Interactive comment on "Planktonic foraminiferal spine versus shell carbonate Na incorporation in relation to salinity" *by* Eveline M. Mezger et al.

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Dear editor and dr. Takashi Toyofuku,

Thank you very much for the useful comments, additions and suggestions on our manuscript. We have changed and/or answered these comments step-by-step in the text below, explaining why we agree or respectfully disagree. Our answers are directly below the individual comments.

Also on behalf of the other authors,

Respectfully yours,

Eveline Mezger

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Takashi Toyofuku: "Uploaded my comments are bit older revision with unexpected re-action of website. I hope authors use my comments indicated below. *** General considerations In this study, detailed sodium (Na) content and distribution of planktonic foraminiferal test. Na distribution of spine and spine base had been not well studied by previous studies. This point is greatly progressed by this study. The authors also suceed to show that presence or absence of spine / spine base enriched with Na can have a significant effect on bulk Na / Ca. Geochemical analysis of numerous shells and organic linings and model calculations are carried out by this study. I can certify this is a good research that has been extensively studied about spine and spine-based Na / Ca, and it is expected that readers of Biogeoscience will be interested with this topic."

Questions and comments

1) Have you not analyzed chlorine by EPMA? Also, please be sure to show the how many times and how long the samples were wash with water (L. 94). In considering Na / Ca, salt NaCl is the most popular and strong contaminant from seawater. It is necessary to know whether the distribution of Na is related to Cl or independent. Authors insist that Na is included in lattice with cited literature, but may Na that is not included in lattice exist, too. It is also necessary to make sure whether there is a change in Na concentration depending on the time and number of washing with water (L. 98) to consider the influence of NaCl. The washing process never change Na contents?

Thank you for this suggestion. Unfortunately, this method does not allow for chlorine (Cl) measurements since their concentrations in calcite are much lower ($\sim$40 times) than those of sodium (Na). This has now been added to the text at line 107. The fact that Cl is much lower is still a valuable addition to our study. This implies that Na incorporation into the shell as (micro-)fluid inclusions (similar to what is suggested for Cl, Kitano et al., 1975), only provides a very small contribution to the total Na. Therefore, the effect of rinsing and potentially losing the fluid-included Na, does not significantly affect our results. Clearly, Na is – as far as resolution permits – homogeneously distributed throughout shell calcite, and higher in spine (base) calcite, with no (visible)

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contamination on the outside of the shells. We rinsed every polished sample three times to avoid contaminants on the calcite surface. As these (polishing powder) particles were very loosely attached to the exposed surface, contact time with the deionized water was kept very brief and is not expected to influence lattice-bound Na. We now added this information to the manuscript (line 98). So far, leaching of Na from the calcite lattice has only been observed on much longer (Myr) timescales (Yoshimura et al., 2017). Furthermore, after extensively testing the effect of the number of rinsing steps on the Na-composition in inorganic calcite powder (Mezger et al., in preparation for submission), this did not show any difference in calcite Na/Ca (Figure R1).

Caption Figure R1: Na/Ca values of inorganic calcite powder, measured with iCAP-Q-ICP-MS at the Royal NIOZ, plotted as a function of cleaning steps with supersaturated $CaCO_3$ solution and de-ionized water (here referred to as milli-Q). The relatively high Na/Ca before rinsing indicates seawater present at the surface of the precipitated calcites.

2) Why authors did not analyze samples of different salinity conditions to examine the relationship between Na / Ca of spine and spine base and salinity? (Section 4.3). In Mezger et al. (2016), the first author analyzed planktonic foraminiferal specimens collected by plankton pump in Red sea with salinity gradient. Therefore, it seems possible to analyze Na / Ca of spine compared with salinity with these samples. However, in this study, as shown in Fig. 8-10, from the consideration based on the model calculation, it is concluded that Na / Ca of spine does not correlate with water temperature. The approach by model calculation is interesting and the conclusion is logical. Robust discussion can be constructed if there is support by measurement. In the future study, I think there is a possibility that samples with different salinity conditions can be measured. For that reason, it is not bad idea to leave room for discussion in the conclusion.

