Biogeosciences
Discussions

Interactive comment on "Modern and Cenozoic records of magnesium behaviour from foraminiferal Mg isotopes" *by* P. A. E. Pogge von Strandmann et al.

Anonymous Referee #1

General comments:

Pogge Von Strandmann and coauthors present new Mg isotope data from foraminifera, both modern day and from the past $\sim$40My, in order to produce a record of past $\delta26$Mg values in the oceans. The authors provide good evidence in this and in an earlier paper (Pogge Von Strandmann et al. 2008) to show that temperature, Mg/Ca ratio, size fraction and carbonate ion saturation do not influence the foram $\delta26$Mg value, while inter-species isotopic effects means wherever possible a single species record is necessary. The $\delta26$Mg value of modern day foraminifera of the same species appears to be quite variable, meaning that the precision of the foraminifera seawater record is fairly limited (0.5‰. Even so, the data from two species of foraminifera shows clear

evidence for past changes in seawater $\delta26$Mg of over a permil, with values becoming more negative over the past 20My. The authors use the seawater $\delta26$Mg record to model potential sources and sinks of Mg to seawater and conclude that the Mg flux from rivers and the Mg sink to dolomite are the main controls over past change in $\delta26$Mg values of the oceans.

This is the first study to show the past isotopic composition of Mg in seawater with both a decent resolution and a level of precision that, although not great, shows resolvable past changes in Mg isotope composition over time. While there are many studies that have investigated Mg isotopes during continental weathering (rivers, soils sediments etc. . .) a seawater record has been lacking from the literature. For that reason this is an important set of data that clearly needs to be published. The modeling aspect is slightly more problematic to me but it is fundamentally a very difficult problem to address. There are several unknowns or poorly defined fluxes of Mg either into or out of the oceans. For example the past continental weathering flux of Mg is not known, and the low temperature Mg sink at the mid ocean ridge flanks has been estimated to be between 5-100% of the riverine input flux in the modern ocean! I think the modeling that has been attempted is OK and the assumptions are for the most part well justified - I don't know of a way to easily improve this. There has been recent evidence to suggest that seafloor production has decreased over the last 20My but this has not been incorporated into the model – it might not make much difference but I'd like to see it discussed. Similarly it would be good to add some discussion as to why there would have been a change in dolomite Mg sink from 10 to 65% of the MOR sink. That is a massive change – how can this be justified? Finally, due to the number of assumptions that are involved in the modeling and the uncertainties involved, some of the conclusions might want to be toned down a little – e.g. the discussion of what is driving the increase in seawater Mg concentration over the past 10-15My.

Once these relatively minor comments have been addressed I think this manuscript should be accepted for publication in Biogeosciences.

Specific comments:

P7459, L10 – Calculating the δ26Mg 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 87Sr/86Sr the dissolved δ26Mg 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 d26Mg value alone.

P7459, L14 – why is the carbonate endmember so heavy? Dolomites have δ26Mg values that are more usually -2‰ and calcite can be significantly lighter (down to -5‰. Where does -1.45‰ come from?!

P7461, L27 – In general if Δ26Mg is used it should be defined – e.g. Δ26Mgsolid-solution. Shouldn't the value be -2.6‰ I am a little confused as to what Δ26Mgorgcarb-SW values of -0.55 to -2.1‰ actually mean? Modern forams have very light d26Mg values of $\sim$-5‰ and seawater is -0.82‰Ṡo surely a Δ26Mgorgcarb-SW value of -4permil is more normal?

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 24Mg 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.

P7462, L9 – How do you calculate ΔMg/Ca? What does a ΔMg/Ca value of -90 actually mean (fig 2b)?

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

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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?

P7463, L2 – It took me a while to figure out what is meant here. Seawater has a Mg/Ca ratio of $\sim$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 δ26Mg is more similar to seawater than foram δ26Mg values. Perhaps the explanation could be slightly reworded to be easier to read.

P7463, L11 – Why wouldn't you see a correlation between foram Mg/Ca and δ26Mg? Why specify organic Mg/Ca? And again, please define what is meant by organic Mg/Ca (at least somewhere in the paper).

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?

P7464, L17 – In the modern ocean the flux of Mg into carbonates is $\sim$11% of the riverine input and the low temperature exchange of Mg for Ca and low temperature basalt alteration removes $\sim$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?

P7465, L26 - . . .shows the effect of using modern day values for the riverine flux and isotopic composition on seawater δ26Mg,

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

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

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

P7467, L3 –I understand the assumption that the $\delta26$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 $\delta26$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.

P7467, L5 – I agree with the interpretation – we do not see large variation in $\delta26$Mg of several ‰ in large rivers so this would seem unreasonable to invoke in the past.

P7467, L7 – There has been recent work that suggests that the seafloor production rates have decreased over the past $\sim$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.

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 $\sim$25My

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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?

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 ($\sim$5% of riverine input, Bach et al. 2003; Alt et al. 1996) to major (up to 100% of riverine input, Wheat & Mottl 2000, Mottle & 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.

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 $\delta26$Mg. This is because the model input says the hydrothermal flux has not changed, which is still debatable isn't it? (see previous comment)

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