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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 CO₂, whose causes are hotly debated (Bernier, 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 DePaolo, 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 CO₂ outgassing) and rates of hydrothermal circulation and basalt alteration (Bernier, 1994; Hardie, 1996). Another set of hypotheses calls on changes in the CaCO₃ system – specifically changes in rate of shallow water carbonate deposition and dolomite formation (Holland and Zimmermann, 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 ²⁶Mg, 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 $\delta^{26}\text{Mg}$ 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 $\delta^{26}\text{Mg}$ value of core-top foraminifera of -4.71‰ (Pogge von Strandmann, 2008). $\delta^{26}\text{Mg}$ values of coccolithophores, as measured in laboratory cultures, are $\sim 2\text{--}3\text{‰}$ 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:

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

where $(^{25,26}\text{Mg}/^{24}\text{Mg})_{\text{STD}}$ is the measured $^{26}\text{Mg}/^{24}\text{Mg}$ 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 $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values of $-1.34 \pm 0.14\text{‰}$ and $-2.62 \pm 0.26\text{‰}$ ($2\sigma_{\text{sd}}$;

$n = 215$) relative to DSM-3. On the Thermo Scientific Neptune, Cambridge-1 Mg standard yielded $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values of $-1.34 \pm 0.06\text{‰}$ and $-2.59 \pm 0.12\text{‰}$ ($2\sigma_{\text{sd}}$; $n = 46$). Both measured values are indistinguishable from published values ($\delta^{25}\text{Mg} = -1.33 \pm 0.07\text{‰}$; $\delta^{26}\text{Mg} = -2.58 \pm 0.14\text{‰}$; 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 $\delta^{25}\text{Mg}$ and $\delta^{26}\text{Mg}$ values to within 0.18‰ ($\delta^{26}\text{Mg}$; $2\sigma_{\text{sd}}$). Plotted in three-isotope space ($\delta^{25}\text{Mg}$ vs. $\delta^{26}\text{Mg}$) 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:

$$\frac{d\text{TCO}_2}{dt} = V + F_{\text{Ca-CW}} + F_{\text{Mg-CW}} - F_{\text{Ca-CB}} \quad (1)$$

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):

$$\begin{aligned} \frac{d\text{ALK}}{dt} = & 2F_{\text{Ca-CW}} + 2F_{\text{Mg-CW}} + 2F_{\text{Mg-SW}} + 2F_{\text{Ca-SW}} \\ & + F_{\text{Na/K-SW}} - F_{\text{RW}} - 2F_{\text{Ca-CB}} \end{aligned} \quad (2)$$

where SW, CW, RW refer to silicate weathering, carbonate weathering, and reverse weathering, respectively. In modern global rivers, Ca makes up $\sim 30\text{--}40\%$ of the silicate alkalinity, but constitutes >90% of the alkalinity in buried carbonates (Bernier and Bernier, 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:

$$\begin{aligned} \frac{d\text{Ca}}{dt} = & F_{\text{Ca-CW}} + F_{\text{Ca-SW}} + F_{\text{Ca-DOL}} + F_{\text{Ca-BA}} + F_{\text{Ca-CLAY}} \\ & - F_{\text{Ca-CB}} \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{d\text{Mg}}{dt} = & F_{\text{Mg-CW}} + F_{\text{Mg-SW}} - F_{\text{Mg-DOL}} - F_{\text{Mg-BA}} - F_{\text{Mg-CLAY}} \\ & - F_{\text{Mg-CB}} \end{aligned} \quad (4)$$

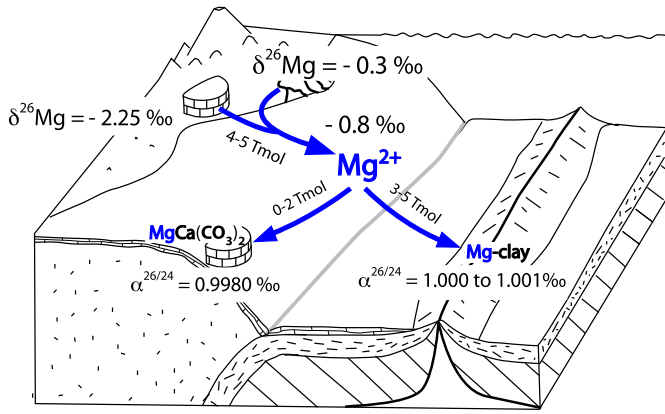


Fig. 1. Illustration of the global modern magnesium cycle in seawater. Mg fluxes and Mg isotopic compositions of seawater and various sources/sinks are taken from the published literature (see text for details).

where CW, SW, and CB are as above, and DOL, BA, and CLAY reflect cation-for-Ca exchange reactions associated with dolomitization, basalt alteration (at high temperatures), and low-temperature clays, respectively. We assume here that the Mg sink associated with marine clays (hydrothermal and sedimentary) is quantitatively balanced by a Ca source with no net source/sink of alkalinity. This is a simplification of complicated systems that in reality involve other cations (notably Na^+ and K^+) and may act as net sources or sinks of alkalinity. The effect of ignoring the alkali metals is to overestimate changes in seawater Ca in the model. These assumptions do not fundamentally alter the conclusions presented here, though further consideration of a more complete model of seawater chemistry is warranted.

