

General points

Both reviewers brought up comments and questions about the underlying assumptions of the model. We agree that any model is constrained by its assumptions. For modelling magnesium isotopes, it is highly debated what effect low-temperature hydrothermalism and off-axis water-rock interactions have on Mg concentrations, with estimates ranging from 0–100% of sinks (see references in the paper). Notably, there are no Mg isotope constraints of any of these processes. Especially off-axis interactions are unconstrained for almost all seawater elements.

As both reviewers state in agreement with our reasoning, it is currently difficult to think of better ways to model seawater Mg and its isotopes, despite its importance for understanding weathering and reconstructing climate. Below, we comment on the effect of changing high-temperature hydrothermal effects, but these are fairly small given the long ocean residence time of Mg (and hence a very buffered response), and the lack of an isotopic fractionation effect due to likely quantitative removal of Mg.

With regards to the comments on the size of the dolomite sink, we agree that one of our models suggests this is larger than other authors have suggested. Previous estimates of dolomite formation are based on models, whereas Mg isotopes could provide some actual constraints. We would re-iterate that the models we have calculated are end-member scenarios providing a possible range of values. It is important to note that off-axis reverse weathering effects could balance Mg to the result that the dolomite sink becomes smaller. While we are happy to consider the possibility in the text, as yet we unfortunately lack the knowledge to constrain it in any way. Hence we believe that our model provides the best constraints possible, given our current level of understanding. As always, the interpretation can change once new data are available.

Reviewer 1

Specific comments

P7459, L10 – Calculating the $\delta^{26}\text{Mg}$ value of the riverine flux is of course very problematic. It clearly will not be a simple mixing between carbonate and silicate sources as unlike $^{87}\text{Sr}/^{86}\text{Sr}$ the dissolved $\delta^{26}\text{Mg}$ value is fractionated by secondary mineral formation. However, broadly speaking this is probably the best you can do in this kind of model. At the very least we know that purely carbonate draining rivers will be isotopically lighter than purely silicate draining rivers. When it gets down to large rivers that mix sources I think that you cannot say anything about the ratio of carbonate vs silicate Mg sources from the $\delta^{26}\text{Mg}$ value alone.

In general, the amount of carbonates vs. silicates appears to be the main controlling factor on river Mg isotopes. We agree that silicate secondary minerals do fractionate Mg isotopes, but this is a somewhat more minor effect (globally) compared to lithology. Certainly in small catchments, lithology seems to be key, and silicate dominated catchments do not show more river $\delta^{26}\text{Mg}$ variability than other types (Tipper et al., 2008). We agree that using this approach to determine inputs on a catchment scale will likely not work, but on a global scale we believe this is a decent approximation. We elaborate on this now in the text (section 2.3).

P7459, L14 – why is the carbonate endmember so heavy? Dolomites have $\delta^{26}\text{Mg}$ values that are more usually -2‰ and calcite can be significantly lighter (down to -5‰. Where does -1.45‰ come from?!

The value is determined by a back-calculation from Sr to Mg isotopes, to explain the modern global mean river values (as stated in the text). The value is within the range of rivers draining dolomite (which can be as heavy as -1‰ – Tipper et al., 2006), which will likely dominate the carbonate Mg budget of rivers.

P7461, L27 – In general if $\Delta^{26}\text{Mg}$ is used it should be defined – e.g. $\Delta^{26}\text{Mg}_{\text{solid-solution}}$. Shouldn't the value be -2.6‰ I am a little confused as to what $\Delta^{26}\text{Mg}_{\text{orgcarb-SW}}$ values of -0.55 to -2.1‰ actually mean? Modern forams have very light $\delta^{26}\text{Mg}$ values of -5‰ and seawater is -0.82‰. So surely a $\Delta^{26}\text{Mg}_{\text{orgcarb-SW}}$ value of -4permil is more normal?

