The Mg isotopic composition of Cenozoic seawater – evidence for a link between Mg-clays, seawater Mg/Ca, and climate

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ABSTRACT

Cooling of Earth's climate over the Cenozoic has been accompanied by large changes in the magnesium and calcium content of seawater whose origins remain enigmatic. The processes that control these changes affect the magnesium isotopic composition of seawater, rendering it a useful tool for elucidating the processes that control seawater chemistry on geologic timescales. Here we present a Cenozoic magnesium isotope record of carbonate sediments and use a numerical model of seawater chemistry and the carbon cycle to test hypotheses for the covariation between Cenozoic seawater chemistry and climate. Records are consistent with a 2–3× increase in seawater Mg/Ca and little change in the Mg isotopic composition of seawater. These observations are best explained by a change in the cycling of Mg-silicates. We propose that Mg/Ca changes were caused by a reduction in removal of Mg from seawater in low-temperature marine clays, though an increase in the weathering of Mg-silicates cannot be excluded. We attribute the reduction in the Mg sink in marine clays to changes in ocean temperature, directly linking the major element chemistry of seawater to global climate and providing a novel explanation for the covariation of seawater Mg/Ca and climate over the Cenozoic.

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1. Introduction

Earth's climate has transitioned from greenhouse to icehouse conditions over the last 65 million years. This climatic change is attributed to a decline in atmospheric CO_2, whose causes are hotly debated (Berner, 1994; France-Lanord and Derry, 1997; Kent and Muttoni, 2008; Raymo and Ruddiman, 1992), and is associated with an increase in the ratio of Mg to Ca in seawater. A two- to three-fold increase in Mg/Ca over the Cenozoic is observed in a variety of records of ancient seawater chemistry, including fluid inclusions in halite (Horita et al., 2002; Lowenstein et al., 2001; Zimmermann, 2000), deep-sea pore fluid profiles (Fantle and De-Paolo, 2006; Higgins and Schrag, 2012), the mineralogy of inorganic marine cements (Sandberg, 1983), low-temperature calcium carbonate veins in oceanic crust (Coggon et al., 2010), and biogenic carbonates (Dickson, 2002; Stanley and Hardie, 1998). Similar covariation between seawater Mg/Ca and climate, observed on hundred million year timescales throughout the Phanerozoic (the so-called 'aragonite' and 'calcite' seas), suggests fundamental connections between the global carbon cycle and the major element chemistry of seawater.

Exactly how climate and seawater chemistry are linked is not well understood. One set of hypotheses for this link invokes changes in seafloor spreading, which can alter both rates of silicate weathering (through changes in CO_2 outgassing) and rates of hydrothermal circulation and basalt alteration (Berner, 1994; Hardie, 1996). Another set of hypotheses calls on changes in the $CaCO_3$ system – specifically changes in rate of shallow water carbonate deposition and dolomite formation (Holland and Zimmerman, 2000) or the rate of carbonate weathering (Wallmann, 2001). These two sets of hypotheses differ in the Mg-bearing minerals they invoke to explain the Cenozoic Mg/Ca rise – Mg-silicates for changes in hydrothermal alteration or the Mg/Ca of silicate weathering, and Mg-carbonates for changes in carbonate weathering or burial, principally as dolomite.

Mg isotope records can be used to quantify the relative contributions of changes in silicate or carbonate fluxes to the global Mg budget. Recent studies of Mg isotope fractionation during mineral formation show that Mg-clays are modestly enriched in ^{26}Mg, whereas Mg-carbonates (calcite and dolomite) are depleted by 1–4‰ relative to the precipitating solution (Galy et al., 2002; Higgins and Schrag, 2010; Pogge von Strandmann, 2008; Teng et al., 2010; Tipper et al., 2012, 2006b). Because Mg-clays and Mg-carbonates represent the principle sources and sinks of Mg in seawater, these opposing isotope effects make the Mg isotopic

