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# Modern and Cenozoic records of magnesium behaviour from foraminiferal Mg isotopes

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**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Magnesium is an element critically involved in the carbon cycle, because weathering of Ca–Mg silicates removes atmospheric CO<sub>2</sub> into rivers, and formation of Ca–Mg carbonates in the oceans removes carbon from the ocean–atmosphere system. Hence the Mg cycle holds the potential to provide valuable insights into Cenozoic climate-system history, and the shift during this time from a greenhouse to icehouse state. We present Mg isotope ratios for the past 40 Myr using planktic foraminifers as an archive. Modern foraminifera, which discriminate against elemental and isotopically heavy Mg during calcification, show no correlation between the Mg isotope composition ( $\delta^{26}\text{Mg}$ ) and temperature, Mg/Ca or other parameters such as carbonate saturation ( $\Delta\text{CO}_3$ ). However, inter-species isotopic differences imply that only well-calibrated single species should be used for reconstruction of past seawater. Seawater  $\delta^{26}\text{Mg}$  inferred from the foraminiferal record decreased from  $\sim 0\text{‰}$  at 15 Ma, to  $-0.83\text{‰}$  at the present day, which coincides with increases in seawater lithium and oxygen isotope ratios. It strongly suggests that neither Mg concentrations nor isotope ratios are at steady-state in modern oceans, given its  $\sim 10$  Myr residence time. From these data, we have developed a dynamic box model to understand and constrain changes in Mg sources to the oceans (rivers) and Mg sinks (dolomitisation and hydrothermal alteration). Our estimates of seawater Mg concentrations through time are similar to those independently determined by pore waters and fluid inclusions. Modelling suggests that dolomite formation and the riverine Mg flux are the primary controls on the  $\delta^{26}\text{Mg}$  of seawater, while hydrothermal Mg removal and the  $\delta^{26}\text{Mg}$  of rivers are more minor controls. Using riverine flux and isotope ratios inferred from the  $^{87}\text{Sr}/^{86}\text{Sr}$  record, the modelled Mg removal by dolomite formation shows minima in the Oligocene and at the present day (with decreasing trends from 15 Ma), both coinciding with rapid decreases in global temperatures.

### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



# 1 Introduction

The weathering of Ca–Mg silicates sequesters atmospheric CO<sub>2</sub> and controls long-term climate (Walker et al., 1981; Berner et al., 1983; Kump et al., 2000). In turn, the history of weathering on land is partly reflected by the Mg evolution of the ocean, recorded by marine carbonates. Given that Mg is critically involved in the long-term carbon cycle, studying Mg offers advantages over trace elements that are not involved so directly, such as strontium or osmium isotopes (Palmer and Edmond, 1992; Levasseur et al., 1999; Georg et al., 2013). The dominant Mg source to the oceans is thought to be continental weathering, via rivers and groundwaters, while the main sinks are removal by hydrothermal fluids, dolomite formation and low-temperature clay formation during alteration of the oceanic crust (Holland, 2005).

Reconstructing past seawater Mg concentrations through time, however, demands deconvolving Mg uptake by these carbonate archives as well as variations in Mg sources and sinks to seawater (Holland, 2005). Importantly, the fundamental question whether Mg in the oceans is in steady-state is still unanswered (Holland, 2005; Tipper et al., 2006b), although most recent studies suggest that seawater Mg concentrations are rapidly evolving with time (Coggon et al., 2010; Higgins and Schrag, 2012; Horita et al., 2002; Fantle and DePaolo, 2006).

The various seawater sources and sinks have different Mg isotope ratios, providing the basis for using Mg isotopes to understand long-term Mg cycling. The flux-weighted mean riverine input has a  $\delta^{26}\text{Mg}$  (‰ deviation of the sample  $^{26}\text{Mg}/^{24}\text{Mg}$  ratio from the standard DSM-3) that is intermediate between that of silicate and carbonate sources. Additional fractionation is caused by Mg uptake into plants, or into secondary minerals formed during weathering (Tipper et al., 2006a, b, 2008, 2010; Pogge von Strandmann et al., 2008, 2011, 2012; Teng et al., 2010a, b; Huang et al., 2012; Black et al., 2006; Bolou-Bi et al., 2010, 2012). Modern oceans, which are isotopically uniform (Foster et al., 2010; Young and Galy, 2004), have an isotope ratio similar to the riverine input. Quantitative removal of Mg from the oceans (i.e., causing no isotope fractionation,

BGD

11, 7451–7484, 2014

Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

(Table 1). The ages are based on the shipboard age models (Zachos et al., 2004). No single species is available throughout the record and hence we spliced records derived from *O. universa* and *Globigerina venezuelana*. Specimens with minimal overgrowths or diagenetic infilling were selected. Given the very long ( $\sim 10$  Myr) modern ocean residence time of Mg (Berner and Berner, 1996), sampling resolution was  $\sim 5$  Myr overall, with up to 1 Myr resolution across the middle Miocene when other isotope systems, such as Li, show major changes which have been related to weathering (Misra and Froelich, 2012).

Assuming that the Mg isotope fractionation from seawater stays constant for individual species through time, our data set allows us to splice together data from *O. universa* from 0–14.7 Ma, and from *G. venezuelana* from 5–40 Ma. We assessed for possible offsets between these species by analysing them from the same samples (1264A 17H6 and 19H1, as well as core-top samples for *O. universa*). The variability in  $\delta^{26}\text{Mg}$  in core-top *O. universa* from this study and Pogge von Strandmann, 2008 is  $\pm 0.18\%$  (2 s.d.), and combined with the analytical uncertainty of  $\delta^{26}\text{Mg}$  in modern seawater ( $\pm 0.06\%$ , 2 s.d., Foster et al., 2010) and of the foraminifer samples themselves (0.01–0.14‰) this gives a compound uncertainty of  $\pm 0.21\%$  on the correction factors applied.

## 2.2 Methods

Our methods of cleaning and chemical purification of foraminiferal carbonate have been published in detail elsewhere (Pogge von Strandmann, 2008). Briefly,  $\sim 20$  tests were picked per sample, crushed and cleaned in methanol and  $18.2\text{M}\Omega$   $\text{H}_2\text{O}$  to remove clays, followed by heating with ammonia buffered with 1%  $\text{H}_2\text{O}_2$  to remove organics. The samples was then split, with  $\sim 50\%$  taken for trace element analysis on an Element 2 Sector ICP-MS (inductively coupled plasma mass spectrometer), with samples matrix-matched against multi-element standards produced from individual high-purity single element standards, with an intercalibrated in-house standard (BSGS, Ni et al., 2007), and the international carbonate reference standard JLs-1 as assessments of

**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

accuracy. These analyses are necessary not just to acquire elemental ratios important for interpretation (e.g. Mg/Ca), but also to determine whether silicate clays have been sufficiently removed to not affect Mg isotope ratios. Many clays contain high Mg abundances with isotope ratios significantly different from that of carbonate, and hence clay content was assessed by determining Al/Ca and Mn/Ca ratios (Pogge von Strandmann, 2008). Low Al and Mn abundances are the main reason 50 % of sample was dedicated to concentration analyses. Low Al/Ca ( $< 300 \mu\text{mol mol}^{-1}$ , Pogge von Strandmann, 2008, where most samples  $< 50 \mu\text{mol mol}^{-1}$ ) and Mn/Ca and a lack of a positive correlation between Al/Ca or Mn/Ca and Mg/Ca or  $\delta^{26}\text{Mg}$  show that silicate clays or Fe–Mn coatings are not a source of Mg in these analyses.

