

A Cenozoic record of seawater Mg isotopes in well-preserved fossil corals

Anne M. Gothmann¹, Jarosław Stolarski², Jess F. Adkins³, and John A. Higgins¹

¹Department of Geosciences, Princeton University, Guyot Hall, Princeton, New Jersey 08544, USA

²Institute of Paleobiology, Polish Academy of Sciences, Twarda 51/55, 00-818, Warsaw, Poland

³Division of Geological and Planetary Sciences, California Institute of Technology, 1200 East California Boulevard, Pasadena, California 91125, USA

ABSTRACT

Reconstructions of seawater Mg isotopic composition ($\delta^{26}\text{Mg}$) can provide novel insights into the processes that control the major ion chemistry of seawater over geologic time scales. A key period of interest is the Cenozoic (ca. 65 Ma to today), during which the Mg/Ca ratio of seawater increased by a factor of 2–3. However, two published records of seawater $\delta^{26}\text{Mg}$ over the Cenozoic disagree, making it difficult to draw conclusions about mechanisms driving seawater Mg/Ca change over the past 65 m.y. Here we present a new record of seawater $\delta^{26}\text{Mg}$ from a set of well-preserved fossil corals, ranging in age from Paleocene to Recent. Fossil coral $\delta^{26}\text{Mg}$ decreases by $\sim 0.3\text{‰}$ between the early Cenozoic and the Oligocene, then increases by $\sim 0.15\text{‰}$ between the Oligocene and present, in strong agreement with the published record derived from bulk pelagic carbonate. Together with this existing record, our fossil coral data suggest that the rise in $[\text{Mg}]_{\text{seawater}}$ over the Cenozoic was mainly driven by an increase in Mg silicate weathering or a decline in Mg uptake in marine silicates. In contrast, we suggest that changes in the rate of carbonate weathering and dolomite formation likely played a minor, but not insignificant, role in the global Mg cycle over the Cenozoic.

INTRODUCTION

Reconstructions of $[\text{Mg}]$ in seawater (sw) over the Cenozoic from fluid inclusions in marine evaporites (Lowenstein et al., 2001) and deep-sea pore-fluid profiles (Higgins and Schrag, 2012; Fantle and DePaolo, 2006) show an increase of $\sim 60\%$, from 30 mM ca. 60 Ma to 53 mM in the modern ocean. This increase in $[\text{Mg}]$ is accompanied by a decrease in seawater $[\text{Ca}]$, leading to a factor of $\sim 2\text{--}3$ increase in the Mg/Ca ratio during the Cenozoic (Fig. 1A). While the mechanisms responsible for these observed changes remain enigmatic, they coincide with other major changes in the Earth system, including eustatic sea level, the mineralogy of inorganically precipitated calcium carbonates and evaporites, continental configuration, global greenhouse gases, and climate (Gothmann et al., 2015; Lowenstein et al., 2001; Holland and Zimmerman, 2000).

The increase in seawater Mg over the Cenozoic implies a sustained imbalance between geologic sources of Mg (carbonate and silicate weathering) and sinks (Mg-rich marine silicate minerals and dolomite) (Holland and Zimmerman, 2000; Tipper et al., 2006a). A simplified case for this imbalance can be mathematically expressed as follows:

$$dM_{\text{Mg}_{\text{sw}}} / dt = F_{\text{riv}} - F_{\text{dol}} - F_{\text{silicate}} > 0, \quad (1)$$

where F_{riv} is the river flux of Mg, F_{dol} and F_{silicate} are the fluxes of Mg removed from seawater by the dolomite and marine silicate sinks, respectively, t is time, and sw is seawater. The silicate flux includes basalt alteration at low and high temperatures, as well as authigenic clay formation.

