

# Effect of ambient Mg/Ca ratio on Mg fractionation in calcareous marine invertebrates: A record of the oceanic Mg/Ca ratio over the Phanerozoic

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## ABSTRACT

The Mg/Ca ratio of seawater has changed significantly over the Phanerozoic, primarily as a function of the rate of ocean-crust production. Echinoids, crabs, shrimps, and calcareous serpulid worms grown in artificial seawaters encompassing the range of Mg/Ca ratios that existed throughout the Phanerozoic exhibit a direct nonlinear relationship between skeletal and ambient Mg/Ca. Specimens grown in seawater with the lowest Mg/Ca ( $\sim 1$ ) changed their mineralogy to low-Mg calcite ( $< 4$  mol%  $\text{MgCO}_3$ ), suggesting that these high-Mg calcareous organisms would have produced low-Mg calcite in the Cretaceous, when oceanic Mg/Ca was lowest ( $\sim 1$ ). These results support the empirical evidence that the skeletal chemistry of calcareous organisms has varied significantly over the Phanerozoic as a function of the Mg/Ca of seawater, and that the Mg/Ca of unaltered fossils of such organisms may be a record of oceanic Mg/Ca throughout the Phanerozoic. Mg fractionation algorithms, which relate skeletal Mg/Ca, seawater Mg/Ca, and temperature, were derived from these and other experiments. They can be used to estimate paleoceanic Mg/Ca ratios and temperatures from fossil skeletal Mg/Ca of the organisms evaluated. Paleoceanic Mg/Ca ratios, recalculated by using the echinoderm Mg fractionation algorithm from published fossil echinoid Mg/Ca, crinoid Mg/Ca, and paleotemperature data, are consistent with other estimates and models of oceanic Mg/Ca over the Phanerozoic.

**Keywords:** seawater Mg/Ca ratio, echinoderms, calcite, Cretaceous, Mg fractionation, paleotemperature.

## INTRODUCTION

Considerable time and effort have been devoted to the reconstruction of the thermochemical history of seawater, owing to its inevitable far-reaching geological, geochemical, and paleontological implications. Ancient seawater Mg/Ca ratios have been reconstructed from the Mg/Ca of fossil echinoderms (Dickson, 2002, 2004), and paleoceanic temperatures have been reconstructed from the Mg/Ca of fossil foraminifera (Lear et al., 2000). These applications have assumed (1) that skeletal Mg/Ca varies with ambient Mg/Ca (Stanley and Hardie, 1998, 1999; Stanley et al., 2002) and (2) that this variation is linear and can therefore be defined with a single fractionation coefficient. In this study, I have conducted experiments on four modern high-Mg calcareous invertebrates to evaluate these assumptions. Although my experiments confirm the first assumption, they disprove the second by showing that skeletal Mg varies nonlinearly with ambient Mg/Ca. Such reconstructions must therefore employ Mg fractionation coefficients that vary with oceanic Mg/Ca, known to have oscillated over the Phanerozoic (Fig. 1) (Ronov, 1964; Folk, 1974; Wilkinson and Algeo, 1989; Hardie, 1996; Morse et al.,

1997; Lowenstein et al., 2001; Siemann, 2003).

The Mg/Ca of seawater is thought to vary primarily as a function of the mixing rate of mid-ocean ridge hydrothermal brines and average river water, driven by the rate of ocean-crust production (Hardie, 1996). As mid-ocean-ridge basalt comes in contact with brine, it is converted to greenstone, thereby releasing  $\text{Ca}^{2+}$  and  $\text{K}^+$  to the seawater and removing  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  from it. The rate of ocean-crust production controls the rate of this ion exchange and, therefore, the relative concentrations of these ions in the oceans. This relationship is evidenced in synchronized transitions between  $\text{MgSO}_4$  and KCl evaporites and aragonite and calcite biotic or abiotic precipitates (Sandberg, 1983; Hardie, 1996; Stanley and Hardie, 1998), fluid inclusions (Lowenstein et al., 2001) and Br (Siemann, 2003) in marine halite, and the Mg/Ca ratios of fossil echinoderms (Dickson, 2002, 2004).