The other  $\sim 50\%$  of sample was purified for Mg isotopes using our previously described method of cation exchange columns (AG-50W X-12) using 2.0 M  $\text{HNO}_3$  as an elution agent (Foster et al., 2010; Pogge von Strandmann, 2008; Pogge von Strandmann et al., 2011, 2012). Purified samples were analysed for Mg isotopes using a Finnigan Neptune multi-collector ICP-MS, with an Elemental Scientific Apex-Q “moist” plasma introduction system. This system has the same benefits as the “wet” plasma quartz spray chambers commonly used for Mg isotopes (suppression of  $\text{C}_2^+$  and  $\text{CN}^+$  interferences and no significant hydride formation) but also higher sensitivity ( $\sim 100 \text{ pA}$  of  $^{24}\text{Mg}^+$  for a  $50 \text{ ng mL}^{-1}$  solution at an uptake rate of  $50 \mu\text{L min}^{-1}$ ) (Pogge von Strandmann et al., 2011). The total procedural blank of this method is  $\sim 0.2\text{--}0.25 \text{ ng}$ , which is insignificant compared to the mass of sample used. Analytical precision and accuracy were assessed by multiple analyses of seawater, yielding  $\delta^{26}\text{Mg} = -0.82 \pm 0.06 \text{ ‰}$  (2 s.d.,  $n = 26$ , Foster et al., 2010). As yet no carbonate reference standard for Mg isotopes exists, so analytical precision on carbonate was assessed by repeated (including diluted) analyses of coral carbonate detailed in Pogge von Strandmann (2008) ( $-3.44 \pm 0.08 \text{ ‰}$ ,  $n = 13$ ).

## 2.3 Modelling seawater Mg using Mg isotopes

A record of seawater  $\delta^{26}\text{Mg}$  gives a possibility of attempting to reconstruct Mg sources and sinks, as well as seawater Mg concentrations. In addition, constraining past riverine Mg fluxes and isotope ratios could provide constraints on changes in weathering and the related atmospheric  $\text{CO}_2$  withdrawal. A series of assumptions must be made about Mg behaviour during this time. For our first model (termed “fixed sink” model), we assume that the hydrothermal Mg sink is proportional to the mid-ocean ridge spreading rate, taken from the GEOCARB II model (Berner, 1994). The dolomite sink is constrained from rates of shallow water carbonate accumulation (Holland and Zimmerman, 2000; Hay, 1994), on the assumption that such carbonate is predominantly dolomitised. Removal onto low-temperature clays is thought to be minimal, with very poor constraints on any isotope fractionation (Tipper et al., 2006b), and are therefore ignored for this model. Given that the isotope fractionation caused by these sinks is reasonably well-constrained (Higgins and Schrag, 2010b), this leaves the river Mg flux and isotope ratio as remaining unknowns. For the riverine flux we use the Sr riverine flux calculated from foraminiferal Sr/Ca and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Lear et al., 2003; McArthur et al., 2001). The relationship between Mg and Sr in rivers is relatively straightforward, and there is little change in Sr/Mg for rivers draining silicate or carbonate terrains (Fig. 1, Gaillardet et al., 1999). Hence the modern global river Sr/Mg ratio and the riverine flux over the past 40 Ma are used to calculate the 40 Myr riverine Mg flux.

The seawater Mg budget  $N$  is calculated by  $dN/dt = F_r - F_{\text{MOR}} - F_{\text{sed}}$ , where  $F$  is the flux from rivers, mid-ocean ridges and sedimentation, given in  $\text{mol yr}^{-1}$ . The isotope ratios are then calculated from the standard mass-balance formula

$$N \frac{dR_{\text{SW}}}{dt} = F_r(R_r - R_{\text{SW}}) - F_{\text{MOR}}(R_{\text{MOR}} - R_{\text{SW}}) - F_{\text{sed}}(R_{\text{sed}} - R_{\text{SW}}) \quad (1)$$

The isotope ratio  $R$  of the sinks is calculated from the equation  $\Delta_{\text{sink}} = R_{\text{sink}} - R_{\text{SW}}$ , where removal at MOR is thought to be quantitative, resulting in no isotope fractionation, and  $\Delta_{\text{sed}} \sim 1.7\text{--}2\text{‰}$  for dolomite (Tipper et al., 2006b; Higgins and Schrag,

**BGD**

11, 7451–7484, 2014

### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





2010b). The equations were then solved in 100 000 year time slices, using the seawater  $\delta^{26}\text{Mg}$  values calculated from the foraminiferal record (see below), and solving for the isotope ratio of river water.

The second main model allows the flux of Mg to dolomite to be a variable (“fixed source” model). Rather than simply solving the flux mass balance, the isotope mass balance equation is solved for  $F_{\text{sed}}$ , using the same assumptions for the hydrothermal flux and riverine flux as in the first model. This then requires a “known” riverine isotope ratio through time, which is constrained from the river  $^{87}\text{Sr}/^{86}\text{Sr}$  of Lear et al. (2003), on the assumption that the river Sr isotope ratio is dominantly controlled by mixing between weathering of carbonate ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.708$ ) and silicate ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.722$ ) endmembers. This allows calculation of the  $\delta^{26}\text{Mg}$  of rivers, by assuming that these endmembers dominantly control the  $\delta^{26}\text{Mg}$  of modern rivers (flux weighted mean  $-1.09\text{‰}$ , de Villiers et al., 2005; Tipper et al., 2006b), and back-calculating to the  $\delta^{26}\text{Mg}$  of the carbonate ( $\delta^{26}\text{Mg} = -1.45\text{‰}$ ) and silicate ( $\delta^{26}\text{Mg} = -0.2\text{‰}$ ) endmembers. Clearly, this approach assumes that Sr isotopes are not anomalously influenced by radiogenic Himalayan carbonates (Palmer and Edmond, 1992), although it has been suggested that the radiogenic Himalayan flux is due to mixing between unradiogenic carbonate and radiogenic silicate weathering (Galy et al., 1999). In any case, as will be shown below, these changes are a relatively minor unknown variable in the Mg system.

### 3 Results

To assess potential diagenesis and/or recrystallisation, Sr/Ca ratios were examined in both modern and ancient foraminifera. In the core-top samples, Sr/Ca from *G. ruber* and *G. sacculifer* were identical to the range of other pristine foraminifera (Ni et al., 2007). The Eocene–Holocene samples have similar Sr/Ca ratios ( $1.19$ – $1.3 \text{ mmol mol}^{-1}$ , compared to core-top  $1.24$ – $1.41 \text{ mmol mol}^{-1}$ ; Table 1), which are higher than the Sr/Ca range thought to characterise diagenetically altered and recryst-

## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tallized foraminifera (Kozdon et al., 2013). Mg/Ca ratios in all foraminifera from this study are also lower than those ratios thought to represent diagenesis.