Ignoring non-Ca/Mg cations and alkalinity contributions from reverse weathering in Eq. (2), solving for a global alkalinity balance in quasi-steady-state ($\frac{d\text{ALK}}{dt} \sim 0$), and substituting it into Eq. (3) yields:

$$\frac{d\text{Ca}}{dt} = F_{\text{Ca-DOL}} + F_{\text{Ca-BA}} + F_{\text{Ca-CLAY}} - F_{\text{Mg-CW}} - F_{\text{Mg-SW}} \quad (5)$$

Note that sinks of Ca in Eq. (5) are the sources of non-Ca alkalinity from silicate and carbonate weathering, whereas exchange reactions associated with dolomitization, basalt alteration, and ion exchange on clays are the only Ca sources. This result explains why an increase in the overall rate of silicate weathering leads to a decline in seawater Ca. The opposite conclusion would be reached if one did not consider a global alkalinity balance at quasi-steady-state. Inspection of Eqs. (4) and (5) indicate that there are four ways in which to explain the increase in seawater Mg/Ca over the Cenozoic: 1) a reduction in the formation of dolomite; 2) an increase in Mg-silicate weathering; 3) an increase in Mg-carbonate weathering; or 4) a reduction in the rate of Mg removal in clays.

The magnesium isotopic composition of seawater provides a window into the global magnesium cycle because Mg isotopes are fractionated very differently during the formation of Mg-carbonates and Mg-silicates (Fig. 1). The magnesium isotopic composition and fractionation factors associated with sources/sinks of Mg in carbonate and silicate rocks used in the model are taken from the published literature (Higgins and Schrag, 2010; Hippler et al., 2009; Tipper et al., 2006b; Wimpenny et al., 2014; Wombacher et al., 2011; Young and Galy, 2004) and measurements of the Mg isotopic composition of modern/recent dolomite (Fantle and Higgins, 2014). $\delta^{26}\text{Mg}$ values for carbonate and silicate weathering are set at -2.25‰ and -0.3‰ , respectively. Recent studies have shown that Mg isotopes can be fractionated during continental silicate weathering due to the formation of secondary mineral

Table 1

Model outputs for our two-box model of the global C, alkalinity, Mg, and Ca cycles over the Cenozoic. (+) and (−) denote sources and sinks, respectively. The range of values reflects different model scenarios and is consistent with estimates of present-day fluxes and their isotopic composition. See text and Supplementary Information for further details.

Model variable	Model output ($t = \text{present}$)	Isotopes $\delta(\text{‰})$ or α/ϵ
Carbon	Flux (Tmol/yr)	
Volcanic outgassing (+) ¹	4.25 to 5.0	
Carbonate weathering (+) ²	11 to 13	
Silicate weathering (+) ¹	4.25 to 5.0	
Carbonate burial (−) ³	15.3 to 18.0	
Calcium	Flux (Tmol/yr)	
Carbonate weathering (+) ⁴	9.0 to 10.8	
Silicate weathering (+) ⁵	2.3 to 2.5	
High T hydrothermal (+) ⁶	1.4 to 1.6	
Low T hydrothermal/clays (+) ⁷	0.6 to 1.5	
Dolomitization (+) ⁸	0.75 to 1.0	
Carbonate burial (−) ³	14.5 to 17.0	
Magnesium	Flux (Tmol/yr)	Isotopes
Carbonate weathering (+) ⁴	2.0 to 2.2	-2.25^9
Silicate weathering (+) ⁵	2.0 to 2.5	-0.3^{10}
High T hydrothermal (−) ⁶	1.4 to 1.6	1.0000^{11}
Low T hydrothermal/clays (−) ⁷	0.6 to 1.5	1.0007^{12}
Dolomitization (−) ⁸	0.75 to 1.0	0.9980^{13}
H₂O	Flux (10^{13} kg/yr)	
Axial hydrothermal ¹⁴	2.7 to 3.0	
Ridge-flank hydrothermal ¹⁵	25 to 70	

¹ Marty and Tolstikhin (1998).

² Gaillardet et al. (1999).

³ To balance^{1,2}.

⁴ Assuming a Mg/Ca of carbonate weathering of 0.16 to 0.20.

⁵ Assuming a Mg/Ca of silicate weathering of 0.9 to 1.1.

⁶ Calculated using high-T water flux and assuming 1:1 exchange with Mg.

⁷ Calculated using low-T water flux and assuming 1:1 exchange with Mg.

⁸ Estimated from difference in $\delta^{26}\text{Mg}$ between seawater and rivers; Tipper et al. (2006b).

⁹ Avg. $\delta^{26}\text{Mg}$ of carbonate rocks; see text.

¹⁰ Avg. $\delta^{26}\text{Mg}$ of silicate rocks; see text.

¹¹ Assuming quantitative Mg removal.

¹² Higgins and Schrag (2010); see text.

¹³ Fantle and Higgins (2014) and Higgins and Schrag (2010); see text.

¹⁴ Elderfield and Schultz (1996).

¹⁵ Tuned to satisfy mass balance.

phases (Pogge von Strandmann et al., 2012; Tipper et al., 2006a; Wimpenny et al., 2010). Thus it is possible that the $\delta^{26}\text{Mg}$ value of the river flux may be shifted from that expected from the Mg isotopic composition of the parent carbonate/silicate rocks. However, on long timescales we expect this effect to be minor as the average Mg isotopic offset between shale and primary silicates appears to be small ($\sim 0.3\text{‰}$; Young and Galy, 2004).

The Mg isotopic composition of weathered carbonates will be dominated by dolomite and high-Mg limestone, both of which appear to exhibit significant natural variability in their Mg isotopic composition (-0.8‰ to -2.8‰ for dolomite and -2.5 to -4.5‰ for limestone), though the total number of measurements is small (Galy et al., 2002; Higgins and Schrag, 2010; Tipper et al., 2006b; Wombacher et al., 2011). We use an average $\delta^{26}\text{Mg}$ value of carbonate weathering, listed in Table 1, of -2.25‰ , but also explore heavier values ($\delta^{26}\text{Mg} = -1.75\text{‰}$).

