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Biogeosciences Discussions

Interactive comment on "The impact of seawater calcite saturation state by modifying Ca ion concentrations on Mg and Sr incorporation in cultured benthic foraminifera" *by* M. Raitzsch et al.

M. Raitzsch et al.

markus@ldeo.columbia.edu

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Dear Dr. Bijma,

We are pleased to have received two constructive and helpful reviews plus one short comment (which was actually an adequate review), which definitely helped to improve our manuscript. We adjusted the manuscript according to the reviewer's suggestions and would like to consider our revised manuscript for publication in Biogeosciences. Detailed responses to the reviewer's comments are below:

Reply to Anonymous reviewer

Major comments: The part on the influence of Mg/Casolution, DMg, and Mg/Cacc concerning A. tepida is slightly confusing. Page 11355, lines 13-15 starts with that the change in Mg/Cacc is negligible indicating no influence of the hardly changed solution Mg/Ca. Indeed, the Mg/Ca in the solution is within errors constant. But, according to Table 2 Mg/Cacc is decreasing from 2.41 to 1.60 (not including the outlier). That is a change of 65%, comparable to temperature change (following general temperature dependency) of 5+C. I would not call that a negligible change. Later in the discussion (4.1, 11358, first lines) you state that DMg (and therewith of course Mg/Cacc) indeed decreased significantly, but as an effect of increased (Ca2+). Then in section 4.2 further evidence is given that not Mg/Casolution but indeed Ca concentration is the controlling factor. I suggest to rephrase the first part on page 11355 to make it more in line with the rest of the discussion.

Reply: We agree that this part was slightly confusing since the variation in Mg/Cacc is significant and the range of Mg/Casw is negligible. The according sentence was rewritten.

At several places the importance of these experiments with regard to reliably reconstruct paleotemperatures is mentioned. The abstract (beginning and end) mentions the importance of knowing the Ca concentration and how this has changed over time. The last part of discussion says that Mg/Ca is more dependent on the Mg/Ca ratio of the sea water than on the Ca concentration. And in the conclusion Sr/Ca is mentioned as potential recorder of past sea water Sr/Ca. But, where is the link which shows how relevant these experiments are for paleoreconstructions? The introduction says that Ca behaves conservatively in the ocean with a residence time of 1.1 Myr. Does this mean then that the remark from the abstract is only valid for records which cover longer time periods? And are there any indications on how the Ca concentration changed in the past? Is this comparable to the range which is used in the experiments? The same goes for Mg/Ca and Sr/Ca of seawater. How did they change in the past? Mg/Casw, for example, changed from 5.2 to over 6 in one of the experiments. But in nature the

modern Mg/Ca of 5.2 is the highest for the whole Cenozoic. Most of the time values have been a lot lower. Taking this together with the fact that some experiments have suggested that at higher omega the response of DMg is not that strong anymore, could it be that a much larger effect could have been detected when Ca concentration (or accidental Mg/Casolution) were lowered instead of increased? How representative are these results for the reconstruction of paleotemperatures? These two shallow living species were used as they are robust and can be subjected to many conditions, but which are never used in paleotemperature reconstructions. However, one of the results is the difference response of them to certain environmental changes. Is it okay to transfer behavior of a shallow living benthic foraminifer to a deep living benthic foraminifer because their Mg/Ca ratios occupy a similar range?

Reply: It is right that these issues were not discussed extensively. A detailed discussion on that is now included in the last section ("Conclusions and implications for paleoreconstructions").

Minor comments: p.11353, line 10: why was A. tepida kept in the dark?

Reply: An explanation was added.

p.11354, line 11: You mention B and U here, but they are not in the results?

Reply: B and U have been removed.

p.11355, line 24: Fig. 4a should be Fig. 5a?

Reply: Yes, changed.

p.11359, line 2: replace "are" with "is".

Reply: Changed.

p.11361, line 4: replace "implies" with "imply".

Reply: Changed.

Table 1 and 2: Just an idea: it seems to me that it would have been more convenient to make one table with all data for H. depressa and one for A. tepida.

Reply: The tables are reorganized now.

Figure 4: make a c) plot from the inset in part a). That makes it a bit clearer.

Reply: Changed.

Reply to Dr. Toyofuku

I have two major points. 1. experimental water chemistry for H. depressa Mg/Ca of seawater (Mg/Ca sw) conditions has changed from 5.2 to 6.2 with calcite saturation state for H. depressa, while the Mg/Ca sw ratios indicate almost same value for A. tepida. This Mg/Ca sw variation for H. depressa can not be ignored. The fact should be mentioned by authors via a comparison between A. tepida and H. depressa in Result and Discussion.