The observation that Mg/Ca has varied in the oceans over the Phanerozoic (Fig. 1) coupled with experiments showing that the amount of Mg incorporated into nonskeletal carbonates increases with the ambient Mg/Ca ratio of seawater (Berner, 1975; Füchtbauer and Hardie, 1976; Mucci and Morse, 1983; Morse et al., 1997) suggests that ambient Mg/Ca would have influenced Mg incorporation

in skeletal carbonates over the Phanerozoic as well. Laboratory experiments have shown that the amount of Mg incorporated into the calcite of *Amphiroa* coralline algae increases with the Mg/Ca ratio of the seawater (Stanley et al., 2002). The purpose of this study is to determine whether calcite-secreting marine invertebrates mimic coralline algae and abiotic calcite with respect to the fractionation of Mg and to evaluate the variability of the coefficients that govern this fractionation, with respect to ambient Mg/Ca, taxonomy, and anatomy.

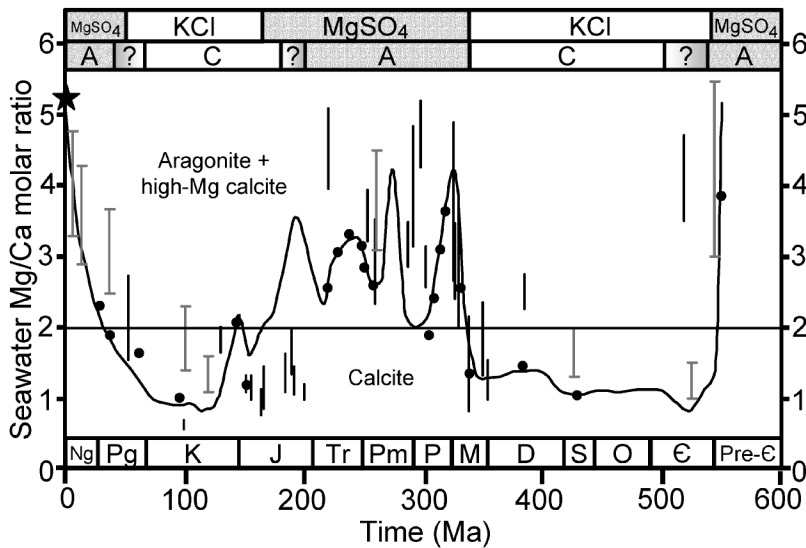
Previous work has shown that the Mg/Ca ratios of the low-Mg calcite produced by the blue mussel *Mytilus edulis* and the euryhaline ostracode crustacean *Cyprideis australiensis* vary with the Mg/Ca ratio of the experimental seawater in which they are raised (Lorens and Bender, 1980; Deckker et al., 1999). However, these results were achieved by employing artificial seawater with Mg/Ca ratios significantly greater than those thought to have existed throughout the Phanerozoic (Hardie, 1996).

## METHODS

Four types of marine invertebrates that secrete high-Mg calcite in modern seas—echinoids (*Eucidaris tribuloides*), crabs (*Perchon gibbesi*), shrimps (*Palaemonetes pugio*), and calcareous serpulid worms (*Hydrooides crucigera*)—were grown in six artificial seawaters (Bidwell and Spotte, 1985) that were identical except for their Mg/Ca molar ratios, which were formulated at values that encompass the range shown to have existed throughout the Phanerozoic ( $\sim 1.0$ – $5.2$ ; Fig. 1; Hardie, 1996): 1.0, 1.5, 2.9, 4.4, 5.4, and 6.7. The ionic strengths of the artificial seawaters were held constant at the modern value of 0.7. The Mg/Ca ratios remained within 5% of their initial values throughout the experiment.

