Invited review

Magnesium isotope fractionation in biogenic and abiogenic carbonates: implications for paleoenvironmental proxies

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Casey Saenger [a,*], Zhengrong Wang [b]

[a] Department of Environmental Science, Alaska Pacific University, 310C Grant Hall, 4101 University Dr, Anchorage, AK 99508, USA
[b] Department of Geology and Geophysics, Yale University, New Haven, CT 06520, USA

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ABSTRACT

Geochemical variations in marine biogenic carbonates that are preserved in the geological record serve as proxies of past environmental change. However, interpreting most proxies is complicated by biologically-mediated vital effects, highlighting the need to develop new tools for reconstructing paleoenvironmental change. Recently, magnesium (Mg) isotope variability in carbonates has been explored extensively to determine its utility as a paleoenvironmental proxy. We review the results of these works, which have yielded valuable information on the factors affecting Mg isotope fractionation between carbonates and solution ($\Delta^{26}Mg_{carb-sol}$) in biogenic and abiogenic carbonate minerals. Strong evidence exists for a mineralogical control on $\Delta^{26}Mg_{carb-sol}$, with the negative offset from $0‰$ following the sequence aragonite < dolomite < magnesite < calcite. Abiogenic carbonates precipitated from solutions with relatively high Mg/Ca ratios ($> \sim 3$ mol/mol) and saturation states ($\Omega > \sim 3$) that are similar to seawater suggest that $\Delta^{26}Mg_{carb-sol}$ has a temperature dependence of $\sim 0.01‰ \, °C^{-1}$ and is insensitive to precipitation rate. In contrast, a significant precipitation rate dependence is observed in calcites precipitated from solutions with relatively low Mg/Ca ratios ($< \sim 3$ mol/mol) and saturation states ($\Omega < \sim 3$). This difference likely reflects varying mineral growth mechanisms and we discuss the degree to which $\Delta^{26}Mg_{carb-sol}$ may be affected by factors such as fluid inclusions, amorphous calcium carbonate precursors, ion attachment/detachment kinetics, surface entrapment and Mg speciation. High-Mg calcite organisms, which likely precipitated from relatively unmodified seawater, also exhibit a temperature dependence of $\sim 0.01‰ \, °C^{-1}$, albeit sometimes with a systematic offset toward smaller fractionations. In contrast, strong vital effects in low-Mg calcite organisms, which exclude Mg from their calcifying fluids, lead to $\Delta^{26}Mg_{carb-sol}$ values that exhibit no clear temperature dependence and are offset from abiogenic experiments. The majority of biogenic aragonites have $\Delta^{26}Mg_{carb-sol}$ values that are slightly more positive than those in abiogenic experiments, but bivalves and one sclerosponge species can exhibit significantly larger fractionations. Although vital effects and analytical uncertainties will limit $\Delta^{26}Mg_{carb-sol}$ paleotemperature reconstructions to anomalies of at least $\pm 10 \, °C$, Mg isotope variability in biogenic carbonates may be a useful proxy for the Mg isotope composition of seawater, which reflects continental weathering, dolomitization and hydrothermal activity.