Reply: We agree with the concern raised by this reviewer, but feel we have covered this matter sufficiently in the texts dealing with the obtained Mg/Ca ratios. For instance, we explained that on p. 11355 line 11-17, p. 11359 line 24-p. 11360 line 3, and p. 11362 line 10-13. I think we came up with that information at the most important passages. In addition, section 4.2 is entirely dedicated to this issue.

2. clear differentiation between calcite saturation state and [Ca2+] The experimental variable is calcite saturation state in this study. 5 times larger [Mg2+] changing is occurred when the [Ca2+] is changed. The variations should be caused by difference of calcite saturation state of seawater and not caused by only [Ca2+]. I think it is inadequate that the result will be argued by the effect of [Ca2+] only.

Reply: The main reason for interpreting our results as a function of [Ca2+], rather than as a function of saturation state, is twofold. Firstly, there is a dataset (Dueñas-Bohórquez et al., in prep) that shows that the foraminiferal response to carbonate ion manipulations is not the same as those after manipulating calcium. Secondly, we be-

lieve that foraminifera may not have some sort of 'omega-receptor'. In a number of published calcifiation models for foraminifera, it is noted that foraminifera should be able to concentrate Ca and (bi)carbonate ions from seawater. Since the ratio between the two ions in sea water is not the same as in calcite, foraminifera likely take up and utilize Ca and (bi)carbonate by different mechanisms. Therefore, we explained our results primarily as a function of Ca-availability and secondarily as the associated change in saturation state.

*** The sequential comments. p.11347 The impact of seawater calcite saturation state by modifying "Ca" ion concentrations on Mg and Sr incorporation in cultured benthic foraminifera. I feel that the experimental variable would be only [Ca2+] in this study from this title. Is it OK?

Reply: As we said in our previous reply, we think that Ca concentration is the main control on the incorporation of Mg and Sr in our results. However, we clarified it now in the title: "Incorporation of Mg and Sr in calcite of cultured benthic foraminifera: impact of calcium concentration and associated saturation state."

p.11352 l.10-15 The Mg/Ca sw has slightly changed among the conditions for H. depressa. I think the fact should be mentioned when you want to compare results between this species and A. tepida.

Reply: Yes, this information is important when comparing the results between A. tepida and H. depressa, but here it comes a bit too early since it would interrupt the reader in getting general information on the experimental setup. Therefore we wrote "similar Mg/Ca ratios between the different solutions" and not "constant...".

p. 11353 L. 20 The information of light source (e.g. intensity or Photosynthetically Active Radiation (PAR)) is required, as far as authors deal with symbiotic species.

Reply: Unfortunately, we don't have information on the light intensity or PAR, but I added information on the lamp including the manufacturer, model and the electric

power. However, we assume to have had run our experiments at the lower range of 100 to 200 μmol photons m-2 s-1. A recent study of Fujita & Fujimura (2008, JFR, Vol. 38) showed that the inorganic carbonate production of large symbiont-bearing foraminifera is not that dependent on the photosynthetically active radiation, compared to the organic carbonate production.

p. 11354-11355 In my impression, growth rate of 29% and 47% is a little bit small for 2-months incubation. Had the specimen already matured from the beginning? Could you give the table about the growth of specimens, too?

Reply: Yes, it is possible that some specimens were already mature when we added them to the experiments. It is now mentioned in the according text. Data on the number of incubated, grown and analyzed foraminifers are now included in Tables 1 and 2.

P. 11355 L. 2 ... specimens precipitated new "calcite". I think "chamber" is good at here.

Reply: Changed.

P. 11356 L. 22 The overgrowth specimen should be pictured in gray in the Sr/Ca plot, too.

Reply: Changed.

P. 11356 L. 23 Could you show the SEM photo? I am interested with the thickness of the wall and looks of the test surface from each condition.

Reply: The SEM pictures are added as Figure 7.

P. 11357 L. 9 Mg/Ca of seawater is modified with calcite saturation state for H. depressa. This fact should be mentioned in the paragraph.

Reply: The change of Mg/Casw in the Heterostegina experiment is already mentioned in section 3.2. However, a possible influence of Mg/Casw on the Sr incorporation is discussed in section 4.2 where we show that only a minor portion of incorporated Sr

can be attributed to this parameter.

P. 11358 L. 11 The varied Mg/Ca of seawater is considered in this discussion?

Reply: The possible influence of Mg/Casw on Mg/Ca in H. depressa has been mentioned in section 3.2. In section 4.2 there is an own discussion only on the influence of Mg/Casw. However, in section 4.1 the decrease in DMg of H. depressa is shown to be so small that it is statistically insignificant. If Mg/Casw was constant between the different solutions, we wouldn't probably see any change in Mg/Cacc at all.

P. 11359 L. 15 with increasing calcite saturation state Is the effect of Mg/Ca sw truly negligible?

Reply: In the next section we show that the influence of Mg/Casw and Mg/Cacc on the Sr incorporation is very small in the Heterostegina experiment. Theoretically, the change should be only 1%, but we observed a change of 23%, which can be only attributed to the varying Ca concentrations.