Changes in each of the flux terms in Equation 1 have been invoked to explain the Cenozoic $[\text{Mg}]_{\text{sw}}$ increase. One suggestion is that the

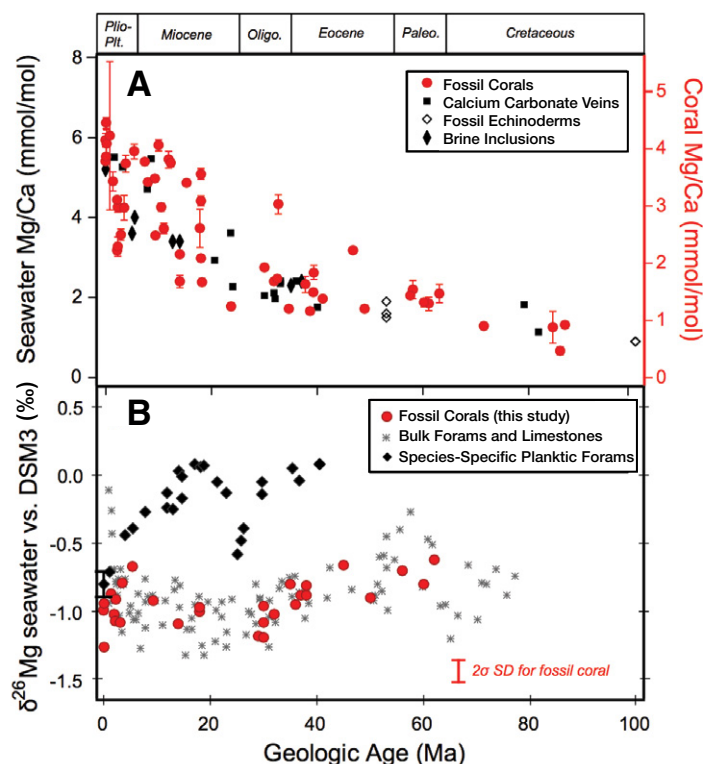


Figure 1. A: Reconstructions of $\text{Mg}/\text{Ca}_{\text{sw}}$ (sw—seawater). Coral error bars denote the 2σ standard error from multiple secondary ion mass spectrometry measurements on the same sample. Uncertainties in growth temperature for fossil corals may account for additional $\sim \pm 25\%$ variability in Mg/Ca data (Gothmann et al., 2015). Fluid inclusion data are from Lowenstein et al. (2001), Brennan et al. (2013), and Timofeeff et al. (2006). Echinoderm data are from Dickson (2004). Hydrothermal carbonate vein data are from Coggon et al. (2010) and Rausch et al. (2013). Fossil coral data are from Gothmann et al. (2015). **B: Cenozoic records of $\delta^{26}\text{Mg}_{\text{sw}}$.** DSM3— ^{26}Mg isotope standard. All coral data (red circles) are converted to seawater values assuming a constant fractionation of -0.9‰ (this study; Saenger and Wang, 2014; Wombacher et al., 2011). Seawater $\delta^{26}\text{Mg}$ records from Higgins and Schrag (2015) and Pogge von Strandmann et al. (2014) are also shown (asterisks and diamonds, respectively). Bulk foraminifera, limestone, and species-specific foraminifera $\delta^{26}\text{Mg}$ data are converted to seawater values using modern fractionation factors. The error bar on the modern planktic foraminifera average corresponds to the uncertainty in the fractionation applied to the record from Pogge von Strandmann et al. (2014), based on a core-top calibration with *Orbulina universa*. Errors shown for fossil coral correspond to the long-term reproducibility of our in-house standard ($\pm 0.11\text{‰}$, 2σ standard deviation, SD). Pit—Pleistocene; Plio—Pliocene; Oligo—Oligocene; Paleo—Paleocene.