Constraints on Mg isotope fractionation during the formation of marine clays comes largely from a single study of deep-sea pore-fluid profiles (Higgins and Schrag, 2010) which indicate Mg isotope fractionation factors ($\alpha^{26/24}$) of between 1.0000 and 1.0010. Similar Mg isotope fractionation factors are observed in terrestrial systems where Mg-clays are being produced from the weathering of primary silicates (Teng et al., 2010; Tipper et al., 2006a; Wimpenny et al., 2010, 2014). Exactly how much of this isotopic fractiona-

tion is expressed in the global Mg-clay sink will depend on the environment of clay formation. For example, in high-temperature hydrothermal systems, removal of Mg is quantitative and thus the $\delta^{26}\text{Mg}$ value of the total high-temperature clay sink must be equal to the $\delta^{26}\text{Mg}$ value of seawater. In low-temperature hydrothermal systems or marine sediments where Mg removal is less quantitative, more isotopic fractionation will be expressed. We assume a fractionation factor of 1.0000 for Mg removed in high-temperature hydrothermal systems and a fractionation factor up to 1.0007 for clays formed in low-temperature environments (Table 1).

There are few published $\delta^{26}\text{Mg}$ values of dolomite, making an estimate of the fractionation factor associated with dolomitization somewhat uncertain. Published values of Pliocene-present ‘organogenic’ dolomites from ODP site 1082 and 1012 give a range from -1.72‰ to -2.52‰ , though we note that the modeled fractionation factor ($\alpha^{26/24}$) for dolomite precipitation at these sites is 0.9980 to 0.9975, corresponding to predicted $\delta^{26}\text{Mg}$ values of -2.8‰ to -3.3‰ (Higgins and Schrag, 2010). The difference between modeled and measured dolomite $\delta^{26}\text{Mg}$ values is due to the fact that these pore-fluid systems are semi-closed with respect to Mg. As a result, removal of pore-fluid Mg by dolomite precipitation drives Rayleigh-type distillation of pore-fluid Mg isotopes, yielding heavier $\delta^{26}\text{Mg}$ values for the dolomite than would be expected based on the modeled fractionation factor. We assume that most volumetrically significant dolomites in the geologic record likely formed from a more open system and a Mg isotope fractionation factor for dolomitization of 0.9980 (Table 1). Recently published and unpublished measurements of Miocene-Pleistocene dolomites from the shallow subsurface in the Marion Plateau and the Bahamas, believed to be formed in a more open system in rapid exchange with seawater (Swart and Melim, 2000; Vahrenkamp et al., 1991), show a narrow range of $\delta^{26}\text{Mg}$ values of $-2.8 \pm 0.20\text{‰}$, $n > 50$, consistent with a fractionation factor of ~ 0.9980 (Fantle and Tipper, 2014). To account for the possibility that more closed-system dolomites constitute a significant fraction of the global dolomite sink, we test the sensitivity of the model to smaller fractionation factors (0.9990).

3. Results

3.1. The Mg isotopic composition of pelagic carbonates over the Cenozoic

Despite differences in size fraction, sedimentation rates and the degree of diagenetic alteration, absolute values and temporal changes in $\delta^{26}\text{Mg}$ values are similar at the two sites (Fig. 2; Table S1). Measured $\delta^{26}\text{Mg}$ values from the $<65\text{ }\mu\text{m}$ size fraction range from -3.89 to -5.14‰ . Measured $\delta^{26}\text{Mg}$ values from the $250\text{--}450\text{ }\mu\text{m}$ size fraction occupy a narrower range, from -4.25 to -4.85‰ . Measured Mg/Ca, Sr/Ca, Mn/Ca, and Al/Ca of carbonate samples from site 807 are listed in Table S2. Measured Mg/Ca, Sr/Ca, Mn/Ca, and Al/Ca ratios for all size fractions range from 1.2 to 4.2 mmol/mol, 0.5 to 2 mmol/mol, 0.1 to 1.6 mmol/mol, and 0.01 to 0.30 mmol/mol, respectively. None of the correlations between trace element ratios and $\delta^{26}\text{Mg}$ values indicate obvious contamination of Mg from Al-silicates or diagenetic Mn crusts. For example, Mn/Ca ratios are systematically higher at site 807 (>0.1 mmol/mol) as compared to site 1265 (<0.05 mmol/mol) but $\delta^{26}\text{Mg}$ values are indistinguishable. Similarly, coherent stratigraphic variability in Sr/Ca, Mn/Ca, and Mg/Ca, where present (e.g. at ~ 200 mbsf at site 1265) is not reflected in variability in measured $\delta^{26}\text{Mg}$ values. We take these observations to indicate that our measurements reflect the Mg isotopic composition of average foraminiferal carbonate, altered by diagenetic recrystallization, with small contributions from silicates, organics, and coccolith calcite. Measured $\delta^{26}\text{Mg}$ values of the two size fractions overlap with

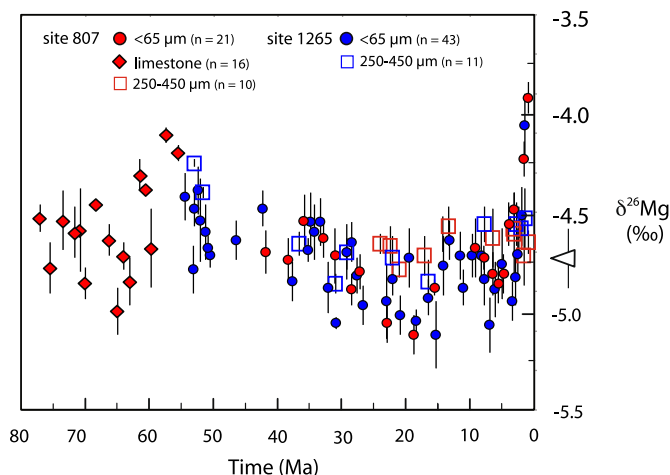


Fig. 2. Measured $\delta^{26}\text{Mg}$ values of pelagic carbonate from ODP sites 1265 and 807. Symbols differentiate $<65\text{ }\mu\text{m}$ (filled circles), $250\text{--}450\text{ }\mu\text{m}$ (open squares), and bulk limestone (filled diamonds) samples. Errors represent 1σ uncertainties associated with repeat measurements of a single sample passed through cation exchange chromatography. Triangle denotes average $\delta^{26}\text{Mg}$ value for a range of modern foraminiferal species (Pogge von Strandmann, 2008; Wombacher et al., 2011).