On average, Mg/Ca temperatures calculated from the core-top samples using species-specific calibration equations (Anand et al., 2003) are within 0.7 °C of the recorded sea surface temperature (SST). There are no overall resolvable correlations between  $\delta^{26}\text{Mg}$  and Mg/Ca (Fig. 2a) or with depth (i.e. dissolution) or  $\text{CO}_3^{2-}$  concentrations. For the latter, *G. ruber* and *Gt. tumida* show an apparently negative trend, that is, however, not truly resolved within the analytical uncertainty of the methodology for  $\delta^{26}\text{Mg}$ . Mg isotope ratios of *G. truncatulinoides*, *G. sacculifer* and *G. ruber* are within the range of previous studies (Chang et al., 2004; Pogge von Strandmann, 2008; Wombacher et al., 2011). The new data for *G. inflata* are similar to *G. truncatulinoides*, its nearest relative in the study with the most similar habitat. *G. conglobatus* records values more positive than the overall foraminifer average and also more positive than the other species in the genus, *G. sacculifer* and *G. ruber*. The new  $\delta^{26}\text{Mg}$  values for *O. universa* and *G. tumida* have expanded the range of the previously published dataset for those species (Fig. 3). The average for  $\delta^{26}\text{Mg}$  in low-Mg foraminifera from this study and others (Pogge von Strandmann, 2008; Wombacher et al., 2011) is  $-4.62 \pm 0.67 \text{‰}$  (2 s.d.), with the main outliers from the average being *G. sacculifer* ( $\leq 0.95 \text{‰}$  lighter than average) and *G. menardii* ( $\leq 0.64 \text{‰}$  heavier than average) (Fig. 3).

The Eocene–Holocene samples show a decrease at  $\sim 14 \text{ Ma}$  from  $-4.14 \text{‰}$  to the present day. For most of the time between the middle Eocene and middle Miocene, values are approximately constant at  $-4.3 \text{‰}$ , aside from several isotopically light data points in the late Oligocene (Fig. 4a).

## BGD

11, 7451–7484, 2014

### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 4 Discussion

### 4.1 Mg incorporation in foraminifera – a window into biomineralisation

Little is as yet understood about the incorporation of Mg into foraminiferal calcite, and in particular on the associated Mg isotope fractionation. This study strengthens the information on species-dependent variability in Mg isotope fractionation (Fig. 3), reiterating that a clear understanding of the controls on Mg isotope fractionation may yield important clues for the incorporation of Mg into tests and hence ultimately the process of biomineralisation. Test growth rate and seawater calcite saturation state have previously been shown not to affect test  $\delta^{26}\text{Mg}$  values (Pogge von Strandmann, 2008). Several studies have established that  $\delta^{26}\text{Mg}$  in planktonic foraminifera does not appear to be dependent on calcification temperature (Chang et al., 2004; Pogge von Strandmann, 2008; Wombacher et al., 2011), in contrast to a weak temperature dependence of  $\delta^{26}\text{Mg}$  in calcitic sclerosponges and corals (Wombacher et al., 2011; Yoshimura et al., 2011). The greatest  $\delta^{26}\text{Mg}$  variation in this study's *G. ruber* and *G. sacculifer* is indeed in samples with almost identical SST.

Consequently, there is no correlation between  $\delta^{26}\text{Mg}$  and Mg/Ca (Fig. 2a). This suggests that the active removal or biocomplexation of Mg, to allow for calcite growth, does not preferentially discriminate by a set amount against an individual Mg isotope, either for individual species, or for planktic foraminifera as a whole. It seems likely, however, that the processes that dramatically reduce the Mg concentrations of foraminiferal tests relative to seawater are the same that drive the Mg isotope composition of the tests significantly lighter than inorganic calcite. Given that the Mg isotope ratio of seawater is well known ( $-0.82 \pm 0.06\text{‰}$ , Foster et al., 2010), and that the thermodynamics and fractionation during the precipitation of inorganic carbonate is reasonably well constrained ( $\Delta^{26}\text{Mg} \sim 2.6\text{‰}$  at  $20^\circ\text{C}$ , Busenberg and Plummer, 1989; Mucci, 1987; Galy et al., 2002; Pogge von Strandmann, 2008; Wombacher et al., 2011; Hippler et al., 2009; Immenhauser et al., 2010), other effects must account for a  $\Delta^{26}\text{Mg}_{\text{orgcarb-SW}}$  of  $-0.55$  to  $-2.1\text{‰}$ .

### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

It has been proposed that Mg is reduced by active pumping out of an intra-cellular vacuole with a seawater starting composition (Bentov and Erez, 2006; Erez, 2003; de Nooijer et al., 2014). Hence, the Mg isotope fractionation could be the result of this pumping, which would be expected to follow a Rayleigh-type isotope fractionation process, with slightly greater fractionation at lower temperature (Wombacher et al., 2011). Calcification from this modified solution would then be an inorganic calcification process (Pogge von Strandmann, 2008). However, no mechanism for active Mg removal has yet been identified. In addition, the wide ranges in Mg/Ca fractionation caused by the “vital-effect” ( $\Delta\text{Mg/Ca}$ , where the inorganic fractionation has been removed) at relatively small variation in  $\Delta^{26}\text{Mg}$  (again corrected for inorganic fractionation) imply that no single process is responsible for both the removal of Mg, and the discrimination against heavy Mg isotopes (Fig. 2b).

Another possible process is active pumping of Ca, via Ca-pumps, from vacuolised seawater into the Ca reservoir, rather than removal of Mg from the Ca reservoir (Raitzsch et al., 2010; ter Kuile, 1991), thereby changing the Mg/Ca ratio. Nehrke et al. (2013) suggest that Ca for test calcification is primarily supplied by a combination of active trans-membrane transport, which has been shown to strongly discriminate against other elements due to differences in surface charge density, and passive transport (i.e., vacuolisation) (Nehrke et al., 2013). In this model, most of the Ca is supplied by trans-membrane transport, which strongly discriminates against Mg, combined with a relatively small amount passive transport, which adds Mg in seawater-like proportions. Hence if trans-membrane transport favours light Mg isotopes, which may be more energetically favourable, then the variability in  $\delta^{26}\text{Mg}$  and Mg/Ca could be explained by either species-specific across-membrane Ca transport mechanisms (which are variably efficient in discriminating against Mg), or species-specific amounts of passive transport of seawater (Nehrke et al., 2013).

