

## A Preliminary Study on Mg Isotopic Compositions of Foraminifera

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This study reports the first high-precision measurements of the Mg isotopic compositions of marine carbonate and seawater. Previous investigations concluded that mass dependent variations of Mg isotopic ratio are restricted to a few permil (Catanzaro and Murphy, 1966). A multiple collector-inductively coupled mass spectrometer is used to measure small isotopic variations. Prior to measurement, Mg is separated from other elements by ion exchange chromatography. We use the standard-sample bracketing technique and the isotopic ratio ( $^{26}\text{Mg}/^{24}\text{Mg}$ ) is expressed as a per mil deviation from the international Mg-isotopic standard, SRM 980. Based on duplicate chemistry and mass spectrometer measurement of a variety of samples, including silicate, seawater, and synthetic solutions, the overall reproducibility of our method is 0.06 per mil/amu ( $2\sigma$ ,  $n=15$ ) for Mg.

### Results

We have measured Mg isotopic compositions of two planktonic foraminiferal species and two surface seawater samples. The seawater samples are from Mediterranean and North Atlantic Ocean. Both have an indistinguishable  $\delta^{26}\text{Mg}$  of about +2.5 per mil. This result is consistent with the long residence time (>10Ma) of Mg in the ocean. The  $\delta^{26}\text{Mg}$  of the two species of foraminifera, *Globigerinoides sacculifer* and *Orbulina universa*, from surface sediment in the South China Sea were also measured. The size of the individuals, in this case, is constrained to be larger than 425 $\mu\text{m}$ . The results show only small differences between these two species,  $\delta^{26}\text{Mg}$  being +0.21 and -0.16 per mil for *G. sacculifer* and *O. universa*, respectively. The absence of the last chamber in *G. sacculifer* does not affect the  $\delta^{26}\text{Mg}$  value. Foraminifera are enriched in the light isotope by about 2.4 per mil with respect to seawater. This is similar to the inorganic fractionation coefficient of  $^{26}\text{Mg}$  relative to  $^{24}\text{Mg}$  ( $\alpha\text{Mg}$ ), estimated from the study of cave deposits (Galy et al., 2000). The speleothems were shown to be enriched in the lighter isotope by 1.9-2.4 permil relative to the host-rock with an average cave temperature of 18 C, which is not far from most sea surface temperatures. We, therefore, assume the inorganic  $\alpha\text{Mg}$  to be 0.9976. In addition, the

isotopic fractionation of  $^{44}\text{Ca}/^{42}\text{Ca}$  ratio between seawater and foraminifera may be estimated from the data reported by Zhu and MacDougall (1998). Their data suggest a depletion of 0.4-0.5 per mil in the  $\delta^{44}\text{Ca}$  (a permil deviation of  $^{44}\text{Ca}/^{42}\text{Ca}$  from the international standard, SRM 915a, Halicz et al., 1999) of Holocene benthic foraminifera relative to modern seawater.