each other and the average $\delta^{26}\text{Mg}$ values of multiple species of core-top foraminifera (Pogge von Strandmann, 2008), consistent with the total Mg budget of the sediment being dominated by foraminiferal calcite. An exception to this are the youngest $<65\text{ }\mu\text{m}$ samples at both sites which are enriched by 0.6 to 0.7‰ compared to samples of the same age in the $250\text{--}450\text{ }\mu\text{m}$ size fraction. We attribute these heavy Mg isotope values to greater contributions from coccolith calcite and possibly silicate or organic Mg. The shift towards lower $\delta^{26}\text{Mg}$ values in the $<65\text{ }\mu\text{m}$ size fraction then reflects mixing due to breakdown of foraminiferal calcite as well as the effects of diagenetic recrystallization (Higgins and Schrag, 2012) and the loss of any silicate/organic Mg. Average $\delta^{26}\text{Mg}$ values from the two sites are within 0.1‰ of each other ($807 = -4.64\text{‰}$; $1265 = -4.72\text{‰}$) and show similar secular variability (Fig. 2).

There are four potential sources of bias to consider in a record of the Mg isotopic composition of seawater from bulk foraminiferal carbonate – diagenetic recrystallization, species-dependent fractionation, temperature-dependent fractionation, and vital effects associated with foraminiferal calcification that may change on geologic timescales in response to evolution or changes in seawater chemistry. We constrain the effects of recrystallization using measurements of Mg isotopes in the pore fluid and a model of sediment diagenesis (see Supplementary Information S3). Model results are consistent with early diagenetic recrystallization leading to little change in the $\delta^{26}\text{Mg}$ value of the bulk foraminiferal carbonate with depth. Depending on model conditions, the bulk may be shifted to both heavier ($<0.1\text{‰}$) and lighter ($<0.3\text{‰}$) $\delta^{26}\text{Mg}$ values. Importantly, because much of the recrystallization appears to occur within the first 5 to 10 Myr, the Mg isotopic composition of the recrystallized calcite should also be sensitive to changes in the $\delta^{26}\text{Mg}$ value of seawater (though this signal is expected to lag the signal in the unrecrystallized calcite by millions of years).

The change in $\delta^{26}\text{Mg}$ value of the bulk sediment due to diagenetic recrystallization is small in spite of the fact that recrystallization results in significant exchange of Mg between sediment and pore fluid – a consequence of similar Mg isotope fractionation factors for recrystallized and foraminiferal calcite. Laboratory experiments of Mg isotope fractionation in calcites precipitated at different rates estimate equilibrium Mg isotopic fractionation factor of $3.5 \pm 0.2\text{‰}$ (Mavromatis et al., 2013), consistent with the large ($\sim 4\text{‰}$) Mg isotope fractionations required by our pore-fluid

and sediment data. In contrast to the small changes in $\delta^{26}\text{Mg}$ values observed in the bulk sediment, recrystallization of coccolith calcite will be associated with a large negative shift in its $\delta^{26}\text{Mg}$ value due to the large difference in the Mg isotopic composition of recrystallized and coccolith calcite (Fig. S6).

Diagenetic recrystallization may also play a role in some of the heavier $\delta^{26}\text{Mg}$ values observed between ~ 60 and 55 Ma at site 807. The heaviest of these samples occurs just beyond the transition from chalk to limestone in site 807 – a transition that is associated with significant destruction of the primary carbonate fabrics. Given the potential for alteration of Mg isotopes during recrystallization and the generally heavy $\delta^{26}\text{Mg}$ values observed in deep pore fluids from site 807 (Higgins and Schrag, 2012), we regard the heavier $\delta^{26}\text{Mg}$ values in the limestone at site 807 as suspect. Better preservation at site 1265 suggests that the heavy $\delta^{26}\text{Mg}$ values observed in samples from the $250\text{--}450\text{ }\mu\text{m}$ size fraction between 50 and 55 Ma may indicate a heavier $\delta^{26}\text{Mg}$ value of seawater at that time.

There are significant inter- and intra-species differences in $\delta^{26}\text{Mg}$ values of foraminiferal carbonate (Chang et al., 2004; Pogge von Strandmann, 2008; Wombacher et al., 2011). Inter-species variability is as large as $\sim 1\text{‰}$, though the majority of measured species are within error of the mean value of $\sim -4.7\text{‰}$. Thus, in an extreme case changes in species composition could produce $\pm 0.5\text{‰}$ of variability in our Mg isotope record. Mg isotope values also vary by as much as 0.3‰ within a given species – and by even larger amounts ($\sim 1\text{‰}$) within the same species measured in different labs (Chang et al., 2004; Pogge von Strandmann, 2008). The source of this variability is uncertain but it highlights the potential for significant bias even in species-specific foraminiferal Mg isotope records. Although our approach averages foraminiferal species, we think it unlikely that variations in species composition have systematically biased our record of Mg isotope variability in bulk pelagic carbonates. This conclusion is supported by the fact that we recover very similar records of Cenozoic Mg isotope variability from sites in two different ocean basins characterized by carbonate accumulation rates that differ by a factor of 2–3 and different extents of diagenetic recrystallization.