The Nehrke et al. (2013) model suggests that trans-membrane transport is the same for coccolithophores (with very low Mg/Ca) and foraminifera (with higher Mg/Ca), and that passive transport of seawater causes the difference in Mg/Ca. However, given

## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



that coccolithophores have Mg isotope ratios similar or higher than inorganic calcite (i.e. lower than seawater, but significantly higher than foraminifera) (Wombacher et al., 2011; Ra et al., 2010), this cannot explain why foraminifera have such low  $\delta^{26}\text{Mg}$ . It is possible that the benthic foraminifera (*A. aomoriensis*) examined by Nehrke et al. (2013) has different calcification mechanisms than planktic ones, although available data for deep sea benthic foraminifera have similar ratios to planktic ones (Pogge von Strandmann, 2008). Importantly, *A. aomoriensis* is a brackish water rather than open ocean species, which might have acquired a different calcification mechanism to deal with the different environmental conditions. In addition, if passive addition of seawater caused the variability in foraminifer Mg/Ca, then a correlation would be expected between the “organic” Mg/Ca and  $\delta^{26}\text{Mg}$  fractionation, which is not observed (Fig. 2b). Hence Mg isotopes suggest that coccolithophores and foraminifera have different Ca transport mechanisms, which have different efficiency with regard to discrimination against Mg. Such a process could also explain why high-Mg foraminifera (*Cyclodypeus* sp. and *Marginopora* sp.) have similar  $\delta^{26}\text{Mg}$  to inorganically precipitated calcite (Yoshimura et al., 2011).

This suggests that Mg isotopes can provide a further insight into calcification mechanisms. Future models into controls on Mg/Ca need to consider Mg and Ca isotope, as well as elemental, fractionation. However, the relatively narrow  $\delta^{26}\text{Mg}$  range exhibited by individual species (*G. sacculifer*:  $\sim 0.6\text{‰}$ , *G. tumida*:  $\sim 0.5\text{‰}$ , *G. ruber*:  $\sim 0.3\text{‰}$ ), and the lack of apparent control by environmental parameters, suggests that changes larger than  $\sim 0.5\text{‰}$  in the past indicate changes in the seawater Mg isotope values. However, equally, these data demonstrate the importance of a calibrated, single-species approach, given that the  $\delta^{26}\text{Mg}$  variation seen in core-top foraminifera of different species is that same as that observed across the past 40 Myr in a single species.

## 4.2 A Cenozoic seawater reconstruction based on foraminiferal calcite

The  $\delta^{26}\text{Mg}$  values calculated for seawater for the past 40 Myr are clearly resolvable from present-day ratios, and suggest that seawater  $\delta^{26}\text{Mg}$  was  $\sim 0\text{‰}$  during the middle Eocene (Fig. 4). For most of the time between the middle Eocene and middle Miocene, seawater had approximately constant  $\delta^{26}\text{Mg}$ , aside from an approximately 10 Myr decrease in isotope ratios in the late Oligocene, with the  $\delta^{26}\text{Mg}$  minimum coinciding with the Late Oligocene warming trend (Zachos et al., 2001). From the middle Miocene ( $< 14\text{ Ma}$ ), seawater  $\delta^{26}\text{Mg}$  begins to decrease sharply.

Given its residence time of  $\sim 10\text{ Myr}$ , this strongly suggests that Mg in the modern oceans is not in steady state (Vance et al., 2009), but is evolving rapidly to more negative  $\delta^{26}\text{Mg}$  values. The lack of steady-state is supported by data inferred from fluid inclusions in halite, as well as from Sr and Mg isotope ratios in pore fluids, which suggest that the Mg concentration in seawater over the last 40 Ma has been increasing, with a gradient that is becoming steeper towards the present (Holland and Zimmermann, 2000; Zimmermann, 2000; Fantle and DePaolo, 2006; Higgins and Schrag, 2012).

There are likely two dominant controls on both the Mg concentration and isotope ratios in the oceans: the riverine input and removal into dolomite. Although reconstructing the flux of any element is highly complex, and no unequivocal riverine flux record has ever been constructed, the river elemental fluxes have likely been highly variable over the past 40 Myr. The Mg isotope ratio of rivers (present global flux-weighted mean  $\sim -1.09\text{‰}$ , Tipper et al., 2006b) will dominantly depend on the ratio of carbonates ( $\delta^{26}\text{Mg} \sim -5$  to  $-1\text{‰}$ ) to silicates ( $-0.25 \pm 0.1\text{‰}$ ) in the catchment area (Pogge von Strandmann et al., 2008, 2012; Tipper et al., 2006a, b, 2008, 2010, 2012; Li et al., 2010; Teng et al., 2010b). Interestingly, the overall decrease in seawater  $\delta^{26}\text{Mg}$  appears to start around 15 Ma, which is also when Li isotopes start increasing (Fig. 4d), which has been interpreted as a decrease in the congruency of continental weathering (Misra and Froelich, 2012). The  $\delta^{26}\text{Mg}$  decrease could also be coupled to the decrease in global temperatures and build-up of ice-sheets (Zachos et al., 2001; Lear et al., 2000). It is

**BGD**

11, 7451–7484, 2014

### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



unlikely that changes in the calcium compensation depth will have resolvably affected Mg isotopes in the Cenozoic as dolomite is predominantly a shallow-water carbonate, and therefore is always likely to have existed above the CCD.

In previous attempts to model Mg concentrations in the ocean (Holland, 2005), the river flux has been kept constant over the entire 35 Ma period, which is unlikely to reflect reality given the large climatic variability during this time (e.g. Zachos et al., 2001). However, Holland (2005) suggests that climate was not important, because the removal of Mg into dolomite is the main factor controlling seawater concentrations. The formation rate of dolomite has varied significantly during the course of the Cenozoic; dolomite deposition is thought to have accounted for  $\sim 3.8 \times 10^{12}$  mol yr<sup>-1</sup> Mg at 35 Myr (Holland, 2005), and estimates for the modern removal are between  $\sim 0.2\text{--}1.7 \times 10^{12}$  mol yr<sup>-1</sup> (Elderfield and Schultz, 1996; Tipper et al., 2006b; Holland, 2005). Factoring in minor changes in the Mg sink at mid-ocean ridges, this significant decrease of the removal of Mg into dolomites is thought to have led to a considerable increase in the Mg concentration of the oceans, resulting in Mg being out of steady-state.

The seawater Mg concentrations from both models used in this study significantly increase towards the present day, and are very similar to models of seawater Mg based on the chemistry and <sup>87</sup>Sr/<sup>86</sup>Sr (Fantle and DePaolo, 2006) and on the  $\delta^{26}$ Mg (Higgins and Schrag, 2012) of deep-sea carbonate pore fluids (Fig. 6e). Overall, these models yield somewhat lower Mg than amounts inferred from ridge axis carbonate veins (Coggon et al., 2010; Horita et al., 2002; Zimmermann, 2000), which tend to suggest a more gradual slope (Fig. 6e).