Reply to Dr. Hathorne

11348, Line 23-25, Actually the effect seems very small and you should put this into the context of the estimates of seawater Ca concentration during the Cenozoic from the literature. What would the impact on Mg/Ca temperature estimates be in the Eocene?

Reply: The anonymous reviewer raised the same questions. This information is now added to the abstract and a more detailed discussion is included in the last section, which is now named "Conclusions and implications for paleoreconstructions".

11349 Line 27, ". . .field studies on benthic foraminifera contradict. . ." but which studies in particular?

Reply: References were added.

11350 Line 15, It was actually Segev and Erez (2006) who did the seawater Mg/Ca culturing experiments.

Reply: Changed.

11350 Line 20, It is a bit forward to call it "calcium ion effect" try simply concentration.

Reply: Changed.

11351 Line 23, ". . .sodium hypochlorite bath. . ." sounds dangerous.

Reply: Indeed. It's just sodium hypochlorite now.

11353 Line 3, ". . .with modified carbonate chemistry." I thought this study was about Ca concentration?

Reply: Changed

11354 Line 8-14, You cannot cite our abstract like this as it is not published properly, like at AGU or Goldschmidt, and I hate it when people cite abstracts. I would cite my 2008 JAAS paper saying non-matrix matched calibration works for many elements in a calcite matrix using a 193nm laser. Concerning the change in laser power, can you show some data for the Utrecht Iceland Spar Calcite versus solution ICP-MS values for it? Just some values for Mg from the period of your analyses would be fine. Then you do not have to mention the paper in prep which will be in prep for some time to come.

Reply: The analyses of the GJR standard are now available as Figure 3. Reference was changed.

11354 Line 16, GLITTER is not made by New Wave Research, check out www.glittergemoc. com/

Reply: Changed.

11355 Line 4-5, This relationship is not clear for depressa with only the highest [Ca2+] experiment showing an increase greater than the error estimates shown.

Reply: Rephrased.

11355 Line 16, The depressa Mg/Ca data points are all within the error estimates

shown. What is the level of confidence shown here? You should try to be consistent and use either 1 or 2 sigma throughout.

Reply: It is true that the overall difference between the population means is statistically insignificant, due to the large standard deviations. However, the regression analysis gives a statistically significant relationship between Mg/Cacc and Mg/Casw. This part is clarified now.

11356 Line 6-8, rephrase

Reply: Rephrased.

11356 Line 21-25, Please provide some evidence for this besides SEM images which are always subjective. Some SEMs are fitted with EDAX which could measure a high Mg phase on the surface. Also try calculating the saturation sate of high Mg phases in the various experimental solutions.

Reply: Unfortunately, we did not have EDAX available during SEM imaging. A new Figure 3 with the SEM images has been added that clearly shows the difference between normal shells and those that were incubated in the solution with the highest Ca concentration.You are right that the interpretation of SEM images is subjective, therefore the text has been partially rewritten.

11358 Line 10-12, rephrase

Reply: Rephrased.

11358 Line 16-, Be careful comparing aragonite to your high Mg and low Mg calcite.

Reply: It is mentioned now that these observations from corals are possibly not applicable to foraminiferal calcite. However, it was not meant as a statement but as a possibility. To my knowledge, there is no culture experiment that shows that Ca concentration increases the growth rate of foraminifera. But I wanted to have mentioned that possibilty as it was shown for coralline aragonite.

11359 Line 9, The growth rate dependence shown in Kisakürek et al. (2008) is very small, especially considering the measurement uncertainties.

Reply: This information was added.

11359 “Role of Mg/Ca SW”, I do not think you have a large enough range of experimental Mg/Ca ratios to really extrapolate your results like this. The results are also all within error of each other and should not be interpreted as currently in Fig 6.

Reply: You are right that our Mg/Casw range is too small to allow for extrapolating the relationship with Mg/Cacc as I did in Figure 6 (now Figure 8). Therefore, I changed the figure with dashed ends of the regression line and question marks. However, the possible influence of Mg/Casw on Mg/Cacc is worth discussing, and to my opinion the data make sense since they are remarkably similar to the results from inorganic and other culturing experiments.

11360 Line 20-22, The variations being discussed seem to be within the error estimates shown on Fig 5c.

Reply: Maybe they seem to be within error estimates, but ANOVA analyses revealed that the differences between the population means are highly significant. See section 3.3.

Finally, something is missing, put the results in the context of the secular variation of seawater Ca. When was the seawater Ca concentration twice that of modern?

Reply: It is right that these issues were not discussed. An extended discussion on this is now included in the last section (“Conclusions and implications for paleoreconstructions”).

Interactive comment on Biogeosciences Discuss., 6, 11347, 2009.