Variations in Mg isotope fractionation in foraminifera on geologic and evolutionary timescales due to temperature or vital effects associated with ocean chemistry may introduce biases that would be recorded globally. Previous studies of core-top foraminifera show no evidence for temperature-dependent Mg isotope fractionation (Pogge von Strandmann, 2008; Wombacher et al., 2011), but there are no data bearing on vital effects related to secular change in seawater chemistry and/or evolution. Ultimately, independent records of the Mg isotopic composition of seawater are needed. However, taking into consideration all of the potential sources of bias discussed above, we conclude that the Mg isotopic composition of bulk pelagic carbonates is an accurate recorder of the Mg isotopic composition of seawater on geologic timescales. Although we cannot exclude small variations in the $\delta^{26}\text{Mg}$ value of seawater of $<0.3\text{‰}$ and perhaps somewhat heavier $\delta^{26}\text{Mg}$ values of seawater in the Paleogene ($+0.3\text{--}0.4\text{‰}$), our record otherwise indicates little variability in the $\delta^{26}\text{Mg}$ value of seawater over the last 75 Myr (Fig. 2).

3.2. Model results for Cenozoic seawater Mg/Ca and $\delta^{26}\text{Mg}$

A simple model of seawater Mg and Ca, described by Eqs. (4) and (5), indicates that there are four ways to explain the increase in seawater Mg/Ca over the Cenozoic: 1) a reduction in the formation of dolomite; 2) an increase in Mg-silicate weathering; 3) an increase in Mg-carbonate weathering; or 4) a reduction in the rate of Mg removal in clays (cation exchange or authigenic). Model results for each of these scenarios indicate that the $\delta^{26}\text{Mg}$ of sea-

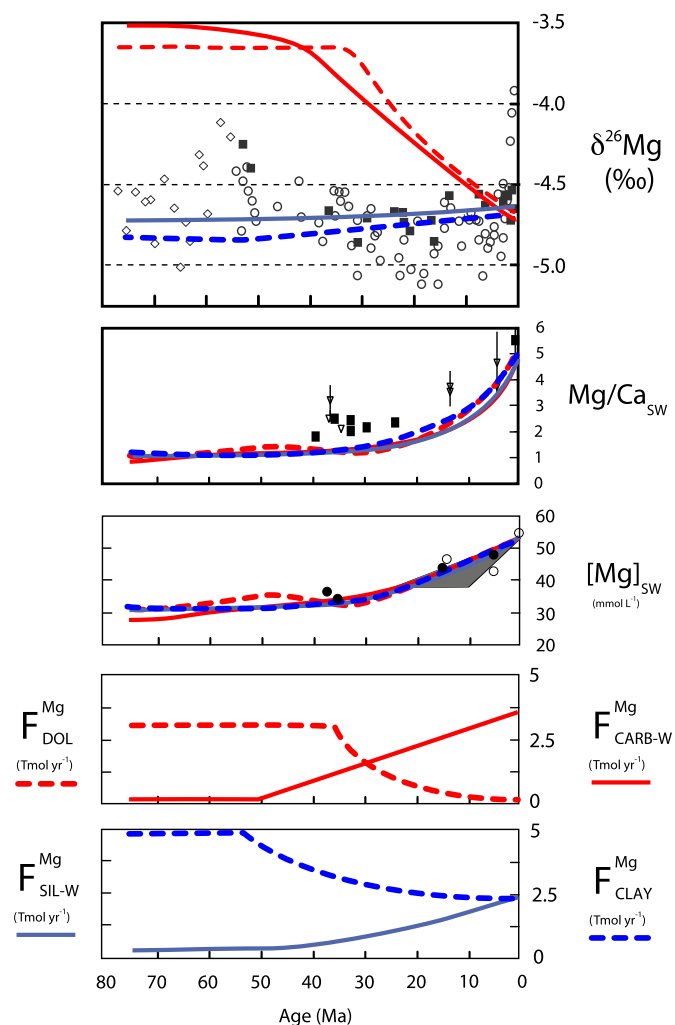


Fig. 3. Model output for different scenarios which can explain the Cenozoic rise in seawater Mg/Ca. The scenarios are 1) a decline in dolomitization (red dashed line); 2) an increase in Mg-carbonate weathering (red solid line); 3) a decline in the sink of Mg in marine clays (blue dashed line); 4) an increase in the Mg/Ca of silicate weathering (blue solid line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

water over the Cenozoic is sensitive to changes in the weathering and burial of Mg-carbonates but relatively insensitive to changes in the weathering and burial of Mg-silicates (Fig. 3, Figs. S10–S12, and Table 1). For example, when the 2–3 fold increase in seawater Mg/Ca is driven by a reduction in dolomitization or increase in Mg-carbonate weathering, the increase in Mg/Ca is associated with a $\sim 1\text{‰}$ drop in the $\delta^{26}\text{Mg}$ of seawater. In contrast, when the increase in seawater Mg/Ca is modeled by increasing the Mg/Ca of silicate weathering or suppressing the precipitation of Mg clays in the ocean, variations in the $\delta^{26}\text{Mg}$ of seawater are smaller and of the opposite sign. Sensitivity tests with different $\delta^{26}\text{Mg}$ values for carbonate weathering and/or dolomite can mute the predicted decline in $\delta^{26}\text{Mg}$ values in seawater over the Neogene, but they cannot reconcile the rise in seawater Mg with our record of variations in the Mg isotopic composition of bulk foraminifera (Figs. S10–S11).

These results suggest that rising seawater Mg/Ca and small changes in the $\delta^{26}\text{Mg}$ of seawater over the Neogene are best explained by an increase in the weathering of Mg-silicates or a decline in the formation and/or Mg content of marine clays. Lower rates of Mg-carbonate weathering and/or higher rates of dolomitization may help explain higher $\delta^{26}\text{Mg}$ values of seawater in the Paleogene, but the large and rapid increase in seawater Mg/Ca

and relatively constant Mg isotopic composition of seawater over the Neogene are best explained by changes in the cycling of Mg-silicates.