1. Introduction

Magnesium (Mg) is a major element in Earth's lithosphere and hydrosphere, and plays important roles in many geological, environmental and biological phenomena. Fractionations among the three stable isotopes of Mg (^{24}Mg 78.99%, ^{25}Mg 10.00% and ^{26}Mg 11.01%) are expected to arise from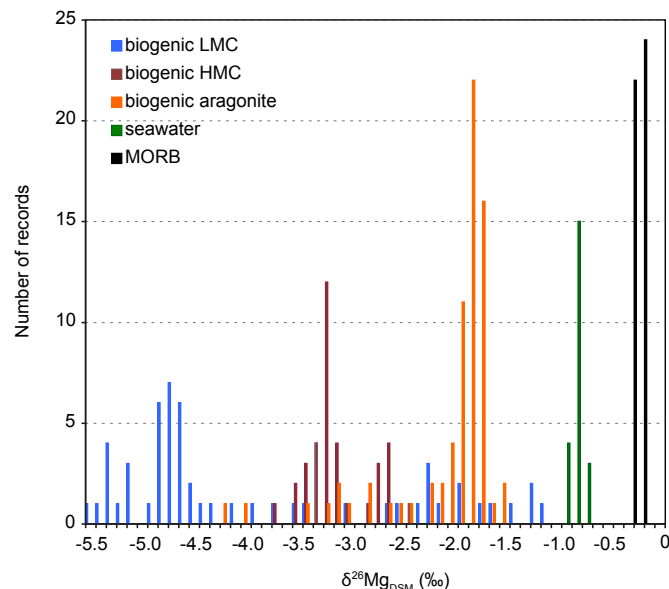 physical, chemical and biological processes, in part, because of their relatively large mass differences. Mg isotope fractionation has been used to constrain various problems including the evolution of the early solar system (e.g. Lee et al., 1976; Hinton and Bischoff, 1984; Bizzarro et al., 2004), continental weathering (e.g. Tipper et al., 2006; Li et al., 2010; Teng et al., 2010), plant growth (e.g. Black et al., 2006; Bolou-Bi et al., 2010) and enzyme synthesis (Buchachenko et al., 2008). This breadth of applications precludes a comprehensive discussion of all aspects of Mg isotope variability in a single review and this paper instead focuses on Mg isotope fractionation with respect to its potential as a paleoenvironmental proxy in marine biogenic carbonates (e.g. foraminifera, coccoliths, corals, bivalves, etc.).

* Corresponding author. Tel.: +1 907 564 8258; fax: +1 907 563 9640.
  E-mail address: csaenger@alaskapacific.edu (C. Saenger).

Analytical advances in the past ~15 years have allowed mass-dependent Mg isotope fractionation to be measured in terrestrial samples. Pioneering studies on the Mg isotope composition of seawater, speleothems and biogenic carbonates (Galy et al., 2001; Galy et al., 2002, 2003; Chang et al., 2003; Chang et al., 2004) yielded a number of important conclusions. These works demonstrated that the Mg isotope composition of surface seawater was depleted in ^{26}Mg relative to the bulk Earth and was relatively constant (Chang et al., 2003, 2004; Young and Galy, 2004; Teng et al., 2010, Fig. 1), consistent with the long (~13 Ma) residence time of Mg in the ocean (Broecker and Peng, 1985). A systematic study of seawater from the surface to a depth of 2.6 km at the East Pacific Rise later demonstrated that the Mg isotope composition of seawater was also constant with depth (within ~0.10‰, de Villiers et al., 2005). These results have recently been confirmed (e.g. Ling et al., 2011) and Foster et al. have suggested the Mg isotope composition of seawater is -0.82 ± 0.01‰ relative to DSM3.

Early work on the Mg isotope composition of natural carbonates suggested considerable natural variations (Fig. 1). Limestone speleothems exhibited a Mg isotope fractionation from their dripwaters of about -2.7‰, while dolostone samples showed much smaller fractionations (Galy et al., 2002). Aragonitic corals had a relatively small fractionation from seawater of about -0.92‰, while a significantly larger fractionation of approximately -4.5‰ was found in LMC foraminifera (Chang et al., 2004). Magnesium occupies a cation site in the carbonate crystal lattice, and exists in aqueous solution primarily as free Mg^{2+} or $Mg(H_2O)_6^{2+}$, or ion pairs in seawater (e.g. $MgCl^+$). The variations observed in natural carbonates clearly show that aqueous Mg isotopes are fractionated during their incorporation into the carbonate lattice, with a strong mineralogical control on the degree to which ^{26}Mg is excluded from the mineral (Fig. 1). However, the Mg isotope composition of carbonates could also be affected by other processes including temperature, growth rate, kinetic isotope fractionation and biologically-mediated vitals effects.