Mg/Ca ratio of rivers (due to changes in carbonate and silicate weathering) increased between ca. 65 Ma and today (Ligi et al., 2013). Others hypothesized that the increase resulted from a decrease in the flux of Mg removed from seawater as dolomite going forward in time (Wilkinson and Algeo, 1989). Third, it has been proposed that the seawater Mg/Ca rise was driven by a decrease in rates of Mg uptake during hydrothermal alteration or formation of marine authigenic clay (e.g., Higgins and Schrag, 2015). It is possible to group these hypotheses into those focusing on (1) flux terms related to silicate minerals, and (2) flux terms related to carbonate minerals.

Mg isotopes ($^{26}\text{Mg}/^{24}\text{Mg}$ and $^{25}\text{Mg}/^{24}\text{Mg}$) offer a way of distinguishing between hypotheses that focus on silicate fluxes and carbonate fluxes because Mg silicates and Mg carbonates have very different $\delta^{26}\text{Mg}$ values (Higgins and Schrag, 2010, 2015; Pogge von Strandmann et al., 2014). Studies of $\delta^{26}\text{Mg}$ fractionation associated with secondary Mg silicate formation during weathering on land, authigenic precipitation in the water column, or basalt alteration indicate that clays preferentially incorporate ^{26}Mg ($\delta^{26}\text{Mg}_{\text{fluid}} - \delta^{26}\text{Mg}_{\text{silicate}} = \epsilon_{\text{silicate}} \sim 0\text{‰}$ to -1.25‰ ; Tipper et al., 2006a; Higgins and Schrag, 2010; Wimpenny et al., 2014). In contrast, studies of Mg carbonates suggest a strong discrimination against ^{26}Mg ($\delta^{26}\text{Mg}_{\text{fluid}} - \delta^{26}\text{Mg}_{\text{carb}} = \epsilon_{\text{fluid-carb}} \sim +1\text{‰}$ to $+4\text{‰}$; Higgins and Schrag, 2015; Galy et al., 2002; Tipper et al., 2006b). Small single-lithology rivers also suggest that silicate weathering products are isotopically distinct (heavier) than carbonate weathering products (Tipper et al., 2006b). Thus, together with records of $\text{Mg}/\text{Ca}_{\text{sw}}$, records of $\delta^{26}\text{Mg}_{\text{sw}}$ can be a powerful tool to test the importance of silicate versus carbonate fluxes for regulating seawater major ion chemistry. It is important to clarify that reconstructions of $\delta^{26}\text{Mg}_{\text{sw}}$ cannot be used to test the relative importance of changes in silicate weathering versus silicate output fluxes as controls on $[\text{Mg}]_{\text{sw}}$. Likewise, it cannot be used to distinguish between changes in carbonate weathering versus dolomite formation through time. Including Mg isotopes in the mass balance given by Equation 1, assuming steady state [$d(\delta^{26}\text{Mg}_{\text{sw}})/dt = 0$], and solving for $\delta^{26}\text{Mg}_{\text{sw}}$ yields:

$$d(\delta^{26}\text{Mg}_{\text{sw}})/dt = F_{\text{riv}} \times (\delta^{26}\text{Mg}_{\text{riv}}) - F_{\text{dol}} \times (\delta^{26}\text{Mg}_{\text{sw}} - \epsilon_{\text{dol}}) - F_{\text{silicate}} \times (\delta^{26}\text{Mg}_{\text{sw}} - \epsilon_{\text{silicate}}), \quad (2)$$

and

$$\delta^{26}\text{Mg}_{\text{sw}} = \delta^{26}\text{Mg}_{\text{riv}} + \epsilon_{\text{dol}} \times f_{\text{dol}} + \epsilon_{\text{silicate}} \times (1 - f_{\text{dol}}), \quad (3)$$