4. Discussion

4.1. Silicate weathering and the rise in seawater Mg/Ca

Is there evidence for large increase in the Mg flux from silicate weathering or a decline in the Mg sink in marine clays over the Cenozoic? The CO₂–silicate weathering thermostat (Walker et al., 1981) indicates that on timescales >100 kyr the flux of CO₂ into the ocean–atmosphere system from the Earth's interior sets the rate of global silicate weathering and the burial of calcium carbonate. Thus one way to increase the Mg flux from silicate weathering is to increase global silicate weathering rates by increasing net CO₂ sources over the Cenozoic. This is consistent with hypotheses that favor an increase in CO₂ sources and silicate weathering rates as a way to explain the Cenozoic rise in seawater ⁸⁷Sr/⁸⁶Sr and ^δ7Li (Misra and Froelich, 2012; Raymo and Ruddiman, 1992). These interpretations are non-unique (Kump, 1989). In addition, lowering pCO₂ while increasing CO₂ sources requires a link between CO₂ sources and increased silicate weatherability (k_{sil} in Eq. (S7)). While it may be possible to couple greater CO₂ sources to increased weatherability using processes such as sulfide oxidation and carbonate weathering associated with tectonic uplift (Torres et al., 2014), it seems unlikely that the magnitude of this effect is large enough to account for the 2–3 additional Tmol/yr of Mg required to explain the Cenozoic rise in seawater Mg.

An alternative way to increase the Mg flux from silicate weathering by 2–3 Tmol/yr over the Cenozoic is to increase the Mg content (or Mg/Ca ratio) of the silicate weathering flux. An increase in the Mg content of the silicate weathering flux could be achieved by either a shift toward the weathering of more mafic terrains or a reduction in the Mg content of secondary clays. Estimates of the Mg/Ca ratio of silicate weathering today range from 0.7 to 1.3 (Bernier and Bernier, 1996; Gaillardet et al., 1999). Model results indicate that the Mg/Ca of silicate weathering would need to increase by a factor of 5 to 10 to account for the rise in Cenozoic seawater Mg (Fig. 3), implying that the Mg/Ca of continental silicate weathering in the Cretaceous was 0.1 to 0.2. This value is extremely low – only 5 of the world's 62 largest rivers have Mg/Ca <0.2 (Gaillardet et al., 1999). In addition, reducing the Mg content of secondary clays to raise the Mg/Ca of the weathering flux appears to be inconsistent with the rise in the ^δ7Li of seawater over the Cenozoic as this record is thought to reflect an increase in the ^δ7Li of continental weathering due to an increase in the removal of Li (and presumably Mg) in secondary clays (Misra and Froelich, 2012).

One intriguing possibility is that modern rivers underestimate the Mg/Ca of silicate weathering due to underappreciated contributions from subaerial weathering of basalt or submarine weathering of peridotite (Dessert et al., 2005; Ligi et al., 2013; Snow and Dick, 1995). There are a number of potential mechanisms – for example an increase in peridotite weathering associated with an increase in the fraction of global seafloor spreading occurring at slow spreading rates or an increase in weathering of flood basalts (Kent and Muttoni, 2008) and/or island arcs. Further research into the quantitative importance of Mg fluxes in these environments and how they may have changed over the Cenozoic is warranted.

4.2. Low-temperature marine clays and the rise in seawater Mg/Ca

The role of Mg clays in the geochemical Mg cycle in the ocean is often limited to consideration of basalt alteration in high temperature axial hydrothermal systems and its dependence on the rate of

seafloor spreading (Bernier, 1994; Hardie, 1996). However, changes in the rate of seafloor spreading over the Cenozoic, and the Neogene in particular, appear to be too small to explain the rise in seawater Mg (Müller et al., 2011; Rowley, 2002). We therefore explore an alternative possibility – that the decline of the Mg sink in marine clays occurred predominately in low-temperature environments in the oceanic crust and marine sediments. We propose that the decline in the formation of low-temperature marine clays was due to the effect of cooler global temperatures on the Mg content and/or kinetics of clay formation in these environments.

4.2.1. The Mg sink in ridge-flank hydrothermal systems

The removal of seawater Mg in clays in low-temperature hydrothermal systems and marine sediments is a poorly quantified but large component of the global Mg cycle (Elderfield and Schultz, 1996; Mottl and Wheat, 1994; Sayles, 1979). Both experiments (Seyfried and Bischoff, 1979) and observations (Elderfield et al., 1999; Fisher and Wheat, 2010; Wheat and Fisher, 2008) indicate that Mg is removed from seawater by the formation of clay minerals during the alteration of oceanic crust at low and moderate temperatures. The size of the Mg sink in these systems depends on the kinetics of reactions between seawater and basalt and the flux of H₂O through ridge-flank hydrothermal systems (Mottl and Wheat, 1994). The magnitude of the H₂O flux through low-temperature hydrothermal systems in turn depends on heat flow from lithospheric cooling and the temperature at which the hydrothermal fluid circulates. Recent studies of the hydrogeology of ridge-flank hydrothermal systems on the Cocos Plate (Wheat and Fisher, 2008), and the flanks of the Juan de Fuca indicate warm spring vent fluid temperatures ranging from 10 to 64 °C. In addition, estimates of the average temperatures of ridge-flank hydrothermal systems from measurements surface heat flow and the ^δ18O values of hydrothermal calcite and aragonite veins indicate temperatures between 10 and 60 °C in oceanic crust of all ages (Johnson and Pruis, 2003; Gillis and Coogan, 2011). At these low temperatures, the fluid fluxes required to transport ~6–7 TW of ridge-flank heat flow (Stein and Stein, 1994) are immense, on the order of 10¹⁵ to 10¹⁶ kg H₂O/yr (continental runoff is ~5 × 10¹⁶ kg H₂O/yr).

Model reconstructions of the volume of ridge-flank hydrothermal systems since the Mesozoic (Müller et al., 2013) suggest that part of the reduction in the low-temperature Mg sink could be due to a decline in heat flow and H₂O fluxes associated with variations in seafloor spreading rates and ridge length through time. While this may contribute to changes in seawater Mg since the Cretaceous, we note that Müller et al. (2013) predict only a ~20% decline in H₂O fluxes over the Cenozoic, with almost no change since ~40 Ma, inconsistent with a large rise in seawater Mg over the Neogene.