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composition of seawater a potentially powerful tool for unraveling the processes that control the geochemical cycling of magnesium in seawater and its link to the carbon cycle and climate on geologic timescales. Here we present measurements of the Mg isotopic composition of pelagic carbonates and associated pore fluids from two sites in the Pacific and Atlantic Ocean basins to reconstruct changes in the Mg isotopic composition of seawater over the Cenozoic. We evaluate potential bias in our record due to diagenetic recrystallization using measurements of the Mg isotopic composition of the associated pore fluids and a numerical model of sediment diagenesis (Higgins and Schrag, 2012). We find that the Mg isotopic composition of bulk foraminifera is likely an accurate, if imperfect, recorder of the Mg isotopic composition of seawater. Using a numerical model of the global carbon, alkalinity, magnesium, and calcium cycles, we show that small changes in the Mg isotopic composition of seawater over the Cenozoic are best explained by changes in the weathering or formation of Mg-silicates. We propose that a temperature-driven reduction in the Mg sink in low-temperature clays can account for the covariation of seawater Mg/Ca and climate over the Cenozoic and discuss implications of this hypothesis for our understanding of the processes which control the chemical and isotopic composition of seawater on geologic timescales.

2. Methods

2.1. Measurements of $\delta^{26}Mg$ values in pelagic carbonates and associated pore fluids

We measured the magnesium isotopic composition of pelagic carbonates and their associated pore fluids from Ocean Drilling Program (ODP) sites on the Ontong Java Plateau in the Pacific (Site 807; Kroenke et al., 1991) and Walvis Ridge in the Atlantic (Site 1265; Zachos et al., 2004). Sediments at both sites are composed almost entirely of pelagic carbonate (>90 wt%) made up of foraminifera and coccoliths and preserve a relatively complete Cenozoic record with sedimentation rates averaging 2–3 cm/kyr at site 807 and <1 cm/kyr at site 1265. Although making up $<50\%$ of the carbonate sediment, foraminiferal calcite contributes $>90\%$ of Mg in bulk pelagic carbonate sediments, due to the high ratio of Mg to Ca in foraminifera (1–5 mmol mol^{-1}) compared to coccoliths (0.1–0.2 mmol mol^{-1}; Stoll et al., 2001). Magnesium isotope fractionation during biological calcification in foraminifera is similar across many species with an average $\delta^{26}Mg$ value of coretop foraminifera of $-4.71\permil$ (Pogge von Strandmann, 2008). $\delta^{26}Mg$ values of coccolithophores, as measured in laboratory cultures, are $\sim$2–3$\permil$ enriched compared to foraminifera (Ra et al., 2010). Mg isotope measurements were carried out on two size fractions of the sediment: <65 μm (coccoliths and small/fragmented foraminifera; $n = 71$), and 250–450 μm (foraminifera; $n = 21$). Below 1100 meters at site 807, Mg isotope measurements were made on bulk limestone ($n = 16$). A description of the analytical methods used to prepare (acidify/dissolve) samples and chromatographically separate Mg from the sample matrix can be found in the Supplementary Information (S1) and Higgins and Schrag (2012).

Magnesium isotope ratios were measured on both a GV Isoprobe P and a Thermo Scientific Neptune multicollector-inductively coupled plasma-mass spectrometer (MC-ICP-MS) and are reported using delta notation:

$$\delta^{25,26}Mg = \left(\frac{(^{25,26}Mg/^{24}Mg)_{SAM}}{(^{25,26}Mg/^{24}Mg)_{STD}} - 1 \right) \times 1000$$

where $(^{25,26}Mg/^{24}Mg)_{STD}$ is the measured $^{26}Mg/^{24}Mg$ ratio of the DSM-3 Mg standard (Galy et al., 2003). Repeat measurements of the Cambridge-1 Mg standard on the GV Isoprobe P yielded $\delta^{25}Mg$ and $\delta^{26}Mg$ values of $-1.34 \pm 0.14\permil$ and $-2.62 \pm 0.26\permil$ ($2\sigma_{sd}$;