### Model

There is no direct measurement relative to SRM 915a of the inorganic  $\alpha\text{Ca}$  available for carbonate-seawater system. However, an indirect estimate can be made using the pool model of Elderfield et al. (1996). These authors propose that Sr and Ba over Ca ratios, measured in benthic foraminifera, can be described by inorganic precipitation of the shell from a pool affected by a Rayleigh distillation process. Furthermore, this model suggests that the fraction of Ca remaining in the pool (fCa) is between 0.01 and 0.11. If we assume that no isotopic fractionation occurs during the transfer of Ca from seawater into the pool, the measured fCa and  $\delta^{44}\text{Ca}$  of shell carbonate predict a range of inorganic  $\alpha\text{Ca}$  between 0.9896 and 0.9982. Figure 1 is a plot of  $\delta^{44}\text{Ca}$  versus  $\delta^{26}\text{Mg}$  when  $\alpha\text{Ca}$  is 0.994. It is clear that Mg isotopes show minimal dependence on fCa while Ca isotopes show a strong dependence. The lack of difference between inorganic  $\alpha\text{Mg}$  and the Mg-isotopic fractionation by foraminifera suggests that there is no significant Mg-isotopic fractionation between the seawater and the pool irrespective to the species. However, the initial Mg/Ca ratio in the pool, unlike Sr and Ba, would have to be adjusted to 1/50 of the seawater value in order to make the calculated Mg/Ca ratio falling into the measured range. Together with intra-cellular measurement of Mg, this indicates that the cytoplasmic membrane acts as a strong barrier with respect to Mg. The Mg-isotopic measurements imply that this biological mechanism inducing elemental fractionation has little effects on Mg-isotopes. These preliminary results clearly show that Mg and Ca isotopes are promising tools for the exploration of vital effects on cation uptake and precipitation of foraminiferal shells. Further, they offer the potential to assess environmental factors on element/Ca ratios.

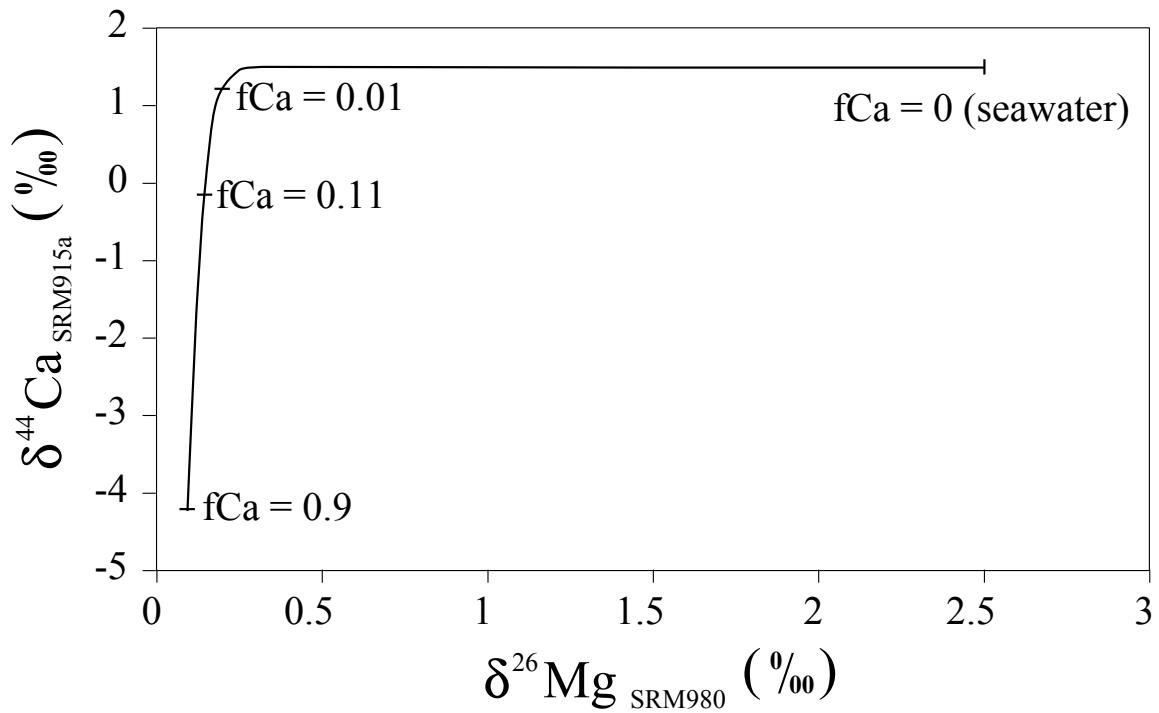


Figure 1: Co-variation of the Ca- and Mg isotopic composition of a foraminiferal shell according to the pool model (Rayleigh distillation of a finite reservoir)

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