We propose that the reduction in the Mg sink in ridge-flank hydrothermal systems was a consequence of a reduction in the average temperature in ridge-flank systems due to cooling of the deep ocean since the Eocene (Coogan and Gillis, 2013). This hypothesis requires that Mg uptake in low-temperature hydrothermal systems must be temperature dependent and that the temperature of these systems must respond to changes in deep ocean temperature. The available evidence suggests that both of these criteria are met in ridge-flank hydrothermal systems.

First, a compilation of data on the chemical composition of ridge-flank fluids indicates that the amount of Mg removed in these systems depends strongly on temperature between ~20 and 60 °C (Fisher and Wheat, 2010). This result is consistent with measurements of Mg/Ca ratios in hydrothermal carbonate veins that indicate a steep decline in the Mg/Ca of the fluid as ^δ18O temperatures increase from 10 to 45 °C (Coggon et al., 2010). The mechanism for temperature-dependent Mg removal in ridge-flank

systems is unknown, though we suspect that both kinetics and the mineralogy (i.e. the Mg content of the secondary mineral assemblage) may play a role. Second, a compilation of $\delta^{18}\text{O}$ temperatures in hydrothermal carbonate veins indicates a shift in the average and minimum temperatures from the Cretaceous through the Cenozoic of $\sim 10^\circ\text{C}$, broadly consistent with the magnitude of secular change in deep ocean temperature over that time (Gillis and Coogan, 2011).

4.2.2. The Mg sink in sedimentary authigenic clays

Evidence for Mg removal due to the formation of authigenic clays in marine sediments is abundant – pore-fluid profiles from shallow and deep marine environments show Mg depletion in the shallow subsurface due to uptake by clay minerals (Michalopoulos and Aller, 1995; Sayles, 1979) and diatoms incubated in shallow water siliclastic sediments from tropical river deltas are observed to rapidly convert to authigenic clays (Michalopoulos and Aller, 2004). However, extrapolation of these studies to global fluxes is difficult, and the importance of this sink in the Mg budget is highly uncertain. As noted by Mackenzie and Garrels (1966), a large flux of Mg from seawater could be accounted for by a small increase in the MgO content of shallow marine sediments. For example, given a sediment flux to the ocean of $1\text{--}2 \times 10^{16}$ g/yr (Milliman and Syvitski, 1992), an increase of 0.2–0.4 wt% MgO due to the formation of marine clays would represent a Mg sink of 1 Tmol/yr.

The temperature dependence of the Mg sink in marine sedimentary authigenic clays is unknown. We speculate that it is similar to temperature dependence of basalt alteration in ridge-flank hydrothermal systems, though we suspect that there are important differences that require further study. Sedimentary clay authigenesis is observed to depend on a number of variables such as reactive-Si supply (Michalopoulos, 2004) and the kinetics of clay dissolution-precipitation reactions (Mackin and Aller, 1984). A temperature-dependent Mg sink could arise from either of these processes or from changes in the mineralogy and/or Mg content of authigenic clay.

4.2.3. Marine Mg-clays as a link between seawater Mg/Ca and global climate

Considered in the context of the covariation of seawater Mg/Ca and climate, our hypothesis predicts that when the ocean is warm, rates of Mg-clay precipitation in low-temperature environments are high and seawater Mg/Ca is kept low. When cooler climates prevail, the removal of Mg in low-temperature marine clays is suppressed and seawater Mg/Ca rises. We explore the link between seawater Mg/Ca and climate in our box model by adding a temperature-dependent term to the parameterization of Mg removal in low-temperature clays (Eqs. S8c, S8d and Fig. 4). Using this empirical relationship and assuming all other variables remain constant the model reproduces to a first order the timing and magnitude of the increase in seawater Mg/Ca and associated changes in the $\delta^{26}\text{Mg}$ of seawater over the Cenozoic (Fig. 5). We model heavier $\delta^{26}\text{Mg}$ values during the Paleogene as reflecting either lower rates of Mg-carbonate weathering or increased dolomitization due to higher eustatic sea level and greater tropical shelf area (Walker et al., 2002). Although we cannot distinguish between these two possibilities they are both consistent with observations of a shallow carbonate compensation depth (CCD) in the Paleogene (van Andel, 1975).

Modeled rates of the Mg sink in marine clays are broadly consistent with available geochemical and geophysical constraints on the abundance of authigenic clays in marine sediments and altered oceanic crust. Considering only the low-temperature hydrothermal sink, the highest rates of Mg removal in the model (~ 3 Tmol/Mg/yr), if assumed to occur over the upper ~ 1 km of newly formed oceanic crust, would be equivalent to filling a rock

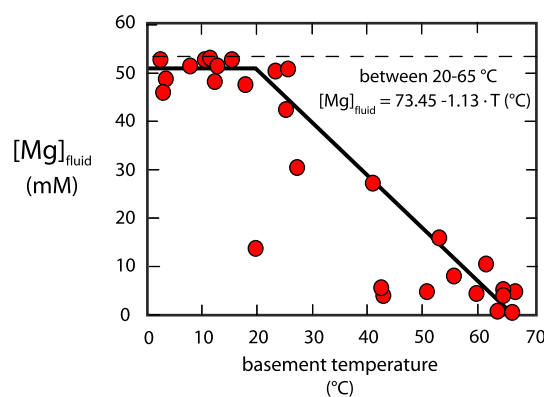


Fig. 4. Concentrations of Mg versus temperature in upper oceanic crust ridge-flank fluids from a compilation of pore water and borehole samples. Taken from Fisher and Wheat (2010). The temperature-dependence used in the model is shown by the solid black line. Alternative parameterizations of the temperature-dependence are possible without changing the conclusions here as long as the temperatures at which low-temperature alteration occurs are sensitive to the temperature of the deep ocean.