$n = 215$) relative to DSM-3. On the Thermo Scientific Neptune, Cambridge-1 Mg standard yielded $\delta^{25}Mg$ and $\delta^{26}Mg$ values of $-1.34 \pm 0.06\permil$ and $-2.59 \pm 0.12\permil$ ($2\sigma_{sd}$; $n = 46$). Both measured values are indistinguishable from published values ($\delta^{25}Mg = -1.33 \pm 0.07\permil$; $\delta^{26}Mg = -2.58 \pm 0.14\permil$; Galy et al., 2003). A total of six samples (two carbonates and four pore fluids), measured on both the GV Isoprobe P and the Thermo Neptune MC-ICP-MS, were found to have the same $\delta^{25}Mg$ and $\delta^{26}Mg$ values to within $0.18\permil$ ($\delta^{26}Mg$; $2\sigma_{sd}$). Plotted in three-isotope space ($\delta^{25}Mg$ vs. $\delta^{26}Mg$) all measured samples ($n = 117$) fall on a line with a slope of 0.5239 ± 0.0014 ($R^2 = 0.9978$), consistent with mass-dependent fractionation of Mg isotopes.

2.2. Box models of seawater chemistry and the carbon cycle

To test our record of the Mg isotopic composition of seawater from pelagic carbonates against the different models for Cenozoic climate and seawater chemistry, we developed a numerical model of the global carbon, alkalinity, magnesium, and calcium cycles. The model links the major element chemistry of seawater, the global carbon cycle and climate through outgassing of CO_2, silicate weathering and the formation and burial of both carbonate and clay minerals. Full details of the model including parameterization of the various sources and sinks can be found in the Supplementary Information (S2). We model only the inorganic carbon cycle:

$$\frac{dTCO_2}{dt} = V + F_{Ca-CW} + F_{Mg-CW} - F_{Ca-CB} \qquad (1)$$

where V is the net source of CO_2 to the ocean–atmosphere system from inorganic carbon (volcanic and metamorphic; Marty and Tolstikhin, 1998), CW is the source of CO_2 from carbonate weathering, and CB is carbonate burial (as $CaCO_3$). The weathering of silicate and carbonate minerals adds cations (Na, Ca, Mg, and K) and alkalinity to seawater that is balanced (less any sinks due to reverse weathering reactions) on timescales of a few kyr by the removal of an equivalent amount of alkalinity in $CaCO_3$ (with minor Mg):

$$\frac{dALK}{dt} = 2F_{Ca-CW} + 2F_{Mg-CW} + 2F_{Mg-SW} + 2F_{Ca-SW}$$
$$+ F_{Na/K-SW} - F_{RW} - 2F_{Ca-CB} \qquad (2)$$

where SW, CW, RW refer to silicate weathering, carbonate weathering, and reverse weathering, respectively. In modern global rivers, Ca makes up $\sim$30–40% of the silicate alkalinity, but constitutes $>90\%$ of the alkalinity in buried carbonates (Berner and Berner, 1996; Gaillardet et al., 1999). The imbalance between Ca sources and sinks implied by Eq. (2) and pointed out by McDuff and Morel (1980) can be satisfied in two ways: 1) reactions that result in a net exchange of non-Ca cations for Ca (e.g. Mg for Ca exchange during dolomitization or in hydrothermal systems on mid ocean ridge axes and flanks, cation exchange on low-temperature clays, or clay authigenesis locally balanced by silicate or carbonate weathering; Sayles and Mangelsdorf, 1977), or 2) reactions that consume non-Ca cations and their associated alkalinity (e.g. F_{RW}; Mackenzie and Garrels, 1966; Michalopoulos and Aller, 1995).

The alkalinity balance defined in Eq. (2) implies that the global geochemical cycle of Ca depends on the other major cations in seawater, principally Mg, Na, and K. This can be shown by considering a simple case that includes only the geochemical cycles of Ca and Mg:

$$\frac{dCa}{dt} = F_{Ca-CW} + F_{Ca-SW} + F_{Ca-DOL} + F_{Ca-BA} + F_{Ca-CLAY}$$
$$- F_{Ca-CB} \qquad (3)$$

$$\frac{dMg}{dt} = F_{Mg-CW} + F_{Mg-SW} - F_{Mg-DOL} - F_{Mg-BA} - F_{Mg-CLAY}$$
$$- F_{Mg-CB} \qquad (4)$$