Because rivers are the dominant source of Mg to the oceans, both their flux and isotopic compositions influence the seawater  $\delta^{26}$ Mg. Hence, the modelled riverine flux and  $\delta^{26}$ Mg cannot be kept constant throughout the studied time period. Figure 5 shows the effect of constant riverine flux and isotope ratio at modern values on seawater  $\delta^{26}$ Mg, assuming that the dolomite and hydrothermal removal fluxes are known (see “fixed sink” model description in Sect. 2.3; Figs. 5 and 6). The addition of riverine flux, based on Lear et al. (2003), shows that although the general trends in seawater  $\delta^{26}$ Mg

## BGD

11, 7451–7484, 2014

### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



are followed, changes of the riverine  $\delta^{26}\text{Mg}$  are required to more accurately reconstruct the seawater trends (Fig. 5). These changes are fairly large, varying between  $-3$  and  $+0.5\%$ , which is approximately the modern range of rivers (Pogge von Strandmann et al., 2008; Tipper et al., 2006b, 2008, 2012; de Villiers et al., 2005; Huang et al., 2012; Wimpenny et al., 2011). However, given that the dominant control over the  $\delta^{26}\text{Mg}$  of rivers is the lithology undergoing weathering (isotopically light carbonates, and heavy silicates), this would require that during most of the Oligocene and Late Miocene rivers were dominated by carbonate weathering, and, for the time between the Early Miocene glaciation and the Miocene climatic optimum, were dominated by an isotopically very heavy source. Hypothetically, mid-Miocene growth of the East Antarctic ice sheet may have lowered sea level (Zachos et al., 2001; Shackleton and Kennett, 1975; John et al., 2011), and exposed shallow marine carbonate platforms to chemical weathering (Li et al., 2009). Reconstructions of riverine Sr isotopes during this time, though, do not show such endmember compositions (Galy et al., 1999; Oliver et al., 2003; Palmer and Edmond, 1992; Lear et al., 2003). Equally, high solid rock  $\delta^{26}\text{Mg}$  values (up to  $+1\%$ ) have been reported in heavily weathered rocks, loess and saprolites (Pogge von Strandmann et al., 2008; Teng et al., 2010b; Li et al., 2010). It has, however, also been shown that generally rivers draining such rocks tend to have lower  $\delta^{26}\text{Mg}$  (Tipper et al., 2012). This suggests that an isotopically heavy global river composition must either be due to the formation of significant amounts of (isotopically light) carbonate on the continents, or weathering and destabilisation of previously weathered, secondary clay-rich material, either of which are unlikely to have occurred on a global scale. Hence it seems unlikely that the “fixed sink” model reproduces Mg sources and sinks accurately, and that riverine  $\delta^{26}\text{Mg}$  did not vary by that amount.

The “fixed source” model (assuming river fluxes and isotope ratios based on Sr isotopes (Lear et al., 2003) and the same hydrothermal flux as in the previous model) allows the dolomite sink to be a variable in controlling the  $\delta^{26}\text{Mg}$  of seawater. If lithology is the main controlling factor on river isotope ratios (deconvolved from Sr isotopes based on two endmember mixing), then this suggests that global river  $\delta^{26}\text{Mg}$  has changed

## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



relatively little, and has, from a mass balance perspective, been more strongly influenced by carbonate over silicate weathering (varying between  $-0.98$  and  $-1.22$ ‰). This seems a more useful approach than the previous model's conclusion of an order of magnitude more variation in river  $\delta^{26}\text{Mg}$ , given that large changes in the isotope ratio of a major element in rivers would require drastic differences in the weathering system.

The fraction of the Mg sink attributed to dolomite relative to hydrothermal uptake ( $f_{\text{dol}}$ ) varies between  $\sim 0.1$  and  $\sim 0.65$  (Fig. 6a), with lowest values at the present day and between  $\sim 25$ – $30$  Ma, and highest values between the Early Miocene glaciation and Miocene climatic optimum. This model appears to demonstrate a more realistic approach to the Cenozoic Mg budget: Mg removal by dolomite across the Cenozoic ( $0.2$ – $3.7 \times 10^{12}$  mol yr $^{-1}$ ) is within estimates by other studies. In addition, the seawater  $\delta^{26}\text{Mg}$  decrease starting at  $\sim 15$  Ma (based on the foraminiferal record) suggests that the modern dolomite sink is at the lower end of estimates from other studies, but agrees well with the only other estimate based on Mg isotopes (Tipper et al., 2006b). In addition, the overall pattern of the modelled dolomite removal flux agrees well with Cenozoic estimates of rates of shallow-water vs. deep-water carbonate accumulation (with the former predominantly dolomite), which also show a minimum between 25 and 30 Ma, and a rapid decrease from  $\sim 20$  Ma towards the present day (Hay, 1994; Opdyke and Wilkinson, 1988). The implication of this is that the increase in seawater Mg concentrations over the past 10–15 Myr was driven by a combination of increasing riverine flux and decreasing dolomite formation (Fantle and DePaolo, 2006), and not by a decrease in the hydrothermal sink.

If the mean global riverine  $\delta^{26}\text{Mg}$  is controlled by lithology, and therefore can be estimated from Sr isotopes, then this implies that dolomite formation (as suggested by Holland, 2005) and the river Mg flux are the dominant controls on both the Mg concentration of seawater, and its isotope ratio. The models suggest that the hydrothermal flux and river isotope ratio are relatively minor controls. Interestingly, seawater Li isotopes are thought to have begun a rapid increase towards heavier values from the mid

## BGD

11, 7451–7484, 2014

### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Miocene climatic optimum at  $\sim 14$  Ma (Fig. 4d), possibly due to a shift in the weathering regime to a more incongruent, weathering-limited system (Misra and Froelich, 2012). Lithium isotope ratios respond only to silicate weathering (Kisakürek et al., 2005; Millot et al., 2010), and therefore there can be no direct link between the concurrent increase in seawater  $\delta^7\text{Li}$  and  $\delta^{18}\text{O}$  and the decrease in  $\delta^{26}\text{Mg}$ . This suggests that the overall control, at least from the Mid-Miocene onwards, is the climatic cooling trend, which affected both the weathering regime and dolomite formation. The model also suggests a rapid decline in Mg taken up by dolomite at the same time as climate cooled in the Early-Mid Oligocene, either due to the cooling, or due to a decrease in the cations supplied from the continents.

## 5 Conclusions

Foraminifera from core-tops and from the past 40 Myr have been analysed for Mg isotope ratios. Core-top foraminifera show no relationship between  $\delta^{26}\text{Mg}$ , Mg/Ca ratios and temperature. Species-specific Mg isotope offsets cannot be readily linked to calcification rate or habitat. As all foraminifera analysed to date are isotopically lighter than inorganic calcite, the data are best explained if Ca is pumped into an intracellular vacuole from seawater. We suggest that the efficiency of this pump determines the Mg isotope fractionation and speculate that this pump selects light Mg isotopes preferentially. A recent model of Mg/Ca fractionation by a combination of trans-membrane transport and passive transport (Nehrke et al., 2013) cannot explain the Mg isotope data, because the direction of isotope fractionation is wrong. This suggests that future models of Mg/Ca fractionation must incorporate Ca and Mg isotope fractionation.

Single, calibrated, foraminifera species may be used to reconstruct past seawater. Seawater  $\delta^{26}\text{Mg}$  values inferred from the foraminiferal record are isotopically heavier than the present for most of the past 40 Ma, by up to  $\sim 0.8\text{‰}$ , aside from isotopically light ratios during the Late Oligocene. Dynamic box models of the various Mg sinks and sources to seawater suggest that the primary controls on seawater Mg concentra-

**BGD**

11, 7451–7484, 2014

### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



tions and isotope ratios are the dolomite formation flux and the riverine flux, with the hydrothermal flux and riverine isotope ratios being more minor controls. Hence the low seawater  $\delta^{26}\text{Mg}$  values observed at the present day and in the Oligocene appear to be due to relatively little dolomite formation, in both cases occurring at the same time as major climate cooling. Concomitant increases in  $\delta^7\text{Li}$  and  $\delta^{18}\text{O}$  together with decreasing  $\delta^{26}\text{Mg}$  from  $\sim 15\text{Ma}$  further suggest strong links between the cooling trend, changes in the weathering regime and significantly lower dolomite formation.