Six individuals of each of the four species were maintained together at  $25 \pm 1$  °C and provided with 10 h/day of identical 15 W irradiance for 160 days in each of the six artificial seawaters, ample time for all of the specimens to generate new skeletal material that could be analyzed for Mg content. The specimens were grown in substrate-free tanks and fed 10 g wet seaweed per week. The high survival rate for these organisms in each of the

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**Figure 1.** Predictions of secular variation in Mg/Ca ratios of seawater during Phanerozoic. Curve is Mg/Ca modeled by Hardie (1996). Black vertical bars are Mg/Ca ranges recalculated from Dickson's (2002, 2004) echinoderm Mg/Ca and temperature data by using echinoderm Mg fractionation algorithm derived in this study. Bars include error associated with Mg fractionation algorithms. Gray vertical bars with T-tops are Mg/Ca ranges estimated from fluid inclusions in marine halites (Lowenstein et al., 2001). Solid black circles are Mg/Ca values estimated from Br in basal marine halite (Siemann, 2003). Star represents modern seawater chemistry (Mg/Ca = ~5.2). Horizontal line is divide between calcite (Mg/Ca <2) and aragonite–high-Mg calcite (Mg/Ca >2) nucleation fields in seawater at 25 °C. Temporal distributions of nonskeletal aragonite and calcite (Sandberg, 1983) and KCl and MgSO<sub>4</sub> marine evaporites (Hardie, 1996) are plotted along top of figure (modified from Lowenstein et al., 2001). A—marine aragonite deposition; C—marine calcite deposition.

seawater treatments suggests that variations in Mg and Ca do not have severe metabolic effects on the organisms. Bellis et al. (1987) showed that reduced levels of ambient Mg (from 50 to 0 mM) did not have significant effects on amino acid retention in sea urchin larvae, whereas Hayashi and Motokawa (1986) demonstrated that elevated Mg levels increased tissue viscosity in echinoderms. However, this increase was observed at Mg concentrations two to five times greater than modern values, well above the range of concentrations evaluated in these experiments.

After 160 days of growth in the artificial seawaters, spines and coronal plates were harvested from the pencil urchins, claws from the sally lightfoot crabs, tails from the grass shrimp, and tube sections from the serpulid worms. New skeletal material, distinguished by its location on the outer perimeter of the skeleton, was embedded in Epotek epoxy resin, sectioned parallel to the longitudinal axis, and analyzed for Mg/Ca molar ratio with the JEOL 8600 Superprobe electron microprobe (EDS, beam current = 0.02 μA, accelerating potential = 15 kV, counting time = 15 s, beam diameter = 1–2 μm). Measurements were made near the periphery of the skeleton to ensure the analysis of new skeletal material that had been deposited sufficiently far from

the original skeleton so as to minimize any topotactic effects.

The skeletal Mg/Ca ratios, Mg/Ca<sub>C</sub>, were plotted against the seawater Mg/Ca ratios, Mg/Ca<sub>SW</sub>, for each of the organisms (Figs. 2A, 2C, 2E). Mg fractionation curves were fit to the data by using least-squares regression.

Mg fractionation coefficients,  $D_cMg$ , were calculated for each of the animals in this study by dividing Mg/Ca<sub>C</sub> by Mg/Ca<sub>SW</sub> (Morse and Bender, 1990):

$$D_cMg = \frac{Mg/Ca_C}{Mg/Ca_{SW}}; \quad (1)$$

$D_cMg$  values were plotted against ambient Mg/Ca<sub>SW</sub> ratios (Figs. 2B, 2D, 2F).

## RESULTS AND DISCUSSION

### Mg Fractionation Curves

It is significant that all of the organisms incorporated less Mg into their skeletons as the Mg/Ca of the artificial seawater decreased (Figs. 2A, 2C, 2E). Organisms grown in the lowest Mg/Ca<sub>SW</sub> (~1) changed their mineralogy to low-Mg calcite (Mg/Ca<sub>C</sub> < 0.04), while organisms grown in the artificial “modern” Mg/Ca<sub>SW</sub> (~5.2) continued to produce high-Mg calcite, remaining within 3% of their preexperimental Mg/Ca<sub>C</sub> ratios.