$\Delta^{26}\text{Mg}_{\text{orgcarb-SW}}$ specifies the amount of fractionation that is due to biotic processes. Inorganic carbonate formation fractionates $\delta^{26}\text{Mg}$ by 2.6‰, so $\Delta^{26}\text{Mg}_{\text{orgcarb-SW}}$ defines the difference between the foram value and seawater, minus the inorganic carbonate effect (i.e. the fractionation between forams, and inorganic calcite precipitated from seawater). This has been added to the text (section 4.1).

P7462, L5 – It would follow Rayleigh fractionation if you assume the cell is a closed system. Is Mg only being pumped out of the cell? Also the fractionation should be kinetic and would favour ^{24}Mg to be pumped out wouldn't it? In this case the resulting Mg would be isotopically heavy which is opposite to what is usually seen in forams.

This is indeed the problem in reconciling Mg isotope fractionation with foraminiferal mineralisation. In this scenario (and note we discuss other, potentially more feasible, scenarios subsequently in the text) all elements that inhibit calcification are pumped out of the vacuole. In this case, yes, ^{26}Mg would have to be preferentially removed from the vacuole. But as yet, we have little knowledge of the mechanisms that would facilitate pumping of Mg (assuming this happens, see later in the text); specifically we do not know whether enzymes are responsible, which could have a preference for heavy Mg isotopes. This is discussed in section 4.1.

P7462, L9 – How do you calculate $\Delta\text{Mg}/\text{Ca}$? What does a $\Delta\text{Mg}/\text{Ca}$ value of -90 actually mean (fig 2b)?

As with the Mg isotopes, we are calculating the Mg/Ca fractionation caused only by biological calcification processes. Given a specific SST, and a Mg/Ca fractionation that would be caused by that temperature in inorganic calcite forming from seawater, we can calculate the residual Mg/Ca fractionation which must be an “organic” processes. The negative value is simply because we are calculating $\text{Mg}/\text{Ca}_{\text{foram}} - \text{Mg}/\text{Ca}_{\text{inorg}}$, and foraminifers have a significantly lower Mg/Ca than inorganic calcite. As for the comments above, this has been expanded in section 4.1.

P7462, L15 – Input of Ca will of course change the Mg/Ca ratio but surely it can have no affect on the Mg isotopic composition if Mg is not being transported? In this context what does discriminating against Mg actually mean? How much Mg

will enter the cell by active trans membrane transport? If this active transport of Ca has such a strong discrimination against Mg it implies that the net input of Mg will be very small – in this case why should it be important when considering bulk isotopic effects? Should we also expect the passive transport of Mg to be isotope specific, I would have thought not? Is there any way to figure out the relative mass balance of Mg addition via an active process and Mg addition via passive transport?

The Mg/Ca fractionation theories say that either Mg is pumped out of vacuolised seawater, or that Ca is pumped from seawater into a vacuole. We agree that if no Mg were pumped at all, there would be no Mg isotope fractionation (and indeed no Mg in foram calcite). This is the basis of our suggestion that the Ca pumping process is not completely efficient, and also (accidentally) occasionally pumps other cations (such as Mg), i.e. discrimination.

Whatever process controls foraminiferal Mg/Ca strongly discriminates against Mg (foram Mg/Ca is at least 1000 times lower than seawater Mg/Ca); so the net input of Mg into the vacuole and subsequently the carbonate is relatively small. The problem is that we as yet have no consensus as to the processes that control Mg/Ca. The key point here is that the Mg isotopes suggest that Nehrke model of passive transport and active transport is not correct, because the passive transport of seawater would drive $\delta^{26}\text{Mg}$ higher (towards seawater), rather than lower as the data show. Hence, we need experiments and theories that incorporate both Mg/Ca and $\delta^{26}\text{Mg}$ – attempting to solve the calcification question from our core-top data is probably not a rigorous method.