### Author Contribution

P. A. E. Pogge von Strandmann wrote the manuscript, designed the model and measured some of the samples. J. Forshaw picked and analysed most of the samples. D. N. Schmidt designed the project with P. A. E. Pogge von Strandmann, picked samples and edited the manuscript.

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**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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### Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. Mg isotope compositions and data from both core-top and past foraminifera.

Core	Species	Size Fraction ( $\mu\text{m}$ )	Depth (m)	Salinity	SST ( $^{\circ}\text{C}$ )	$\text{CO}_3^{2-}$ ( $\text{mmol L}^{-1}$ )	Mg/Ca ( $\text{mmol mol}^{-1}$ )	Sr/Ca ( $\text{mmol mol}^{-1}$ )	$\delta^{25}\text{Mg}$ (‰)	2s.e.	$\delta^{26}\text{Mg}$ (‰)	2s.e.	$\Delta^{25}\text{Mg}$ (‰)	Age (Myr)
Core-top foraminifera														
1206-1	<i>G. tumida</i>	> 500	940	35.63	19.71	73	1.9	1.28	-2.58	0.02	-4.95	0.03	0.00	
1208-1	<i>G. tumida</i>	> 500	2971	35.57	17.71	108	2.0	1.28	-2.72	0.01	-5.21	0.01	-0.01	
1211-1	<i>G. tumida</i>	> 500	4089	35.57	19.52	90	1.5	1.24	-2.71	0.03	-5.15	0.02	-0.03	
1206-1	<i>G. ruber</i>	> 300	940	35.63	19.71	73	2.6	1.39	-2.44	0.01	-4.63	0.03	-0.03	
1208-1	<i>G. ruber</i>	> 300	2971	35.57	17.71	108	2.6	1.41	-2.53	0.05	-4.86	0.02	0.00	
1211-1	<i>G. ruber</i>	> 300	4089	35.57	19.52	90	2.0	1.37	-2.4	0.02	-4.65	0.03	0.02	
5142-2	<i>G. ruber</i>	> 300	3946	36.8	23.88	93	3.9	1.38	-2.46	0.01	-4.69	0.02	-0.02	
1206-1	<i>G. sacculifer</i>	> 300	940	35.63	19.71	73	3.1	1.35	-2.6	0.03	-5.01	0.03	0.01	
1208-1	<i>G. sacculifer</i>	> 300	2971	35.57	17.71	108	2.8	1.36	-2.71	0.02	-5.23	0.02	0.01	
1211-1	<i>G. sacculifer</i>	> 300	4089	35.57	19.52	90	2.6	1.31	-2.61	0.02	-4.96	0.03	-0.03	
1206-1	<i>O. universa</i>	> 300	940	35.63	19.71	73	4.5	1.39	-2.56	0.01	-4.93	0.01	0.01	
5142-2	<i>O. universa</i>	> 300	3946	36.8	23.88	93	5.4	1.28	-2.53	0.03	-4.87	0.03	0.01	
1206-1	<i>G. trunculinoides</i>	> 300	940	35.63	19.71	73	2.6	1.38	-2.45	0.04	-4.66	0.04	-0.02	
1206-1	<i>G. inflata</i>	> 300	940	35.63	19.71	73	2.2	1.37	-2.38	0.01	-4.56	0.02	0.00	
5142-2	<i>G. conglobatus</i>	> 300	3946	36.8	23.88	93	2.7	1.35	-2.29	0.01	-4.34	0.02	-0.03	
Sediment foraminifera														
1264B 1H1	<i>O. universa</i>	> 300					5.31	1.36	-2.61	0.03	-4.97	0.02	-0.02	0.06
1264B 1H5	<i>O. universa</i>	> 300					5.59	1.32	-2.52	0.01	-4.88	0.02	0.02	1.15
1264A 3H6	<i>O. universa</i>	> 300					5.69	1.21	-2.40	0.02	-4.61	0.03	0.00	4.04
1263A 4Hcc	<i>G. venezuelana</i>	> 355					3.02	1.20	-2.37	0.04	-4.56	0.01	0.01	5.50
1264A 11H6	<i>O. universa</i>	> 300					4.49	1.10	-2.27	0.03	-4.44	0.05	0.03	7.82
1264A 17H6	<i>O. universa</i>	> 300					3.91	1.21	-2.30	0.03	-4.41	0.05	0.00	11.90
1264A 17H6	<i>G. venezuelana</i>	> 300					2.09	1.21	-2.24	0.00	-4.30	0.01	0.00	11.90
1264A 18H1	<i>G. venezuelana</i>	> 300					1.96	1.23	-2.32	0.01	-4.42	0.01	-0.02	13.00
1264A 18H6	<i>G. venezuelana</i>	> 300					2.03	1.24	-2.16	0.01	-4.14	0.01	0.00	14.10
1264A 19H1	<i>O. universa</i>	> 300					3.89	1.16	-2.28	0.03	-4.34	0.05	-0.02	14.70
1264A 19H1	<i>G. venezuelana</i>	> 300					2.28	1.26	-2.21	0.04	-4.18	0.02	-0.03	14.70
1264A 19H6	<i>G. venezuelana</i>	> 300					2.39	1.27	-2.10	0.01	-4.09	0.01	0.03	17.10
1264A 20H1	<i>G. venezuelana</i>	> 300					2.15	1.26	-2.15	0.03	-4.11	0.04	-0.01	18.20
1264A 20H7	<i>G. venezuelana</i>	> 300					3.48	1.19	-2.14	0.02	-4.10	0.01	0.00	18.80
1264A 21Hcc	<i>G. venezuelana</i>	> 355					2.05	1.25	-2.20	0.03	-4.22	0.01	0.00	21.30
1264A 24cc	<i>G. venezuelana</i>	> 300					2.54	1.16	-2.26	0.02	-4.30	0.03	-0.02	23.01
1264B 26Hcc	<i>G. venezuelana</i>	> 355							-2.45	0.01	-4.75	0.02	0.02	25.10
1264A 26Hcc	<i>G. venezuelana</i>	> 355					2.87	1.28	-2.45	0.03	-4.85	0.01	-0.03	25.80
1264A 27cc	<i>G. venezuelana</i>	> 300					2.19	1.38	-2.37	0.01	-4.56	0.04	0.01	26.25
1264A 29Hcc	<i>G. venezuelana</i>	> 355					2.78	1.30	-2.24	0.01	-4.31	0.01	0.01	29.70
1264B 29Hcc	<i>G. venezuelana</i>	> 355					2.77	1.22	-2.20	0.05	-4.22	0.02	0.00	29.70
1263A 11Hcc	<i>G. venezuelana</i>	> 355					2.43	1.26	-2.16	0.02	-4.12	0.04	-0.02	35.40
1263B 6Hcc	<i>G. venezuelana</i>	> 300					2.55	1.28	-2.20	0.01	-4.21	0.01	0.00	36.70
1263A 14hcc	<i>G. venezuelana</i>	> 355					2.30	1.28	-2.11	0.02	-4.09	0.05	0.02	40.50

## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

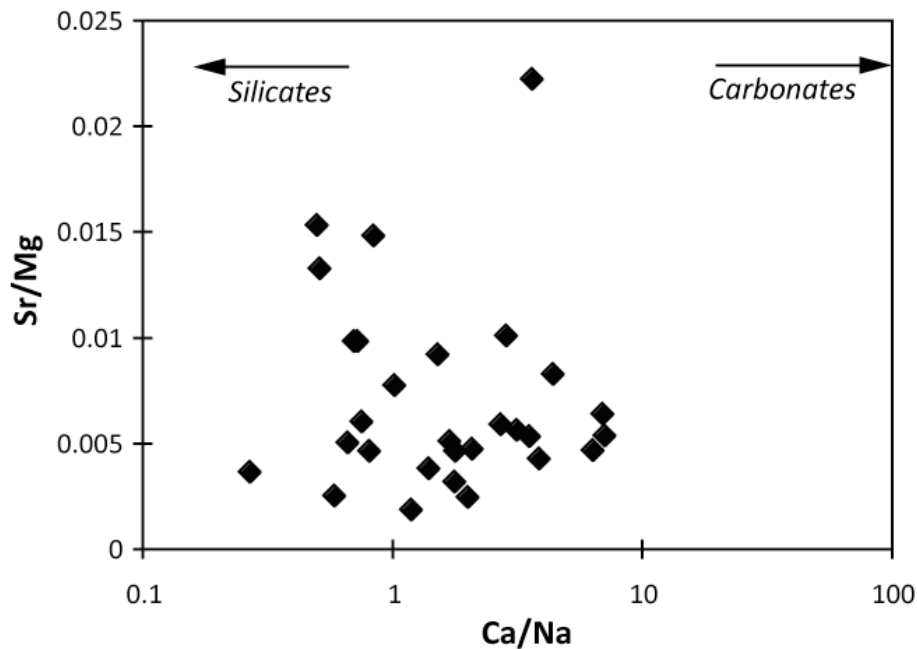
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Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Figure 1.** Mg/Sr and Ca/Na from the Earth's major rivers (Gaillardet et al., 1999), showing that Mg/Sr does not vary between carbonate (high Ca/Na) and silicate (low Ca/Na) weathering, allowing use of riverine Sr fluxes (Lear et al., 2003) to calculate river Mg fluxes.

Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

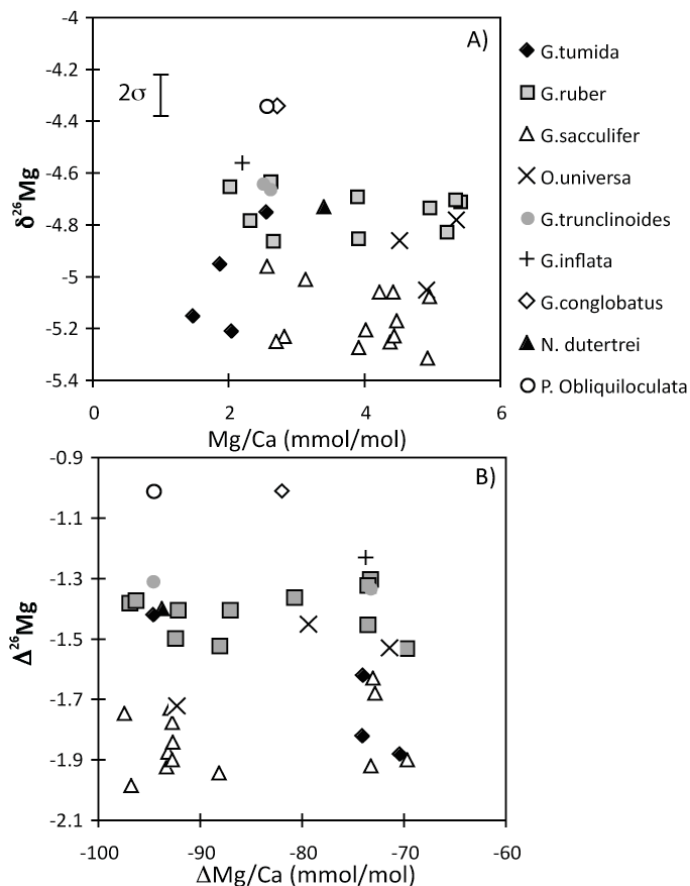
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Interactive Discussion



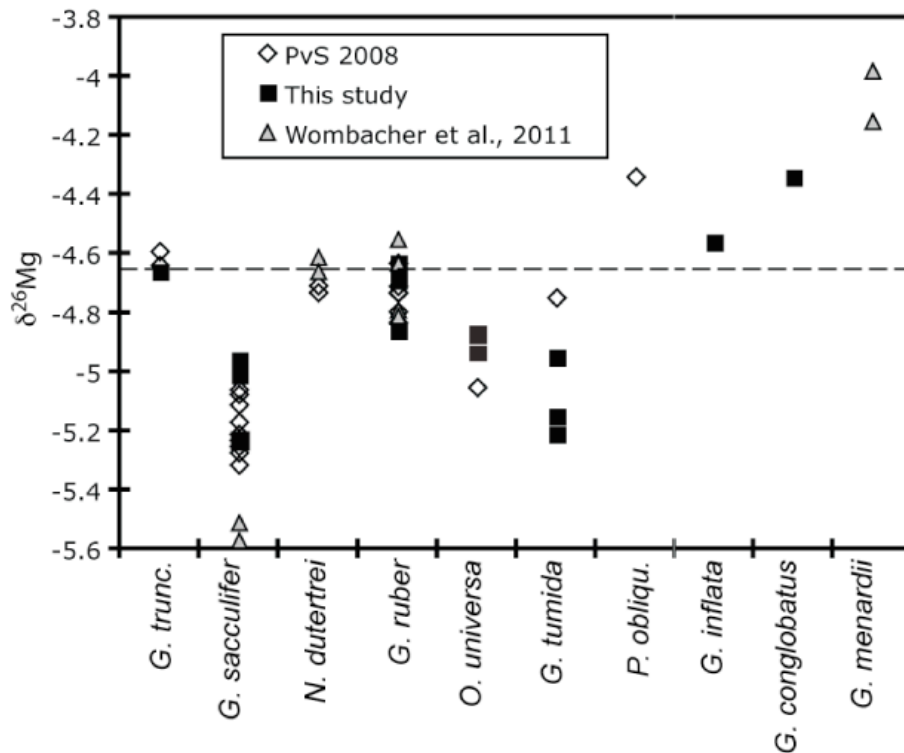
## Past seawater Mg isotope behaviour from foraminifera