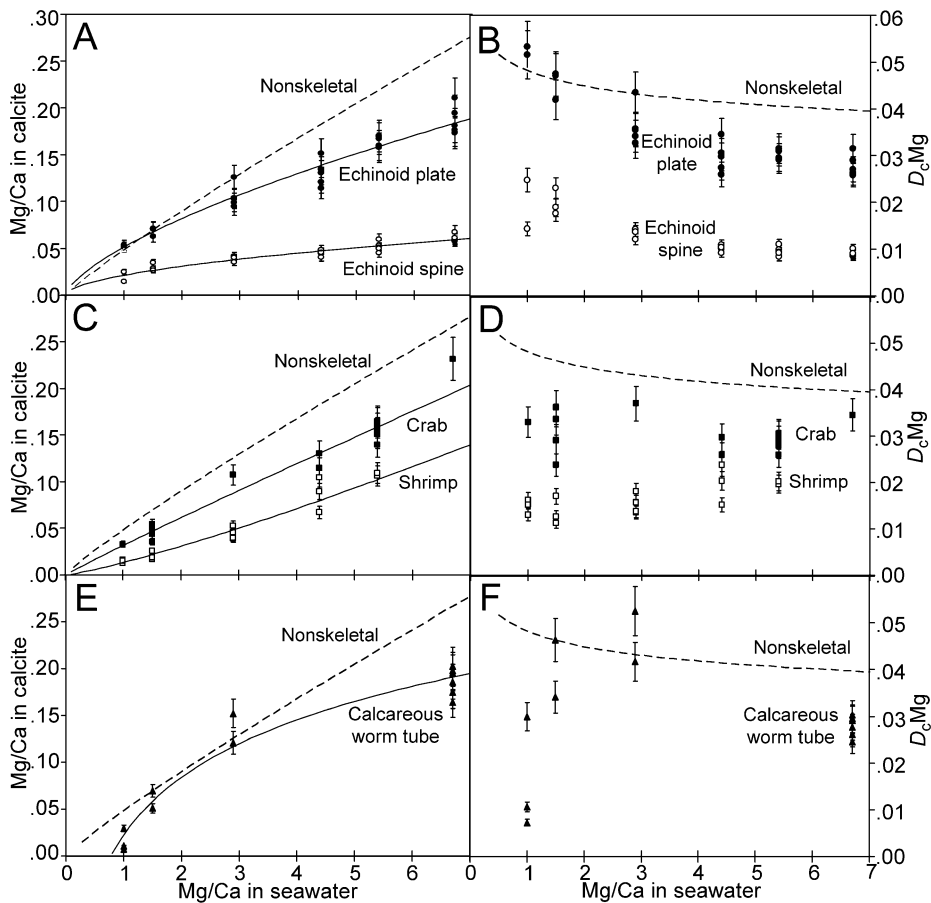
Each type of animal produced a unique Mg fractionation curve. The spines and coronal plates of the echinoids also yielded different fractionation curves (Fig. 2A). Furthermore, each of the curves was lower than the experimentally determined curve for abiotic magnesian calcite (Füchtbauer and Hardie, 1976). This deviation of the biotic fractionation curves from the abiotic curve suggests that these organisms influence, to varying degrees, the incorporation of Mg in their calcite skeletons. However, ranking the organisms by increasing Mg content—echinoid spine, shrimp, crab—echinoid plate—worm—suggests that the degree of Mg fractionation is not, as previously suggested, linked to taxonomic complexity (Chave, 1954). While the biological consequences of skeletal Mg incorporation are unknown, Mg has been shown to retard abiotic calcite-crystal growth (Davis et al., 2000) and decrease the unit-cell volume of skeletal calcite (Bischoff et al., 1983).

### Mg Fractionation Coefficients ( $D_cMg$ )

The calculation of  $D_cMg$  at various Mg/Ca<sub>SW</sub> ratios revealed that the coefficient varied with the ambient Mg/Ca<sub>SW</sub> (Figs. 2B, 2D, 2F).  $D_cMg$  decreased for the echinoid spines—coronal plates and crabs as Mg/Ca<sub>SW</sub> increased (Figs. 2B, 2D). This result is consistent with the experiments on the coralline algae (Stanley et al., 2002) and abiotic magnesian calcite (Füchtbauer and Hardie, 1976; Mucci and Morse, 1983). However,  $D_cMg$  values increased for the grass shrimps as Mg/Ca<sub>SW</sub> increased (Fig. 2D) and were scattered for the serpulid worm tubes (Fig. 2F). The discrepancies among the organisms may be attributable to differences among the organic templates thought to control crystal growth and/or differences in the mechanisms that transport Mg<sup>2+</sup> and Ca<sup>2+</sup> ions into or out of the skeleton-precipitating solutions.