P7463, L2 – It took me a while to figure out what is meant here. Seawater has a Mg/Ca ratio of 5 (at least modern day), so in a coccolith with low Mg/Ca ratios you would expect passive transport of seawater to be less important. In contrast forams have much higher Mg/Ca ratios (more similar to seawater), which would suggest a greater importance of passive transport. However this does not make sense with the isotope data as coccolith $\delta^{26}\text{Mg}$ is more similar to seawater than foram $\delta^{26}\text{Mg}$ values. Perhaps the explanation could be slightly reworded to be easier to read.

Yes, we have provided a better explanation in the revised text (section 4.1). In the Nehrke model, trans-membrane transport results in a low coccolith-like Mg/Ca in both coccoliths and forams. Additionally in this model, in forams, passive transport adds seawater to bring the foram Mg/Ca higher (see Nehrke Fig. 3). As described in our text, this cannot explain the Mg isotope ratios. The explanation could indeed be that forams have simply less trans membrane transport than coccoliths, but something like this has not yet been observed for Mg/Ca.

P7463, L11 – Why wouldn't you see a correlation between foram Mg/Ca and $\delta^{26}\text{Mg}$? Why specify organic Mg/Ca? And again, please define what is meant by organic Mg/Ca (at least somewhere in the paper).

Yes, we have provided a better explanation in the revised text (section 4.1). The problem is that one would expect a correlation between Mg/Ca and $\delta^{26}\text{Mg}$ in forams, because the same process should be removing Mg, and fractionating Mg isotopes, but such a correlation is not observed. "Organic" Mg/Ca and Mg isotope fractionation, here, is the fractionation that is observed after the inorganic component has been removed, i.e. calcification in forams is thought to be simple

inorganic calcification from a modified solution (this should indeed be called “organic Mg/Ca fractionation” in the text). By removing the “inorganic” fraction, this reveals, in theory, the fractionation to Mg/Ca and $\delta^{26}\text{Mg}$ caused by this modification (by pumping or vacuolisation).

P7463, L14 – This is a little vague, what process is meant here? Also, out of interest, how is a high Mg foram defined? Is this also a higher Mg/Ca ratio?

A “high-Mg” foram means a foraminifer that makes its test out of high-Mg calcite (as opposed to the low-Mg calcite tests studied here). High-Mg forams have a much heavier Mg isotope composition than low-Mg forams (see for example Wombacher et al 2011, or Yoshimura et al 2011). More Mg in high-Mg foraminiferal tests corresponds to a higher $\delta^{26}\text{Mg}$. A greater passive addition of Mg would drive $\delta^{26}\text{Mg}$ higher due to addition of seawater into the calcifying fluid. However, it may also be that low- and high-Mg tests calcify in different ways.

P7464, L17 – In the modern ocean the flux of Mg into carbonates is ~11% of the riverine input and the low temperature exchange of Mg for Ca and low temperature basalt alteration removes ~9% (according to Elderfield & Schulz 1996). In the model the low temperature removal of Mg into clays and basalt weathering is ignored because it is assumed to be relatively unimportant. As it appears to be of similar importance to the dolomite sink in the modern ocean is that assumption justified?

The removal of Mg during low-T alteration is incredibly poorly constrained. Estimates range from <7% (Tipper et al., 2006) to 23% (Holland, 2005) of the dolomite sink in the modern ocean, as well as the estimate quoted above. There are no Mg isotope constraints at all on how much isotopic fractionation occurs in low-T alteration (if any). Further, while there are some constraints on dolomite formation over the Cenozoic, there are none for low temperature alteration. If the latter stayed approximately constant through time, its relative importance would decrease back in time, due to increasing dolomite formation. The lack of constraints therefore makes it impossible to include it in any even moderately-constrained model. This is stated in Section 2.3 of the original manuscript, but is now explained better. In general, more (or indeed any) data are needed on this before it can be fully explained.

P7465, L26 - . . . shows the effect of using modern day values for the riverine flux and isotopic composition on seawater $\delta^{26}\text{Mg}$,
Adopted.

P7465, L27 – maybe say ‘using published values for the dolomite and hydrothermal Mg sinks.’
Adopted.