Thank you very much for this useful comment. Unfortunately, we did not have enough material left to study the chemical (EPMA-measured) shell composition for the whole

salinity range (Mezger et al., 2016). These surface water collected specimens were very thin and fragile, and therefore often severely damaged upon laser ablation analyses. Furthermore, due to cleaning procedures, different life stages and the vulnerability of spines, it was challenging to assemble enough material to measure spine composition at all. Spine compositions could only be measured reliably on 'new' multinet collected specimens, which were cleaned differently compared to the other samples used in previous studies. The relationship between salinity and shell Na was based so far on averages of multiple measurements on many different specimens, as the inter- and intra-specimen Na variability is quite large. In this study, we analyze a limited number of individuals and therefore, more specimens and measurements are probably necessary to investigate the potential relationship between spine Na and salinity. We added an extra sentence on this discussion subject in line 428.

3) L. 101: Gentle setting for measurement of Na. Did you check reproducibility of Na measurement with this setting on standard materials? Further, this voltage seems bit weak (not impossible) for calcium detection. Authors will explain about the meaning of optimization of measurement setting of EPMA.

The JCP-1 standard was measured multiple times (n=6) with the same (optimized) settings as the samples, we now clarified this at line 130. The gentle settings of the EPMA allowed us to increase the measurement time on the calcite, since the material and resin is too delicate for more intense beam settings.

4) L. 132: SEM 3000 means "Miniscope TM 3000"? I can not find this type of SEM on Internet.

You are correct, the official name would be 'Hitachi High-Tech TM3000 TableTop scanning electron microscope', which we now changed at line 135.

5) L. 201; I prefer more informative subtitle of paragraph. e.g. SEM measurement of spine morphology and densities.

We now changed the text accordingly at line 203.

6) Figure 5: Can you indicate the difference in species by color? e.g. T. sacculifer is bluegreen colors, G. ruber is red-orange colors. Describe the meanings of shown lines in this caption. Further, could you indicate which data were measured by EPAM or LA-ICP-MS?

Thank you for the suggestion, we now changed figure 5 and its caption accordingly.

7) 4.1 Organic Linings: Authors could show that organic lining were poor with Na. Why EPMA Na mapping never show OM as low concentration bands?

As explained in line 155, organic linings in these species only account for a very limited part of the total shell weight, 0.4-0.7% of the total shell. But the carbonate deposited at or close to the organic lining could even be relatively high in Na. Here we cannot observe the linings as such using EPMA imaging. We now added an extra sentence about this in line 280.

8) Figure 6: It is not appropriate to show "?" here. Describe possible explanation for "Spine Na/Ca" and "Outliers" in the plot Instead of indicating "?".

We changed the figure (6) and caption and agree that this '?' might be confusing.

9) L. 331: This is important consideration because the measured results are variable at part by part by such partial measuement method as LA-ICP-MS, SIMS, EPMA and more. The authors will mention the importance about the choice of measurement portion on the test.

We now added some extra information on the measured portion of the test in line 96

10) Figure 7: It is good useful compilation figure of Na/Ca understanding. Could you explain all indicated knowledge of these in the main text? It would be fit the paragraph started from L333 or around the sentence.

We now added some extra text at line 337.

11) L. 355: Some figure and/or previous study should be referred after "function of salinity".

Thank you, we now changed the text accordingly.

12) Figure 10: Explanations about the lines in the fig. 10a is necessary in the figure caption.

Thank you, we now changed the text accordingly.

Please also note the supplement to this comment:
https://www.biogeosciences-discuss.net/bg-2018-454/bg-2018-454-AC1-supplement.pdf
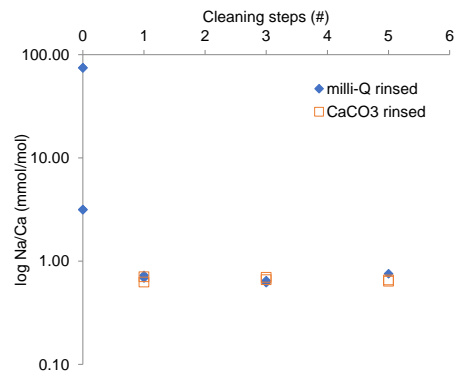
Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-454, 2018.

Fig. 1. Figure R1

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