where $\delta^{26}\text{Mg}_{\text{sw}}$ is the isotopic composition of seawater, $\delta^{26}\text{Mg}_{\text{riv}}$ is the isotopic composition of Mg from rivers, ϵ_{dol} and $\epsilon_{\text{silicate}}$ are the fractionations associated with the formation of dolomite and secondary silicate minerals (i.e., clays), and f_{dol} is the fraction of Mg that leaves the ocean as dolomite. Here we group carbonate and silicate weathering components into a single term: $F_{\text{riv}} \times (\delta^{26}\text{Mg}_{\text{riv}})$. Inspection of Equation 3 indicates that changing $[\text{Mg}]_{\text{sw}}$ by changing the dolomite output flux should have an effect on seawater $\delta^{26}\text{Mg}$ that is of a larger magnitude (and opposite direction) than the effect of changing the silicate output flux. Similarly, a change toward more silicate-dominated rivers would shift $\delta^{26}\text{Mg}_{\text{riv}}$ toward heavier values.

There are two published records of seawater $\delta^{26}\text{Mg}$ for the Cenozoic (Higgins and Schrag, 2015; Pogge von Strandmann et al., 2014), but they are in disagreement. A $\delta^{26}\text{Mg}$ record from species-specific planktic foraminifera (Pogge von Strandmann et al., 2014) shows three large and relatively rapid changes in seawater $\delta^{26}\text{Mg}$ over the past 40 m.y. (black diamonds, Fig. 1B). In contrast, a seawater $\delta^{26}\text{Mg}$ reconstruction from bulk foraminifera and limestones (Higgins and Schrag, 2015) indicates more modest, $\pm 0.15\text{‰}$, changes about the modern value over the past ~ 60 m.y. These two records also point to different geological mechanisms as drivers of seawater Mg/Ca change. The species-specific record is interpreted as reflecting a large decrease in dolomitization rates between ca. 20 Ma and today. The bulk pelagic carbonate record is interpreted to reflect the

dominance of silicate processes at play over the course of the Cenozoic, due to the small ($\sim \pm 0.15\text{‰}$) variations of inferred seawater $\delta^{26}\text{Mg}$ about the modern value. A record of Mg isotopes from well-preserved fossil corals can offer an independent constraint on seawater $\delta^{26}\text{Mg}$. Studies of $\delta^{26}\text{Mg}$ in modern corals suggest that fossil corals should faithfully track $\delta^{26}\text{Mg}_{\text{sw}}$. Corals exhibit a relatively constant fractionation factor regardless of species, with an $\sim \pm 0.2\text{‰}$ range in the isotopic composition of modern corals measured to date ($n = 51$) (Saenger and Wang, 2014). The coral Mg isotope fractionation factor is also within uncertainty of the inorganic aragonite fractionation factor (Saenger and Wang, 2014).

SAMPLES AND METHODS

Well-preserved fossil corals measured for $\delta^{26}\text{Mg}$ range in age from Paleocene to Recent (Gothmann et al., 2015; see the GSA Data Repository¹). Coral samples weighing ~ 2 – 5 mg were chipped from hand specimens, powdered using a mortar and pestle, and dissolved in 1N HNO_3 . To isolate Mg from the CaCO_3 matrix, samples were processed using either a two-step ion-exchange gravity column method or a Thermo Scientific Dionex DCS5000+ ion chromatography system (Husson et al., 2015). Both methods have been shown to isolate Mg without additional isotopic fractionation. $\delta^{26}\text{Mg}$ analyses were conducted using a Thermo Scientific Neptune Plus multicollector–inductively coupled plasma–mass spectrometer (MC-ICP-MS) at Princeton University (USA) as described by Husson et al. (2015). Sample Mg isotope compositions were referenced to the DSM3 isotope standard (Young and Galy, 2004). For additional methodological details and assessments of quality control, see the Data Repository.