P7465, L28 – Add a sentence here saying that a fixed riverine flux and isotopic composition cannot reproduce what is observed.
Done.

P7465, L28 – By varying the riverine flux, based on data by Lear (2003),
Adopted.

P7467, L3 – I understand the assumption that the $\delta^{26}\text{Mg}$ of global rivers can be calculated from the riverine Sr composition – I suppose that there is little other choice in this case. But it should be remembered that the weathering of silicate minerals causes fluid phases to be enriched in light Mg as clay minerals preferentially uptake isotopically heavy Mg. This means that even purely silicate draining rivers can have $\delta^{26}\text{Mg}$ values that are lighter than -0.2‰ . So riverine values of -1‰ might suggest that rivers derive an important component of Mg from carbonates if you assume simple two-component mixing. However silicate weathering will complicate the interpretation. This sentence should be re-worded.

Yes, this is a good point, and studies of weathering of pure silicate terrains have yielded variable Mg isotope ratios, albeit variable to a lesser degree than that between rivers draining silicate vs. carbonate terrains. There is a further uncertainty with most river studies: almost none of them have been corrected for rainwater input, which is often quite significant, and in some cases has a seawater composition (-0.8‰). So it is unknown how much of the river variability beyond basic lithological controls is controlled by varying proportions. This is discussed in the text now.

It has also now been pointed out that the 2 different models are clearly endmember scenarios.

P7467, L5 – I agree with the interpretation – we do not see large variation in $\delta^{26}\text{Mg}$ of several ‰ in large rivers so this would seem unreasonable to invoke in the past.

Indeed.

P7467, L7 – There has been recent work that suggests that the seafloor production rates have decreased over the past 20My (e.g. Conrad & Lithgow-Bertollini 2007, Geology; Muller et al. 2008, Science, Coltice et al. 2013, EPSL). Wouldn't this influence the amount of Mg removed from seawater? In Fig 6B it shows the hydrothermal Mg flux used in the model as being constant over the last 20My – what would happen if the model considered more recent data suggesting a change in seafloor production rate? Also – no references are provided for the data used in Fig 6B and C.

The model we use for seafloor spreading rates is GEOCARB II, which is also the one used by Lear et al, 2003 (which gives the river Sr data). It makes sense to use the same model as Lear, so that additional complications are not added to our Mg model.

However, Conrad and Lithgow-Bertelloni suggest less than a $\sim 4\%$ global decrease of Mg removed over the past 40Ma. Muller et al suggests a $\sim 15\%$ decrease since 20Ma, and Coltice et al a $\sim 10\%$ decrease.

To determine the effect on both of our models, we added a monotonic decrease in the hydrothermal removal flux of Mg by 15% over the past 20Ma (assuming that the hydrothermal flux is proportional to the spreading rate, as discussed in the text). The effect on seawater $\delta^{26}\text{Mg}$ in both models is $\leq 0.02\text{‰}$, much less than analytical uncertainty. The effect on N (the seawater Mg budget) is a 4-6% increase in the resulting modern Mg budget (for the model where N is not fixed). If a step-change is imposed at 20Ma (unlikely, but an extreme scenario), this increases N of the fixed sink model by $\sim 12\%$, which brings it more in line with

the measured concentration data of Horita (and modern concentrations – see figure in original manuscript).

Therefore changes in the hydrothermal sink primarily make a difference in seawater concentrations, rather than isotope ratio, and this effect is slow, given the very long residence time of Mg. This is now detailed and discussed in Section 4.2.

P7467, L17 – The modeled sink of Mg to dolomite in Fig 6A does broadly correspond with the sink calculated from shallow water carbonate accumulation but there are also noticeable differences. For example, the modeled change in dolomitization at 25My is huge, the Mg sink to dolomite increasing by a factor of 6. The change in shallow water carbonate accumulation is not correspondingly large at this time (from the fixed sink model), so how can such a large change in dolomitization be justified in this case? Is direct precipitation of dolomite from seawater being advocated here?