### Ocean-Chemistry Reconstructions

The proportionality between the Mg/Ca of these animals' skeletons and the Mg/Ca of the seawater in which they grew suggests that such animals should have recorded oceanic Mg/Ca throughout the Phanerozoic. Dickson (2002, 2004) innovatively employed a fixed  $D_cMg$ , derived from echinoderms in modern seawater at 25 °C, to reconstruct paleoceanic Mg/Ca from the Mg/Ca of fossil crinoid ossicles and echinoid plates. This study shows that this reconstruction can be improved by employing an Mg fractionation curve, instead of a single  $D_cMg$ , to convert skeletal Mg/Ca to seawater Mg/Ca. The effect of ancient seawater temperature on fossil Mg/Ca can also be corrected for in the reconstruction by using Chave's (1954) observations on the relationship between skeletal Mg fractionation and temperature.



**Figure 2.** Mg fractionation data for four high-Mg calcareous marine organisms. **A:** Mg fractionation curves for echinoid spines (*Eucidaris tribuloides*, open circles,  $y = 0.0213x^{0.538}$ ,  $R^2 = 0.873$ ,  $n = 23$ ) and coronal plates (*Eucidaris tribuloides*, solid circles,  $y = 0.0516x^{0.668}$ ,  $R^2 = 0.959$ ,  $n = 23$ ). **B:** Mg fractionation coefficients for echinoid spines (open circles) and coronal plates (solid circles). **C:** Mg fractionation curves for crabs (*Perchon gibbesi*, solid squares,  $y = 0.0317x^{0.956}$ ,  $R^2 = 0.964$ ,  $n = 16$ ) and shrimps (*Palaemonetes pugio*, open squares,  $y = 0.0134x^{1.21}$ ,  $R^2 = 0.955$ ,  $n = 15$ ). **D:** Mg fractionation coefficients for crabs (solid squares) and shrimps (open squares). **E:** Mg fractionation curve for calcareous serpulid worm tubes (*Hydroides crucigera*, closed triangles,  $y = 0.0883 \ln x + 0.0227$ ,  $R^2 = 0.956$ ,  $n = 13$ ). **F:** Mg fractionation coefficients for calcareous serpulid worm tubes (closed triangles). Broken lines are Mg fractionation curves and coefficients for nonskeletal calcite (Füchtbauer and Hardie, 1976). Mg/Ca in calcite and Mg/Ca in seawater are molar Mg/Ca ratios of skeletal calcite precipitates and artificial seawater solutions, respectively.  $D_cMg$  is Mg fractionation coefficient equal to Mg/Ca in calcite divided by its corresponding Mg/Ca in seawater. Mg fractionation curves are fit to data by using least-squares regression. Vertical bars represent uncertainty due to analytical error.

Mg fractionation curves for echinoid plates, echinoid spines, crabs, serpulid worm tubes, coralline algae (Stanley et al., 2002), and nonskeletal calcite (Füchtbauer and Hardie, 1976) were species normalized with a factor equal to Chave's (1954) average skeletal Mg/Ca of the given higher taxon at  $Mg/Ca_{SW} = 5.2$ , temperature,  $T = 25^\circ C$  divided by the skeletal Mg/Ca of the species in that taxon evaluated in this study at  $Mg/Ca_{SW} = 5.2$ ,  $T = 25^\circ C$  (Table 1). The species-normalization factors for the echinoid plates, echinoid spines, crabs, serpulid worm tubes, and coralline algae are 0.913, 1.708, 0.868, 1.140, and 1.3297, respectively.