RESULTS AND DISCUSSION

$\delta^{26}\text{Mg}$ Records

Results of fossil coral $\delta^{26}\text{Mg}$ analyses are presented in Figure 1B. Data were converted to inferred seawater values by assuming a constant fractionation factor over time between coral aragonite and seawater equal to -0.9‰ . This value is consistent with previous studies (Saenger and Wang, 2014; Wombacher et al., 2011). Cenozoic cooling is not expected to significantly bias coral-based seawater $\delta^{26}\text{Mg}$ records. Initial studies investigating coral $\delta^{26}\text{Mg}$ -temperature relationships found a very minor dependence of $+0.001\text{‰ } ^\circ\text{C}^{-1}$ (Wombacher et al., 2011). Considering this sensitivity, estimated ~ 4 $^\circ\text{C}$ Cenozoic cooling of subtropical sea-surface temperatures since the Eocene (Keating-Bitonti et al., 2011) would translate to an $\sim 0.004\text{‰}$ change in coral $\delta^{26}\text{Mg}$ fractionation. More recent work suggests that inorganic aragonite exhibits a greater sensitivity of $+0.01\text{‰ } ^\circ\text{C}^{-1}$, and measurements of subannually sampled coral suggest that the sensitivity could be as large as $\sim +0.03\text{‰ } ^\circ\text{C}^{-1}$, possibly as a result of seasonal changes in Mg-rich fluid-inclusion incorporation (Saenger and Wang, 2014). If the larger dependences apply, then cooling could drive changes in coral $\delta^{26}\text{Mg}$ of $\sim \pm 0.1\text{‰}$, similar to analytical uncertainties (Husson et al., 2015).

The fossil coral record and the bulk foraminifera and limestone record (Higgins and Schrag, 2015) are in excellent agreement over the Cenozoic. Both reconstructions show a small decline in seawater $\delta^{26}\text{Mg}$ values between 65 and 30 Ma and a slight rise from 30 Ma to the present. Given the many differences between the two archives (e.g., mineralogy, preservation histories, distinct Mg isotope vital effects for corals and foraminifera), the observed agreement provides strong evidence that the two archives accurately record changes in the $\delta^{26}\text{Mg}$ of seawater over the past 65 m.y.

In contrast, there is considerable disagreement between the species-specific record and the records from fossil corals and bulk carbonates. The

¹GSA Data Repository item 2017356, extended methods, Figure DR1 (triple isotope plot for Mg), Figure DR2 (comparison of Mg/Ca ratios measured by SIMS and ICP-MS), Figures DR3–DR5 (additional model scenarios to explore Mg isotope records), Table DR1 (Mg isotope results), and Table DR2 (model parameters and initial conditions), is available online at <http://www.geosociety.org/datarepository/2017/> or on request from editing@geosociety.org.