There is no easy explanation for this – Figure 6A simply shows what the numerical model requires with the listed inputs. The two models we present are endmembers, but in any case, the increase in foraminiferal (and hence seawater) $\delta^{26}\text{Mg}$ at this time must be a cause in either or both river input and dolomitisation. We point out that the rates of shallow water carbonate accumulation are also calculations, rather than observations. It may therefore be that this must be re-evaluated in light of Mg isotope evidence.

P7467, L21 – The modeling obviously has many uncertainties associated with it and I think that this final sentence can be toned down a little. In particular, the modeled dolomite sink seems to change in magnitude in a far more extreme way than could be explained by the shallow water carbonate accumulation (Fig 6A). Also, the more recent evidence suggesting that seafloor production has altered over the last 20My is not considered. Finally the low temperature off axis Mg sink is not well constrained but estimates range from minor (5% of riverine input, Bach et al. 2003; Alt et al. 1996) to major (up to 100% of riverine input, Wheat & Mottl 2000, Mottl & Wheat 1994), and due to the sensitivity of Mg isotopes to secondary mineral formation this could cause Mg to be fractionated in seawater. Perhaps it should be stated that the increase in Mg concentration in seawater can theoretically be driven by increased riverine input and decreased dolomite formation and not necessarily by just a decrease in the hydrothermal sink. Or something along those lines.

We agree that there are significant uncertainties in the model, both with our knowledge of how elemental Mg behaves, and in the lack of isotope fractionation data, and that this should be stated. Our models are endmembers and this is now more clearly stated in the text. As mentioned above, small variations in high-temperature hydrothermal fluxes have little effect. Low-temperature off-axis fluxes are as yet not well understood for any element or isotopic system, and need to be investigated.

P7467, L28 – How can the hydrothermal flux be a minor control over the Mg concentration in seawater? It's the major Mg sink. The model says the hydrothermal flux is unimportant in terms of changes in seawater Mg and $\delta^{26}\text{Mg}$.

This is because the model input says the hydrothermal flux has not changed, which is still debatable isn't it? (see previous comment)

While the hydrothermal flux is a major control over concentration, it has relatively little effect on isotope ratio, given that it is thought to be quantitative. Changes in the hydrothermal flux would eventually have an effect, but are buffered by the long oceanic residence time. Hence dolomite formation, because it imposes a large isotopic fractionation factor, becomes a more important control on the seawater isotope ratio, because it has more isotopic leverage. This is now more clearly stated in section 4.2.

Reviewer 2 (Frank Wombacher)

Title: to me "records of Mg behaviour" sounds odd and in my opinion the title should be improved

Done.

Abstract: The abstract does not mention that the mechanisms of Mg uptake in foraminifera are evaluated in the paper.

That is true, but we feel that our speculation on this subject is best kept to the discussion, and not added to the abstract.

You should add that $d^{26}\text{Mg}$ is given relative to DSM3 Mg. line 23: "Mg" isotope ratios inferred ...

Done.

page 7453 line 6: I guess you mean Mg "isotopes" compared to Sr and Os isotopes.
Yes. Changed.

page 7453 line 10: removal (i.e. from the ocean) by hydrothermal fluids is a bit short and could be explained in more detail.

We have amended the manuscript and described that Mg is lost almost entirely to the oceanic crust during high-temperature interaction between seawater and basalt.

page 7453 line 12 onwards: comment: reconstruction of past seawater Mg contents or Mg/Ca can be achieved from (carbonate) archives alone. Characterizing sources and sinks via isotopes, however, will allow to evaluate the importance of different sources and sinks, i.e. the causes of changes in seawater composition (as written further below).