Evaluating if the Mg isotope compostion of biogenic carbonates may be a useful paleoenvironmental proxy requires an understanding of how the processes mentioned above affect Mg isotope fractionation. Furthermore, a thorough understanding of Mg isotope fractionation in carbonates may help to elucidate the isotope fractionation mechanism of other elements (e.g. oxygen, strontium, calcium) and the partitioning of cations (e.g. magnesium, strontium) between carbonate and solution, many of which have been applied as paleotemperature proxies (e.g. McCrea, 1950; Emiliani, 1955; Kinsman and Holland, 1969; O'Neil et al., 1969; Lear et al., 2002; Böhm et al., 2006). Following a brief discussion of nomenclature and analytical methods, we compare Mg isotope fractionation in abiogenic precipitation experiments with those in calcareous marine organisms and theoretical predictions of equilibrium fractionation factors. The compiled results suggest that Mg isotope variability has some promise as a paleoclimate proxy, but its practical application will be significantly complicated by vital effects and analytical challenges.

2. Nomenclature and analytical methods

2.1. Nomenclature

The data in this paper presents the ratio of ^{26}Mg or ^{25}Mg to ^{24}Mg using standard delta notation:

$$\delta^x Mg = \left(\frac{(^xMg/^{24}Mg)_{sample}}{(^xMg/^{24}Mg)_{standard}} - 1 \right) \times 1000 \quad (1)$$

where x is either 25 or 26. In most manuscripts published after 2003, $\delta^{26}Mg$ values are reported relative to DSM3, a standard of 10g of pure Mg metal from the Dead Sea Metal Company dissolved in one liter of 0.3 N HNO_3 (Galy et al., 2003) whose Mg isotopic signature is slightly heavier than the condritic and/or mantle value (Teng et al., 2007, 2010). However, in select cases data has been reported relative to seawater (e.g. Yoshimura et al., 2011) or SRM980 (e.g. Chang et al., 2004), which has been abandoned due to its heterogeneity (Galy et al., 2003). Additionally, a new solution standard (SRM 3131a) from NIST has recently been reported as $\delta^{26}Mg = -3.05 \pm 0.02$‰ ($1\sigma$, Wang et al., 2013b).

The fractionation factor of Mg isotopes between carbonate mineral and solution ($\alpha_{carb-sol}$) is defined using standard notation:

$$\alpha_{carb-sol} = \frac{(^xMg/^{24}Mg)_{carb}}{(^xMg/^{24}Mg)_{solution}} = \frac{1000 + \delta^x Mg_{carb}}{1000 + \delta^x Mg_{solution}} \quad (2)$$

where x is 25 or 26. Because $\alpha_{carb-sol}$ is close to unity, there is precedence for expressing Mg isotope fractionation between carbonate and solution either as $1000 \ln \alpha_{carb-sol}$ (Wang et al., 2013a) or $\Delta^{26}Mg_{carb-sol}$ (Wombacher et al., 2011; Li et al., 2012; Mavromatis et al., 2013), where $\Delta^{26}Mg_{carb-sol} = \delta^{26}Mg_{carbonate} - \delta^{26}Mg_{solution}$. These values are approximately equivalent, and differ by only $0.001-0.003$‰ for typical biogenic carbonate $\delta^{26}Mg$ values, which is well within analytical uncertainty (~0.1‰, 2σ). The total uncertainty of $\Delta^{26}Mg_{carb-sol}$ (σ_T) can be propagated using the relationship:

$$\sigma_{\Delta 26} = \sqrt{(\sigma_{carb})^2 + (\sigma_{sol})^2} \quad (3)$$

where σ_{carb} and σ_{sol} are the 2σ standard deviations of $\delta^{26}Mg_{carb}$ and $\delta^{26}Mg_{solution}$, respectively.

Discussions of carbonate $\delta^{26}Mg$ also frequently include a comparison with $\delta^{25}Mg$ in three isotope plots. This approach is based on the assumption that the isotope fractionation among ^{24}Mg, ^{25}Mg

Fig. 1. Histogram of $\delta^{26}Mg$ values in biogenic low magnesium calcite (blue), high magnesium calcite (red) and aragonite (orange), compared with those for seawater (green) and mid-ocean ridge basalts (MORB, black). The biogenic carbonate data in this plot is compiled in the Supplementary Online Material. Seawater data are from Foster et al. (2010) and MORB data are from Teng et al. (2010). All values are expressed relative to DSM. See online full color version.