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## ***Interactive comment on “A novel salinity proxy based on Na incorporation into foraminiferal calcite” by J. C. Wit et al.***

### **Anonymous Referee #1**

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Review on A novel salinity proxy based on Na incorporation into foraminiferal calcite by J. C. Wit et al,

In this work the authors are trying to develop a novel proxy for seawater salinity using Na/Ca composition of foraminiferal calcite. Foraminifera were cultured under controlled conditions where seawater parameters, except salinity, were kept constant. LA-ICPMS was used to measure the geochemistry of the cultured shells, in particular, Na/Ca and Mg/Ca values. This advanced analytical method offered the possibility to compare geochemistry of individual shells with their size as well as distribution of trace metals across the shell wall.

The authors found a strong correlation between seawater salinity and shell geochemistry Na/Ca and Mg/Ca which they interpreted as a result of strong salinity control on

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incorporation of Na and, to some extent, Mg into foraminiferal calcite. If found to be true these results present a significant step forward in developing an independent proxy for reconstructing past ocean salinities. Developing a proxy for past ocean salinity is one of the major topics in paleoceanography and I have no doubts this work will be of high interest in the scientific community.

Unfortunately, the manuscript lacks some key information on culturing experiment and analytical method and, in my opinion, also does not have enough information to support its major conclusion (i.e., development of new salinity proxy). The authors completely overlooked the potential effect of calcification rates on Me/Ca values, which could explain the observed relationship without invoking salinity dependence. I hope I am wrong and that the authors will reinforce their conclusions but I think the work would require major revisions, which is what I will recommend to the editor.

\*\*\*\*\* Please see below my detailed comments regarding the manuscript. I split them into two categories: MINOR = requires additional information or explanations and MAJOR= requires significant re-evaluation or additional data.

1- (Minor) –Methods-page6042-lines25-27

Carbonate system is very difficult to maintain during the culturing experiment. All discussed data can completely have different meaning if, for example, pH was drifting significantly during the experiments as it will have major implication for foraminiferal Me/Ca values.

The authors stated that they monitored it during the experiment and found it constant. This statement has to be accompanied by data. At minimum they will need to provide DIC, alkalinity, pH or pCO<sub>2</sub> at the beginning and at the end of each experiment. If they monitored it then it would be best to provide a time series plot.

2- (Major) –Methods -page6043-lines12-25

Description of LA-ICPMS analytical method is inadequate. Na/Ca analysis by itself is

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not a straightforward exercise because Na has one of the largest matrix effects (on itself and other ion in ICP plasma). Authors must provide sufficient proof that measurements were done appropriately and a few references to early publication of the same research group cannot be accepted here.

First, authors used NIST 610 for cross calibration but I am not sure this is a safe approach especially as they used different energy outputs during ablation of the standard. Note that there is ~14% of Na<sub>2</sub>O in the NIST610 and only few hundreds of ppm in foraminifera where there is already huge matrix differences, and on top the standard is ablated with 5 times more energy. NIST610 is ok for Mg/Ca in forams but Na/Ca is a risky and unproven approach.

Second, there is potential ICP front-end contamination (e.g., cones, injector) with Na and drift in signal-to-background ratio. In normal practice, we for example, have specially dedicated 'low-Na' ICPMS cones for measuring Na/Ca in biogenic calcite. This is because after introduction samples with high Na concentrations (like NIST610) the Na background will be higher than the foraminiferal signal. And worse, this background is increasing in each consecutive high-Na sample which will degrade the quality of Na/Ca measurements. So I am puzzled how the authors managed to measure NIST610 and foraminifera using the same ICP front-end. What is the signal-to-background ratio on the forams samples? Was it constant through time (throughout the experiment)?

I think without robust proof and detailed description of the analytical methods all presented dataset could be compromised.

3- (minor) –Methods-page6042-lines17-27

There is very limited information given about Me/Ca composition of culturing media. Surprisingly, Na/Ca (value?) of seawater is missing. The authors have Dna so they should have Na/Ca which has to be provided. It is also important to understand if seawater Na/Ca affects foraminiferal Na/Ca. Note salinity is not = Na/Ca because there can be changes in Ca concentration.

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Were Na/Ca and Ma/Ca values constant during the culturing experiment? Note authors are dealing with chemical cocktail and inorganic precipitation is possible, which is sometimes difficult to identify by simple visual examination.

#### 4- (minor) –Methods -general

There is no description on how the shells were cleaned prior to geochemical analyses. The main focus of this work is Na/Ca and seawater contains high amounts of Na and therefore shell contamination is expected. How did the authors clean their shells and how did they make sure they are cleaned well?