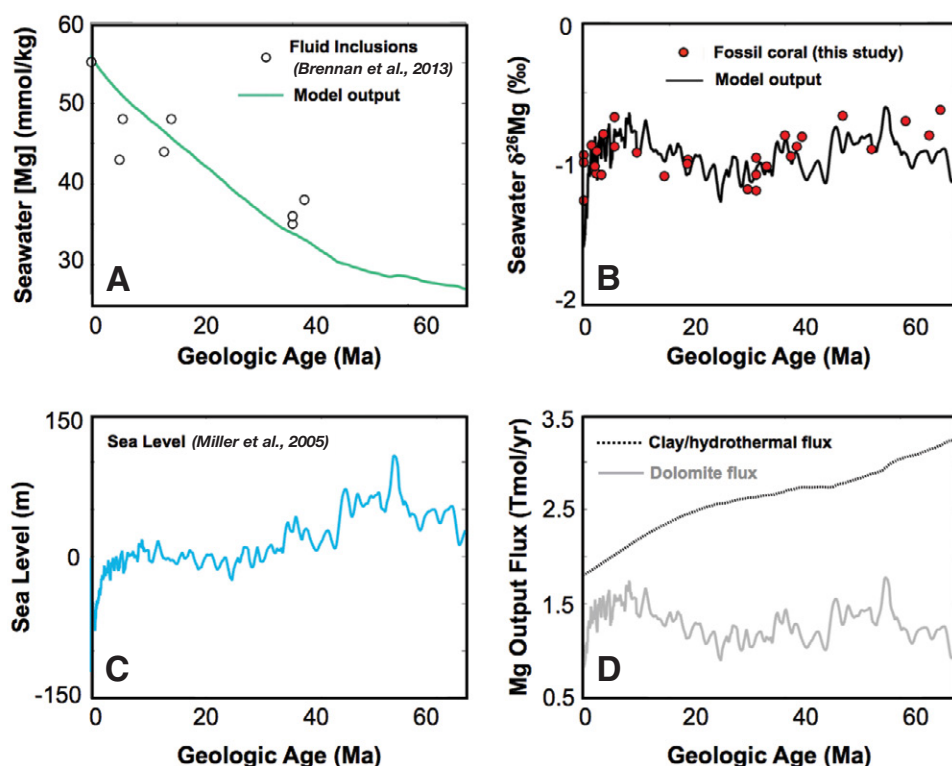


Figure 2. A: Reconstructions of $[Mg]_{sw}$ (sw—seawater) from Brennan et al. (2013) and results of our model history for $[Mg]_{sw}$ (green dashed line). B: Record of $\delta^{26}Mg_{sw}$ from fossil coral and model results (black line). C: Reconstructed sea level used in the model for the size of the dolomite sink in meters relative to modern. Sea-level data were smoothed from the compilation of Miller et al. (2005) using a running 1 m.y. average. D: Model output for dolomite and clay hydrothermal fluxes. River input of Mg and $\delta^{26}Mg$ is assumed to be constant.

source of this disagreement is uncertain, but possibilities include vital effects and diagenetic alteration. The range in $\delta^{26}Mg$ values in modern planktic foraminifera is $>1.5\text{‰}$, indicating a large role for vital effects in foraminifera, possibly related to active discrimination against uptake of Mg into foraminiferal calcite (Pogge von Strandmann et al., 2014). While species-specific groups show a smaller range (*Globigerinoides sacculifer* $\sim 0.6\text{‰}$, *Globorotalia tumida* $\sim 0.5\text{‰}$, *Globigerinoides ruber* $\sim 0.3\text{‰}$), it is still larger than the range shown across all corals (Pogge von Strandmann et al., 2014; Saenger and Wang, 2014). Pogge von Strandmann et al. (2014) assumed that vital effects remain constant with time, but the large magnitude of foraminifera vital effects suggests that this may not be a good assumption, especially considering that $[Mg]_{sw}$, an important boundary condition, varies over the same period of time. Recrystallization of foraminiferal calcite is another possible explanation for the disagreement between the records. Whereas fossil coral samples were screened for diagenetic alteration using seven different techniques (Gothmann et al., 2015; see the Data Repository), species-specific foraminifera were screened using Sr/Ca ratios and visual inspection (Pogge von Strandmann et al., 2014). Neither of these two metrics is sufficiently diagnostic to eliminate the possibility of diagenesis. Previous studies on bulk carbonate sediments have shown that recrystallization is associated with fractionation factors as great as 4‰ for $\delta^{26}Mg$ (Higgins and Schrag, 2012, 2015). While the effects of diagenetic alteration can be corrected in bulk sediment records where recrystallization rates can be quantified using pore-fluid profiles and diagenetic models (Higgins and Schrag, 2012, 2015), this is not the case for species-specific records because the degree of alteration may vary significantly from sample to sample. The effects of recrystallization on the $\delta^{26}Mg$ value of a particular foraminifera species will also be species dependent because they depend on the difference between the $\delta^{26}Mg$ value of that species and the $\delta^{26}Mg$ value of the diagenetic calcite.