with 18% porosity with alteration products containing on average 8 wt% MgO. These values are consistent with studies of altered oceanic crust that show little change in the bulk MgO content (Kelley et al., 2003) but large declines in porosity (Carlson and Herrick, 1990) (Figs. S13–S14). However, we note that estimates of the size of the Mg sink associated with low-temperature alteration of the oceanic crust from compilations of the chemistry of altered and fresh samples in drilled sections of upper oceanic crust from DSDP/ODP sites 417/418 (Spivack and Staudigel, 1994), 504B (Alt et al., 1986), and 801 (Kelley et al., 2003) and sampled ophiolite sections in Cyprus (Bednarz and Schmincke, 1990) vary considerably. ODP sites 504B and the Troodos ophiolite both indicate net uptake of Mg from seawater, whereas sites 417/418 and 504B show either no change or a slight loss of Mg to seawater. The magnitude of the estimated low-temperature Mg sink in these studies is generally ≤ 1 Tmol/Mg/yr, suggesting that if representative of the oceanic crust as a whole, our maximum modeled fluxes of 3 Tmol/yr may be too large. However, the errors in these calculations may be large and systematic given difficulties in estimating the average degree of alteration in a core, the small number of sites that have been drilled, and the fact that much of the fluid flow (and alteration) may be concentrated in thin very permeable zones which are under sampled (Fisher and Becker, 2000; Fisher and Wheat, 2010).

The ~ 3 Tmol/Mg/yr flux in the model, if consumed entirely by the formation of authigenic sedimentary clays, would increase the average detrital sediment Mg content by 0.6 to 1.2 wt% MgO. This is equivalent to a 17–40% increase in Mg content for an average shale (2.5 to 3.5 wt% MgO; Gromet et al., 1984). Evidence for an enhanced Mg sink in authigenic marine clays in the Cretaceous and Paleogene comes from peaks in both shallow and deep-sea sediments in the abundance of authigenic palygorskite, a clay mineral that contains up to 12 wt% Mg and whose appearance in deep-sea marine sediments has been attributed to warmer bottom water temperatures (Couture, 1977; Pletsch et al., 1996; Thiry and Pletsch, 2011).

5. Conclusions

Covariation between the Mg/Ca of seawater and climate over Phanerozoic time suggests a fundamental link between the major element chemistry of seawater, the global carbon cycle, and climate. Reconstructions of the Mg isotopic composition of seawater using measurements of the Mg isotopic composition of pelagic car-

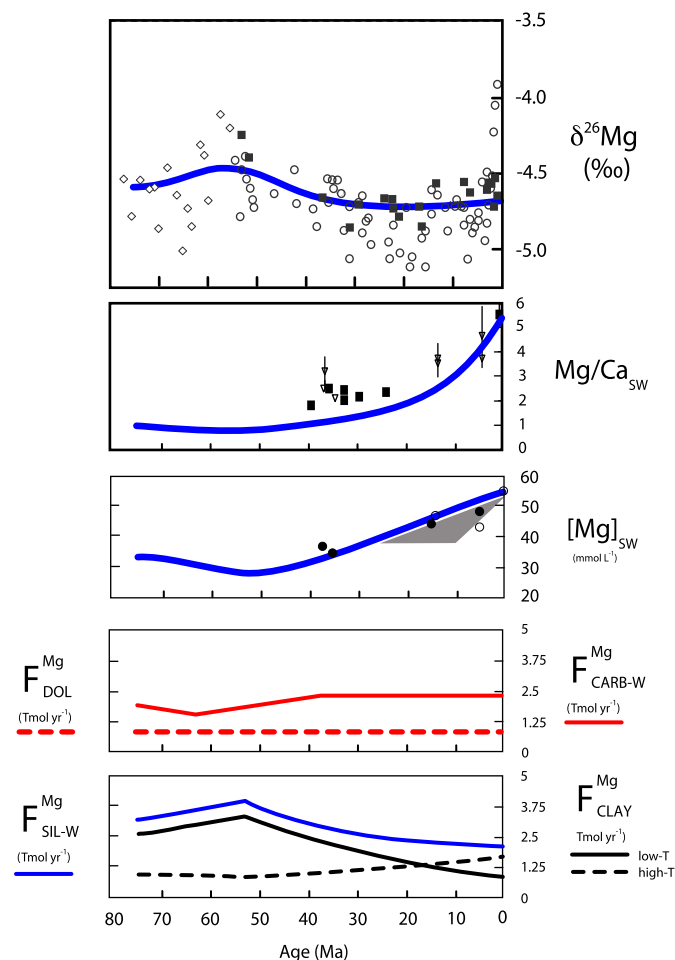


Fig. 5. Model output for our preferred scenario for reconstructed changes in the concentration and isotopic composition of Mg in seawater over the Cenozoic. Reconstructions of Mg/Ca ratios and $[Mg]_{sw}$ over the Cenozoic taken from the published literature (see text for details).

bonates indicate that seawater Mg/Ca has increased by a factor of 2–3 over the Cenozoic and that this increase has been accompanied by small changes in the $\delta^{26}Mg$ value of seawater. Changes in Mg/Ca and Mg isotopes over the Cenozoic cannot be explained by changes in carbonate weathering or deposition; the increase in Mg/Ca over the Cenozoic is best explained by a change in the cycling of Mg-silicates. There are two possibilities – an increase in Mg sources from silicate weathering or a decrease in Mg sinks in low-temperature authigenic sedimentary and hydrothermal marine clays. We favor a decline in Mg sinks in authigenic marine clays due to the effect of cooler deep-ocean temperatures on the kinetics and/or Mg content of the clay sink. This mechanism provides a link between the Mg/Ca of seawater and global climate that does not depend on the cause of climatic change with broad implications for our understanding of the processes that regulate the chemistry of seawater on geologic timescales.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2015.01.003>.

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