#### 5- (minor) –Results-general

Results section is only half page long!!! This is a research paper with big claims and only half page results??? I think this is unacceptable and in fact the lack of results became quickly obvious in the discussion.

To my knowledge, this first paper is describing Na/Ca in forams using LA-ICPMS. So far, there is limited information in the literature on how Na is distributed within the foram shells and how it is different in different chambers. The authors clearly have this information but failed to present it. Arguably, it is not vital in the context of this manuscript but in my opinion this is a MUST HAVE information, which can help interpret some of the correlations identified in this work. I strongly suggest adding a few profiles of Na/Ca and chamber comparison. Also, it would be nice to see Na/Ca profile/chamber values correlated with Mg/Ca.

#### 6- (minor) –Discussion-page6044-lines20-page6043 –line 14

On few occasions, the authors discussed Na/Ca banding in forams and refer to Erez 200x. I am a bit confused here because if I remember correctly I have not seen (published) a single profile of Na/Ca across foraminifera. Definitely Jonathan Erez has none of them. Are the authors referring to their findings? I think for this discussion the authors need a separate section in the results.

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The same goes for the authors comment on lack of 'hot-spot' distribution of Na/Ca across the shell. Please present it in the results.

7- (major) –Discussion-page6046-lines10-27

The authors found a strong intercorrelation between shell size, Na/Ca, Mg/Ca and seawater. Although I understand that establishing a salinity proxy is the primary goal of this study I think the dataset, as it stands, can be interpreted differently. One of the striking features of the dataset is the strong correlation of Me/Ca not only with salinity but also with shell size. The authors argue in the discussion that ontogenetic effect, to which they attributed shell size, by itself does not have effect on foraminiferal Me/Ca. However, a major potential factor, such as calcification rate, was not considered. Shell size is potentially a direct measure of calcification rate, which has a huge (orders of magnitude) effect on trace metal incorporation into calcite. It has been argued for ages that the relationship between Mg/Ca values of foraminifera or ostracoda and their shell size is related to calcification rate. Also, there are numerous inorganic experiments, which clearly establish the link between Me/Ca and calcification/precipitation rate. Therefore, it is quite possible that the increase in Me/Ca reported in this work is due to decrease in calcification rate in experiments with higher salinities. In fact, it may not be related to salinity at all but to concentration of Ca in seawater, for example. I may be wrong but these potential problems have to be one of the major points of the discussion.

Please also note that the argument used by the authors in discussing ontogenetic effect (i.e. individual shell size vs Na/Ca value) is incorrect. Processes which controls Me/Ca at individual shell level and bulk/average Me/Ca level could be different. For example, at individual level there is no correlation between individual shell Mg/Ca values and temperature (just biological noise) but the average Mg/Ca value of 20-30 shells has a strong correlation with temperature. And again, it is not ontogenetic changes but calcification rate which is primary the driving force behind shell size effect. I would like to suggest a few hints which may be helpful for the authors in their rebuttal.

**BGD**

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- Try to estimate thickness of the shells which would be a more accurate measure of calcification rate. Use either LA profile or SEM measurements of few shells if they are still available. Compare this with culturing log book and life span of each foraminifera.
- Use Sr/Ca ratio. Sr was also measured as mentioned in the method section. It could help the argument because Sr response to calcification rate is opposite to that of Mg.

8- (minor) –Discussion-page6047-page6048

The section on Mg correction is completely out of place in my opinion. First, effect of salinity on Mg/Ca is still debated and by itself controversial. Second, this section is badly structured and has many controversial and subjective statement/arguments (e.g. Mg/Ca seawater not affecting Mg/Ca in forams; calcification pathways; individual shell Mg/Ca correlated with size at one salinity but does not in others). And last, it is absolutely not applicable for paleorecords. Let us assume that things work as suggested. Changes in paleosalinity were usually 1-2% which would be 5-10% in Mg/Ca values and is equivalent of 0.5-1C. So in theory, we should correct these very small changes using Na/Ca values. However, error bars on Na/Ca and Ma/Ca are already larger than this, plus there are uncertainties associated with calibration curves (e.g Mg/Ca vs. T and Salinity plus Na/Ca vs. salinity). So if errors are correctly propagated through calculation 'corrected' temperature, estimates will be much worse (more uncertain) than initial temperature estimates.

I think that Na/Ca vs salinity is sufficient and a major topic by itself and it would be beneficial to focus on it adequately rather than adding unnecessary and controversial topics, such as Mg/Ca correction.

I believe that this work has great potentials and could be an important starting point in developing a new and exciting proxy for paleoclimate studies. But as for all novel ideas, it requires a solid base with meticulously detailed description/ evaluation/discussions which I hope I will see in the revised version of the manuscript.

Interactive comment on Biogeosciences Discuss., 10, 6039, 2013.

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