Implications for the Controls on Cenozoic Seawater Chemistry

As discussed in Higgins and Schrag (2015), small changes in seawater $\delta^{26}Mg$ indicate that the partitioning of Mg between carbonate and silicate sources and sinks has not changed greatly over the Cenozoic. In

the modern ocean, the principal sink for Mg is altered silicates and the major source is continental silicate weathering (Tipper et al., 2006b). As a result, it is likely that most of the rise in seawater Mg/Ca over the Cenozoic (Fig. 1A) was driven by changes in the cycling of Mg silicates. The data set presented here, however, is not able to distinguish whether the changes are driven by silicate weathering or by the silicate output flux.

While our results indicate that silicate fluxes dominate the Cenozoic seawater Mg budget, some of the minor variability in seawater $\delta^{26}Mg$ may be due to changes in carbonate weathering rates and/or dolomite formation. Several previous researchers have drawn connections between sedimentary dolomite abundances and records of global sea level (e.g., Holland and Zimmerman, 2000). Formation of dolomite is favored and carbonate weathering is suppressed during times of high sea level due to the greater extent of shallow seaways (e.g., Mackenzie and Morse, 1992). To explore the minor variability in our coral record and in the bulk carbonate record of Higgins and Schrag (2015), we consider one of many possible scenarios for how carbonate and silicate fluxes may have changed over the Cenozoic. We used a simple one box model (see the Data Repository for details), based on Equations 1 and 2, to examine whether the timing and rates of changes in Cenozoic sea level are compatible with our record of seawater $\delta^{26}Mg$ (Fig. 2). In the model we assume that the flux of Mg to seawater from rivers and its isotopic composition are constant through time. It is unclear whether this assumption is appropriate, but as noted in Tipper et al. (2006b), there is not a clear relationship between lithology and riverine $\delta^{26}Mg$, or climate and riverine $\delta^{26}Mg$, at a global scale. We also prescribe that rates of Mg uptake in marine silicates decrease between the early Cenozoic and the present such that the model increase in $[Mg]_{sw}$ matches records from fluid inclusions (Brennan et al., 2013). A similar result would be achieved if rates of Mg silicate weathering were increased toward the present. Rates of dolomitization are parameterized to have a primary dependence on both the global sea-level curve (Miller et al., 2005) and $[Mg]_{sw}$.

We find that the model-derived $\delta^{26}Mg$ curve, which is influenced both by a decrease in Mg uptake in marine silicates and changing dolomitization rates, varies as a function of global sea level and agrees well with

$\delta^{26}\text{Mg}$ records derived from fossil coral samples and from bulk carbonates. We also note that the required changes in dolomitization rates are small ($\pm 35\%$) compared to predictions based on records of sedimentary abundance over the Cenozoic (e.g., 200%; Holland and Zimmerman, 2000). We note again that this model case describes one of many possible histories, and that it is strongly dependent on the assumptions and parameterizations described here and in the Data Repository. For example, removal of $\sim 25\%$ more Mg as dolomite in the early Cenozoic as compared with today, combined with a decrease in the silicate Mg flux between 35 Ma and today, could also explain our record (see Fig. DR5). Nevertheless, all scenarios demonstrate that silicate fluxes likely dominate the rise in seawater Mg/Ca over the Cenozoic, $\sim 75\%$ of which occurs between 35 Ma and today, whereas changes in carbonate flux terms are of secondary importance.

CONCLUSIONS

We find that well-preserved aragonitic fossil corals are robust recorders of past seawater $\delta^{26}\text{Mg}$ and use this archive to distinguish between two existing histories of Cenozoic seawater $\delta^{26}\text{Mg}$. The fossil coral $\delta^{26}\text{Mg}$ record shows $\pm 0.15\%$ change over the Cenozoic and agrees with the published record from bulk carbonates. Together, these records suggest that the increase in $[\text{Mg}]_{\text{sw}}$ between the early Cenozoic and today must have been driven primarily by changes in Mg cycling in silicate rocks. However, the small, $\pm 0.15\%$, variations in inferred seawater $\delta^{26}\text{Mg}$ may be related to changing rates of dolomitization.

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