Yes, agreed. Although of course the fractionation effect between the carbonate archive and seawater must still be determined. This is now stated in the text.

page 7453 line 20 onwards: please give the $d^{26}\text{Mg}$ values and their uncertainties for sources and sinks. At least the mean values of seawater (-0.83) and river water (-1.09) Mg isotope compositions differ from each other and this should be presented more precisely (just stating that the isotope ratio of ocean water and riverine input is similar may be misleading)

This is stated in Section 2.3, but is now re-stated in this section. Seawater is $-0.83 \pm 0.01\text{‰}$ (2se) (Foster et al., 2010), and the river mean is $-1.09 \pm 0.05\text{‰}$ (Tipper et al., 2006). Hydrothermal removal is quantitative, and dolomite formation imposes a fractionation of 1.7–2‰ (Higgins and Schrag, 2010).

page 7454 line 7: "Using planktic foraminifers as an archive demands a mechanistic understanding of the uptake of Mg into the calcite ..." If this were the case, all Mg/Ca proxy work so far is useless. We do not have this mechanistic understanding and your study cannot claim this (but is a welcome contribution). Maybe just write that mechanistic understanding is desirable.

Agreed, and we certainly would not dare to claim that we have determined a complete understanding of Mg incorporation, although our data jointly with our isotope and trace element data provide important constraints which must be met by any model of foraminiferal calcification. A mechanistic understanding of Mg/Ca incorporation mechanisms, though, will provide the means to use the proxy in a wide range of environments with additional controls on the incorporation other than temperature controls, such as salinity, carbonate ion etc. without amending calibration equations at rather unconstrained points in the equation. We now state this in the text.

page 7454 line 10: "with test concentrations 1000 times lower than seawater (Lea et al., 1999)." Better refer to Mg/Ca instead of comparing concentrations of solution and solids.

Seawater Mg/Ca = 5077 mmol/mol. This study's core-top foraminifera Mg/Ca = ~1.5–4.5 mmol/mol. So Mg/Ca changes by a factor of ~1000–3000. The text has been amended.

page 7455 line 6: consider to replace "fractionation causes" by "causes for Mg isotope fractionation"

Done.

page 7457 line 23: "As yet no carbonate reference standard for Mg isotopes exists..." There is JCp-1, JDo-1 and Cal- S as reference materials (e.g. Wombacher et al., J. Anal. At. Spectrom. 2008; Hippler et al., 2009). Perhaps delete this sentence.

Yes, good point. This has been deleted.

page 7457 line 26: uncertainty is 2 sd?

Yes, 2sd.

page 7458 line 27: "Dsed ~ 1.7–2‰ for dolomite" please give the exact values that enter your model

Good point. We used 1.7‰ in the model. Now explicitly stated in the text.

page 7459 line 14: minor thing: "d26Mg of modern rivers (flux weighted mean -1.09 ‰, de Villiers et al., 2005; Tipper et al., 2006b)". Relative to seawater (-0.83) this is -0.26. I think the value obtained by de Villiers et al., 2005 relative to seawater is somewhat different -0.46 (please check).

Yes, that is correct. We now state that we used -1.09 from Tipper et al., 2006, but that (within the uncertainty of that study) the de Villiers result agrees with that.

page 7460 line 1: please give Kozdons range in Sr/Ca for diagenetically altered foraminifera for comparison. Same for Mg/Ca, also give a reference for Mg/Ca if it matters.

The Kozdon range for unaltered modern tests is Sr/Ca > ~1.2 mmol/mol, and Mg/Ca 1–5.5‰, and has been added to the paper.

*page 7460: consider to add figures of $\delta^{26}\text{Mg}$ vs. carbonate ion conc., depth and perhaps Sr/Ca, respectively. There seems to be a general tendency of lower $\delta^{26}\text{Mg}$ values at great depth, but this is usually within measurement uncertainty. In Fig. 2B, *G. tumida* seems to show a correlation between Mg/Ca and Mg isotopes (o.k. it hinges on one data point).*

A figure of carbonate concentration relative to $\delta^{26}\text{Mg}$ has been added to Fig. 2. As shown in the open reply, the other proposed figures show no correlations.

page 7461 line 17: "... the active removal or biocomplexation ..." there are alternatives like the Ca enrichment discussed below. So why state these two?