Temperature-dependent Mg-fractionation curves were determined from Chave's (1954) and Füchtbauer and Hardie's (1976) data by using least-square regressions (Table 1). The species-normalized Mg fractionation curves and temperature-dependent Mg-fractionation curves were solved simultaneously at  $Mg/Ca_{SW} = 5.2$ , thereby yielding a single Mg fractionation algorithm varying as a function of temperature and  $Mg/Ca_{SW}$  (Table 1). The  $R^2$  coefficients of the Mg fractionation algorithms for the echinoid plates, echinoid spines, crabs, serpulid worm tubes, coralline algae, and nonskeletal precipitates are 0.661, 0.767, 0.927, 0.938, 0.881, and 0.981, respectively.

The derived Mg fractionation algorithms can be used to calculate paleoceanic Mg/Ca ratios from unaltered fossils of the taxa evaluated. Although these Mg-fractionation algorithms have been species normalized, they are easily calibrated for extant species with a species coefficient equal to the skeletal Mg/Ca ratio of that species in the wild divided by the skeletal Mg/Ca ratio predicted by the algorithm, given the temperature and seawater Mg/Ca ratio ( $\sim 5.2$ ) in which the wild specimen lived (Table 1). However, the accuracy of the ancient seawater Mg/Ca calculations will be inherently limited for fossils whose Mg fractionation algorithms cannot be calibrated with living representatives. The accuracy of the algorithms may also be limited by other factors

TABLE 1. ALGORITHMS RELATING  $Mg/Ca_{SW}$ ,  $Mg/Ca_C$ , AND TEMPERATURE

CaCO <sub>3</sub> source	$Mg/Ca_C = f(Mg/Ca_{SW})$ (species-normalized, $T = 25^\circ C$ )	$Mg/Ca_C = f(T)$ ( $Mg/Ca = 5.2$ )	$Mg/Ca_C = f(Mg/Ca_{SW}, T)$
Echinoid plate	$Mg/Ca_C = 0.0471Mg/Ca_{SW}^{0.668}$	$Mg/Ca_C = 0.00216T + 0.0876^*$	$Mg/Ca_C = S(0.000719T + 0.0292)Mg/Ca_{SW}^{0.668}$
Echinoid spine	$Mg/Ca_C = 0.0364Mg/Ca_{SW}^{0.538}$	$Mg/Ca_C = 0.00203T + 0.0375^\dagger$	$Mg/Ca_C = S(0.000837T + 0.0155)Mg/Ca_{SW}^{0.538}$
Crab carapace	$Mg/Ca_C = 0.0275Mg/Ca_{SW}^{0.956}$	$Mg/Ca_C = 0.00299T + 0.0582^\S$	$Mg/Ca_C = S(0.000619T + 0.0120)Mg/Ca_{SW}^{0.956}$
Serpulid worm	$Mg/Ca_C = 0.101 \ln Mg/Ca_{SW} + 0.0259$	$Mg/Ca_C = 0.00463T + 0.0761^\#$	$Mg/Ca_C = S(0.00243T + 0.0399)(\ln Mg/Ca_{SW} + 0.257)$
Coralline algae	$Mg/Ca_C = 0.0582Mg/Ca_{SW}^{0.904**}$	$Mg/Ca_C = 0.0825e^{0.0457T}^\ddagger$	$Mg/Ca_C = S(0.0186e^{0.0457T}Mg/Ca_{SW}^{0.904})$
Nonskeletal	$Mg/Ca_C = 0.0482Mg/Ca_{SW}^{0.898\S\S}$	$Mg/Ca_C = 0.00672T + 0.0392^\S\S$	$Mg/Ca_C = (0.00158T + 0.00924)Mg/Ca_{SW}^{0.898}$

Note: SW is seawater; C is calcite; T is temperature; S is species coefficient.

\*Algorithm based on Chave's (1954) echinoid and crinoid data ( $R^2 = 0.417$ ).

†Algorithm based on Chave's (1954) echinoid data ( $R^2 = 0.490$ ).

‡Algorithm based on Chave's (1954) decapod crustacean data ( $R^2 = 0.734$ ).

#Algorithm based on Chave's (1954) annelid worm data ( $R^2 = 0.777$ ).