P. A. E. Pogge von Strandmann et al.



**Figure 2.** (A) Mg/Ca ratios vs.  $\delta^{26}\text{Mg}$  of all species analysed. No relationship exists between these two factors. (B) The Mg/Ca and  $\delta^{26}\text{Mg}$  fractionation after inorganic calcification (temperature-dependent for Mg/Ca) has been removed, showing the extent of biologically controlled impacts on magnesium and its isotopes in foraminifers.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)



**Figure 3.** A compilation of Mg isotope data (Pogge von Strandmann, 2008; Wombacher et al., 2011) from low-Mg planktonic foraminifera. Data from Chang et al. (2004) are not included, due to the lack of a data table in that publication. The dotted line represents the average of the data.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

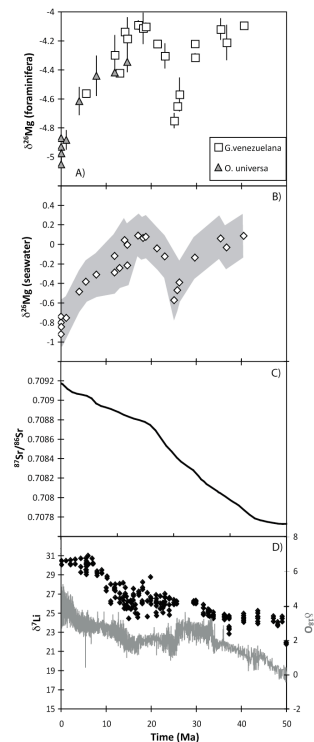
Printer-friendly Version

Interactive Discussion



## Past seawater Mg isotope behaviour from foraminifera

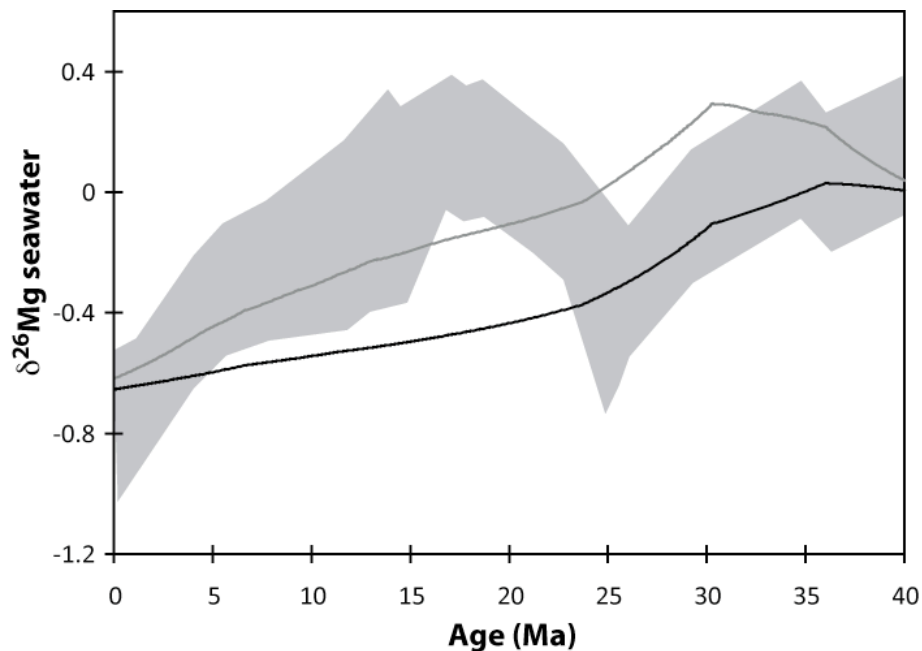
P. A. E. Pogge von Strandmann et al.



**Figure 4.** (A) Foraminiferal  $\delta^{26}\text{Mg}$  values from the past 40 Myr. Uncertainty on the age model is smaller than the symbol size. The error bars represent the 2 s.d. analytical reproducibility of the individual samples. (B) Reconstructed seawater  $\delta^{26}\text{Mg}$  from the foraminiferal record. The grey band shows the extent of uncertainty, including analytical uncertainty and scatter due to the spread in modern *O. universa* and the offset between the two analysed species ( $\pm 0.28\%$ ). (C) LOWESS Cenozoic Sr isotope data (McArthur et al., 2001) (D) Li (Black diamonds) and O (grey line) isotope ratios of planktonic foraminifera (Misra and Froelich, 2012; Zachos et al., 2001).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)





**Figure 5.** Model showing the effect on the fixed sink model when the river flux and isotope ratios are held constant at modern values (black line), and when only the riverine isotope ratios are held constant (grey line – river flux derived from Lear et al., 2003; see text for details). The grey field represents the seawater record derived from foraminifera.

**Past seawater Mg isotope behaviour from foraminifera**

P. A. E. Pogge von Strandmann et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

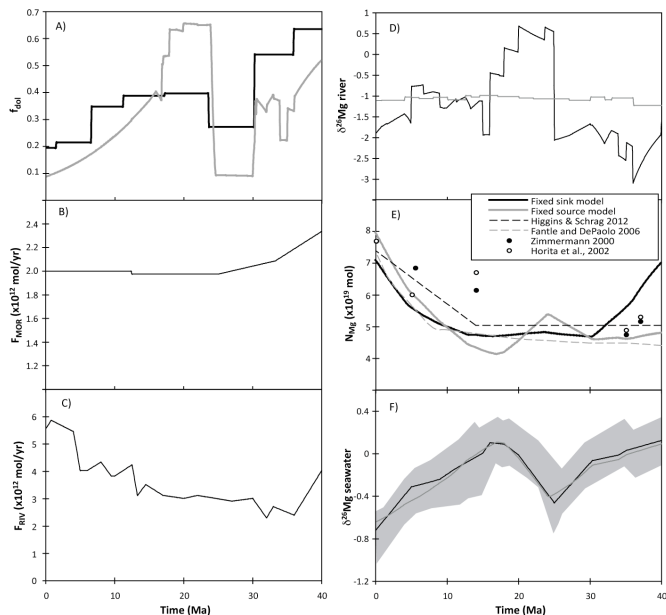
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Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Figure 6.** The inputs and outputs from the models (grey line: fixed source model, black line: fixed sink model). **(A)** Fraction of Mg removed by dolomite, relative to that hydrothermal removal. Due to the relative flatness of the hydrothermal flux at 30 Ma, the Mg removal flux by dolomite is essentially parallel to these curves. **(B)** Mg removal flux at mid-ocean ridges, from estimates of past spreading rates. Both models use these values. **(C)** Riverine input flux, which is identical for both models. **(D)** Riverine  $\delta^{26}\text{Mg}$ . The fixed sink model derives the river  $\delta^{26}\text{Mg}$  from the isotope mass balance equation, while the fixed source model derives it from the riverine  $^{87}\text{Sr}/^{86}\text{Sr}$  (Lear et al., 2003). **(E)** Model output seawater Mg reservoir. The dashed lines represent other models (Fantle and DePaolo, 2006; Higgins and Schrag, 2012) based on pore waters, and the data points are inferred seawater concentrations from fluid inclusions. **(F)** Model results for the seawater  $\delta^{26}\text{Mg}$ . The grey band represents the same uncertainty on the seawater  $\delta^{26}\text{Mg}$  reconstruction as in Fig. 4b.