Only because active removal and biocomplexation are the two methods that have been discussed by previous Mg isotope papers (Pogge von Strandmann 2008, and Wombacher et al., 2011). So, yes, Ca enrichment is now mentioned here.

page 7461 line 18: "... set amount ..." Do you mean by a constant fractionation factor? "individual Mg isotope" consider "heavy Mg isotopes" instead.

Yes, a constant fractionation factor that is universal to that mechanism. Now in the text.

page 7461 line 19: "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." I have problems to understand that logic: why would it be the same? The two most simple cases may be that either i) part of the light isotope enrichment in foraminifera corresponds to the inorganic seawater-calcite Mg isotope fractionation + some vital effect. This would be expected if Mg were removed from a vacuole from which calcite then precipitates or ii) there is some mechanism that just sets the Mg isotope fractionation factor with some modifications for different planktic foraminifera species. Or is there an error and "relative to seawater" in your sentence should be "relative to inorganic calcite precipitated from seawater"?

For both Mg concentrations and Mg isotope ratios this should read "relative to inorganic calcite", and has been changed.

*page 7461 line 27: I do not understand the -0.55 value, I guess it is for *G. menardii* (which is for not in Fig 2b as no Mg/Ca is available). To avoid confusion point out that this range is from *G. menardii* to *G. sacculifer*. Perhaps name the extra fractionation in foraminifera ~ "excess $\Delta^{26}\text{Mg}_{\text{foram-inorg Cc}}$ ".*

The $\Delta^{26}\text{Mg}$ represents the difference between inorganic calcite precipitated from seawater ($\delta^{26}\text{Mg} \sim -3.5\text{‰}$) and foraminifer $\delta^{26}\text{Mg}$. This is now called $\Delta^{26}\text{Mg}_{\text{foram-inorg Cc}}$ to remove ambiguities.

page 7462 line 3: if you like you could point out that the temperature effect (that results from more efficient Mg removal at lower T) is not observed ~ “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, which is not observed (Pogge von Strandmann, 2008; Wombacher et al., 2011). “ However Furthermore, no ...”

Yes, agreed.

page 7463 line 3: “...this (the Nehrke model) cannot explain why foraminifera have such low $\delta^{26}\text{Mg}$.” I think the Nehrke model just cannot explain both foraminifera and coccolithophores at the same time, it may still explain the foraminifera. I guess the Nehrke model should lead to some relationship between Mg/Ca and $\delta^{26}\text{Mg}$ for single species at different temperatures (just saw that this is pointed out below; perhaps restructure this paragraph). Concerning coccolithophores, you could check the paper(s) by Marius Müller (GCA 2011).

See comments to reviewer 1

The point we are making is simply that if Mg isotopes are not incorporated into calcification models, a significant resource is being ignored, and the models could be wrong.

page 7463 line 14: “Such a process ...” Do you mean different Ca transport mechanisms for coccolithophores, foraminifera etc.?

See reply to reviewer 1

We agree that this can be better explained: more Mg in high-Mg tests corresponds to a higher $\delta^{26}\text{Mg}$. Hence, greater passive addition of Mg would drive $\delta^{26}\text{Mg}$ higher due to addition of seawater.

page 7463 line 15: some data for high Mg foraminifera is also given by Wombacher et al. (2011)

This reference has been added.

page 7464 line 19: “... the river elemental fluxes have likely been highly variable over the past 40Myr.” Why? Citations?

Because of significant variations in temperature, physical erosion by ice sheets, mountain uplift, evolution of grasses, etc. We have added reference such as Wanner et al., 2014; Li and West, 2014, which model both river fluxes and weathering rates as changing significantly.

page 7464 line 26 onwards: I think this section needs some explanation. Do you suggest that incongruent weathering plays a role for Mg isotopes (as suggested for Li)? How would the $\delta^{26}\text{Mg}$ be coupled to global temperatures and/or the build-up of ice sheets? Maybe start with ~ “there are four principal explanations for the increase in $\delta^{26}\text{Mg}$...” and then explain them.

