

**Modern and Cenozoic records of magnesium behaviour from foraminiferal Mg isotopes
by Pogge von Strandmann, Forshaw and Schmidt**

submitted to: Biogeosciences

GENERAL COMMENTS

The authors present a set of Mg isotope data for modern and Cenozoic (up to 40 Ma) planktic foraminifera. The data is used to discuss i) possible mechanisms of discrimination against Mg in foraminifera tests. This is of relevance given the widespread use of Mg/Ca in foraminifera e.g. for paleothermometry and ii) the change of seawater Mg isotope composition and concentration during the last 40 Myr. The paper is within the scope of *Biogeosciences*. Getting reliable and precise Mg isotope compositions from foraminifera is not easy. The data presented appears robust and precise and since no such record is published for foraminifera, the study presents a significant advancement. The contribution to the calcification mechanism is in my mind reasonable, but (as previous ones) remains speculative. The modeling of changes of sources and sinks for Mg in the ocean contains several good arguments and approaches, e.g. using the Sr isotope record to estimate the source of Mg in rivers (carbonate vs. silicate weathering) or the realisation that changes in river water Mg isotope compositions cannot explain the change in seawater Mg isotope compositions. There may be some complexity with the hydrothermal sink (see details) but I am no expert in this regard.

In my opinion, the paper can be published with minor (but careful) revision on the discretion of the authors.

SPECIFIC COMMENTS ON SCIENTIFIC ISSUES

There are only minor comments, see below.

DETAILS

Title:

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

Abstract:

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

You should add that $\delta^{26}\text{Mg}$ is given relative to DSM3 Mg.

line 23: "Mg" isotope ratios inferred ...

Introduction:

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

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

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).

page 7453 line 20 onwards: please give the $\delta^{26}\text{Mg}$ 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)

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.

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.

page 7454 line 19: consider to replace or delete “although”.

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

Materials and methods:

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.

page 7457 line 26: uncertainty is 2 sd?

page 7458 line 27: “ $D_{sed} \sim 1.7-2\%$ for dolomite” please give the exact values that enter your model

page 7459 line 14: minor thing: “ $d_{26}Mg$ 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).

Results:

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.

page 7460: consider to add figures of $d_{26}Mg$ vs. carbonate ion conc., depth and perhaps Sr/Ca, respectively. There seems to be a general tendency of lower $d_{26}Mg$ 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).

Discussion:

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

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

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”?

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 $D_{26}Mg_{foram-inorg Cc}$ ”.

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 ...”

page 7462 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).

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

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

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

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.

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.

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

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?

Conclusions:

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?

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”.

Table 1.

Please give Al/Ca and Mn/Ca too.

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

Fig.2:

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

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

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

Frank Wombacher 3rd July 2014 (sorry for being late)