\*\*Algorithm based on Stanley et al.'s (2002) coralline algae data ( $R^2 = 0.891$ ).

‡‡Algorithm based on Chave's (1954) calcareous algae data ( $R^2 = 0.762$ ).

§§Algorithms based on Füchtbauer and Hardie's (1976) nonskeletal precipitates data ( $R^2 = 0.930$  for  $Mg/Ca_C = f[Mg/Ca_{SW}]$ ;  $R^2 = 0.861$  for  $Mg/Ca_C = f[T] @ Mg/Ca_{SW} = 5.0$ ).

that could have influenced biogenic Mg fractionation in the past, yet are not incorporated into the model (e.g., variations in growth rates, fluctuations of other ions in seawater).

Dickson's (2002, 2004) paleoceanic Mg/Ca ratios were recalculated by using the echinoid plate Mg fractionation algorithm (calibrated for crinoid ossicles when applicable) that accounts for ambient temperature and variable  $D_c\text{Mg}$  values (Fig. 1). Paleotemperatures were estimated by Dickson (2002; see Dickson's supplementary data) from paleogeographic and paleotemperature maps (Golonka et al., 1994). The resulting Mg/Ca ratios are consistent with other estimates and models of paleoceanic Mg/Ca over the Phanerozoic (Hardie, 1996; Lowenstein et al., 2001; Siemann, 2003).

### Ocean-Temperature Reconstructions

The correlation between temperature and skeletal Mg incorporation (Chave, 1954) also permits the reconstruction of ancient seawater temperatures from skeletal Mg/Ca ratios. However, such reconstructions must correct skeletal Mg/Ca for the effect of varying ambient Mg/Ca<sub>SW</sub>. A recent temperature reconstruction from the Mg/Ca<sub>C</sub> of fossil foraminifera (Lear et al., 2000) has, like the echinoderm reconstruction (Dickson, 2002, 2004), employed a fixed  $D_c\text{Mg}$  to make this correction. This paleotemperature reconstruction can be improved by using an empirically derived Mg fractionation algorithm, which accounts for  $D_c\text{Mg}$  varying with Mg/Ca<sub>SW</sub>.

### Paleontological Implications

The production of low-Mg calcite by all four organisms in the artificial seawater with Mg/Ca = ~1 suggests that these organisms, which produce high-Mg calcite in modern seas, probably produced low-Mg calcite in middle and Late Cretaceous seas, when Mg/Ca ratios are thought to have been near unity. The wide variety of organisms that exhibit this proportionality between skeletal and ambient Mg/Ca suggests that this is a general trend for modern high-Mg calcareous organisms.

### CONCLUSIONS

These experiments show that the Mg/Ca ratios in the skeletons of four modern high-Mg calcareous organisms—echinoids, shrimp, crabs, and serpulid worms—vary proportionally with the Mg/Ca ratio of the seawater in which they are grown. Therefore, the Mg/Ca of unaltered fossils of such organisms should have tracked changes in oceanic Mg/Ca throughout the Phanerozoic. Reconstructions of paleoceanic Mg/Ca and temperature from echinoderms and foraminifera, respectively, have already assumed that this relationship exists for these organisms. However, these re-

constructions employ a fixed Mg fractionation coefficient ( $D_c\text{Mg}$ ) over a range of ambient Mg/Ca ratios. The results of this study show that  $D_c\text{Mg}$  varies with the Mg/Ca of the ambient seawater. Such reconstructions are improved by employing Mg fractionation algorithms that define how  $D_c\text{Mg}$  varies as a function of ambient Mg/Ca and temperature. The variation of Mg fractionation curves among closely related organisms, such as crabs and shrimps, and among different skeletal components within the same organism, such as echinoid spines and coronal plates, underscores the importance of employing only Mg fractionation algorithms known to characterize the specific anatomy of the given organism. Furthermore, the organisms evaluated in this study, which all produce high-Mg calcite in modern seas, probably produced low-Mg calcite in middle and Late Cretaceous seas, when Mg/Ca values are thought to have been near their lowest.

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