Temperature affects whether silicates or carbonates dissolve easier. Ice-sheets provide physical erosion that will enhance chemical weathering of material the ice sheets are eroding. As discussed in reply to reviewer 1, secondary mineral formation (weathering incongruency) will likely have some effect on river $\delta^{26}\text{Mg}$, although it could be thought to be relatively more minor than a lithological control.

As an observation, it is interesting that $\delta^{26}\text{Mg}$ and $\delta^7\text{Li}$ appear to start changing more rapidly at the same time (15–20 Ma – see Figure 4 in original manuscript). Given that Li substitutes for Mg in silicates, it seems likely that the two isotopic systems are coupled to a degree. This is now more clearly stated in the text.

page 7465 line 12: “Factoring in minor changes in the Mg sink at mid-ocean ridges, this ...” Is this based on the GEOCARB II model? Note that Ligi et al. (Nature 2013) suggest that slow spreading ridges can actually be a source of Mg via seawater peridotite interaction. Also it appears that Coggen et al. (Science 2010) consider changes in the hydrothermal sink to be significant during the Tertiary.

Yes, this is also brought up by the reviewer 1. Both high- and low-temperature hydrothermalism are very unconstrained, and have been proposed to have changed between 0 and ~15% during the past 20Ma. In addition, off-axis interaction could also be a significant factor for many seawater elements. In general, we use GEOCARB II because the Sr data was calculated using this (Lear et al., 2003), so then both models use the same hydrothermal fluxes. This is clearly one of the major assumptions of the model, but given the proposed variability, and unknown Mg isotope fractionation factors, this approach is the best we can do. Hydrothermal changes (in their effect on the model) are now discussed in detail in section 4.2.

page 7466 line 6: “heavy silicates” Heavy rel. to modern seawater?

Yes, although with a $\delta^{26}\text{Mg}$ of about -0.2‰, silicates are heavy relative to pretty much most things.

page 7467 line 23: “... and not by a decrease in the hydrothermal sink.” The above discussion is well written, but here I am a bit lost. Why would the decrease in the hydrothermal sink not add to the increase in Mg concentration?

It is probably more correct to say that our models are less sensitive to changes in the hydrothermal sink, mainly because it imposes no isotope fractionation, and therefore exerts less leverage on seawater $\delta^{26}\text{Mg}$. This is now clearly stated in the text.

page 7468 line 15: “Species-specific Mg isotope offsets cannot be readily linked to calcification rate” Does this refer to the absence of correlation with carbonate ion concentration?

Yes, and to a lack of correlation with size, which is thought to represent growth rate in planktic foraminifers (the latter is now referenced with Pogge von Strandmann, 2008).

page 7468 line 15: “This suggests that future models of Mg/Ca fractionation must incorporate Ca and Mg isotope fractionation.” I agree, but I do not like being told what I have to do, so maybe replace “must”.

Has been changed.

Table 1. Please give Al/Ca and Mn/Ca too.

Added to table 1.

Fig. 1: Any explanation for the high Sr/Mg in some samples?

These are data from Gaillardet et al., 1999. The sample with the highest Sr/Mg is the Rhone, followed by the Huanghe, the Wisla and the Rhine. Is it therefore possible that anthropogenic pollution is responsible for the relatively high Sr. This has been added to the caption.

Fig.2: shows P. Obliquiloculata, but the data is not in table 1.

This figure shows all available data, including published data. O. obliquiloculata is from Pogge von Strandmann 2008. This has been referenced in the caption.

Fig.4: "2 sd analytical reproducibility of individual samples". Single measurements or single species?

Single measurements.

Fig. 6: "(E) Model output seawater Mg reservoir. The dashed lines represent other models ..." No, the solid lines.

No, the dashed lines... The solid lines are our models.