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Discussions

Interactive comment on "Distribution of chlorine and fluorine in benthic foraminifera" *by* Anne Roepert et al.

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Referee Comments Anonymous Referee #2

Roepert et al present NanoSIMS results looking at the distribution of chlorine and fluorine in cultured benthic foraminifera; two rotaliid species where calcite test walls are constructed via calcification around a primary organic sheet (hyaline calcification), and two miliolid species where test walls are constructed from calcite needles within an organic matrix. The preliminary results show that the calcification pathway of benthic foraminifera determines the incorporation and distribution of Cl, F, P and other elements in their calcite shells. The paper is interesting and well written and a good fit to Biogeosciences. One thing that is missing from the text relates to what kind of proxy

the authors think the various halogen elements versus calcium ratios would represent? I have a couple of minor comments that can easily be addressed with minor revisions:

Thank you for your constructive feedback: our detailed responses are given below.

Comment RC2.0: One thing that is missing from the text relates to what kind of proxy the authors think the various halogen elements versus calcium ratios would represent?

Answer: This information is given in the introduction in lines 42-44.

Comment RC2.1: The study takes advantage of benthic foraminifera cultured for different purposes, under different conditions (Figure 4). Were all the samples cultured in the same artificial/natural seawater, and were halogen concentrations monitored?

Answer: The specimen were not cultured in the same artificial/natural seawater. However, the range of salinities created in the culture media by modifications of the natural and artificial seawater based culture media were larger than expected differences between natural and artificial seawater at the same salinity. For the experiments with A. lessonii and A. tepida, the culture media were produced from natural seawater, while for the culture experiments of S. marginalis and A. angulatus, artificial seawater based culture media were used. As halogen concentrations in seawater are tightly linked with salinity, we chose to determine, for practical reasons, salinity in the culture media stocks rather than halogen concentrations. See also answer to comment RC1.6.

Changes: More detail on culturing is provided in the methods section in the revised version: for the detailed changes, see comment RC1.6.

Comment RC2.2: Several of the environmental parameters were calculated from other relationship (salinity-alkalinity) rather than measured. How constant would these parameters have been during the culture experiments?

Answer: As it was not feasible to measure these parameters in the small Petri dishes the foraminifera were grown in, the parameters were measured once when preparing the seawater stock. During the experiment, these variables may have varied slightly

due to evaporation when feeding/cleaning. However, the media were replaced with fresh stock seawaters with the fixed parameters twice a week. Furthermore, culture media were in equilibrium with atmospheric pCO2. Changes in DIC due to calcification are expected to be negligible given the high ratio of culture media volume to foraminiferal calcite per Petri dish.

Changes: We have added more information on the culturing to the Methods section: "Due to the small culturing volumes (Petri dishes), the parameters of the media could not be monitored during the experiments. However, potential changes due to evaporation during feeding or cleaning of the cultures are expected to be negligible, because the culture media were renewed regularly (twice a week), when compared to the large differences between the treatments."

Comment RC2.3: It would be good to see a discussion of error estimates relating to the parameters the halogen/Ca are being compared with.

Answer: see also comment RC2.2. The ranges of the environmental parameters to which the halogen/Ca ratios are compared to, are in the extremes of what is found in natural seawaters, e.g. total alkalinity ranged from 1350 – 4477 μmol/kg. We therefore expected that slight variations in the culture media had little impact with respect to the large differences between the culture media.

Changes: We have added more information on the culturing to the Methods section.

Comment RC2.4: Furthermore, a brief discussion about halogen/Ca errors/variability also seems appropriate.

Answer: see Comment RC1.2.

Changes: see Comment RC1.2.

Comment RC2.5: All results are grouped together in Figure 3 and 4. Why would you expect a similar relationship between halogen/Ca and environmental parameters in hyaline and miliolid species?

Answer: Since this is the first detailed study of Cl and F incorporation into benthic foraminiferal calcite, we presented the data both in terms of co-variance with cations that have been investigated in detail before and in terms of carbonate system parameters. We made no a priori assumption about the absence or presence of a relationship. When halogen incorporation would not be dominated by biomineralization pathway differences of rotaliid and miliolid species, but governed (mainly) by environmental parameters, then a relationship may be expected, as discussed in lines 199-200.

Comment RC2.6: Correlations. Tone down discussion concerning correlations as only very few specimens were used of the same species etc in abstract and results section.

Answer: This comment echoes RC1.1. We are aware that the number of specimens measured in this study does not allow a robust interpretation of the effects of environmental parameters. We have nevertheless included figures showing our data in comparison to culture media properties for visualization.

Changes: see changes to comment RC1.1.

Comment RC2.7: Spatial distribution of halogen/Ca (Figure 1). For the hyaline species higher values are found in the primary organic sheet for all three halogens. Have the authors taken into consideration that Ca in the primary organic sheet will be much lower than in the calcite? Halogen/Ca ratios are hence higher, but it doesn't mean that halogens are actually higher in concentration than they are in the calcite. Do the anion counts show elevated concentrations in these bands?

Answers: Yes, we have taken into consideration that Ca intensities may be lower in the locations of the organic sheet compared to the calcite. However, due to the spatial resolution this is hardly visible in the Ca intensities and the anion intensities are elevated in the locations of the bands, see added figure A6.

Changes: We have added Figure A6 to the appendix showing the elemental intensity profiles for the same transects as in Figure 1, illustrating that elevated halogen/Ca

ratios at the locations of organic linings are not caused by lower Ca intensities. We furthermore added “These bands are not caused by lower Ca intensities at these locations (Figure A6).” to the Results section.

Other comments: Comment RC2.8: Abstract: The discussion of the results is vague. What is meant by ‘Cl and F were highly heterogeneous and correlated within the shell walls’ (line 7, 8), and ‘In these species Cl and P were correlated’ (line 10)? was the correlation positive or negative, and how significant?

Answer: ‘Cl and F were highly heterogeneous and correlated within the shell walls’ (line 7, 8) refers to the spatial distribution of Cl and F within shell walls. ‘In these species Cl and P were correlated’ (line 10) refers to a positive spatial correlation of Cl and P.

Changes: the text was adapted as follows: “Cl and F were distributed highly heterogeneously within the shell walls, forming bands that were co-located with the bands observed in the distribution of phosphorus (significant positive correlation of both Cl and F with P; $p < 0.001$)” and “In these species Cl and P were spatially positively correlated ($p < 0.001$)”

Comment RC2.9: Lines 14, 15 ‘We further propose that in the miliolid species Cl may be incorporated as a solid solution of chlorapatite or associated with organic molecules in the calcite’. It is unclear what is meant with solid solution? Do you mean chloroapatite that has dissolved?

Answer: The term “solid solution” is a standard term used in thermodynamics and mineralogy for mixtures of solid phases that have similar crystal structures (similar to aqueous solutions in aquatic environments).

Comment RC2.10: Perhaps not use the word organic lining as a pseudonym for primary organic sheet, as foraminifera sometimes have an organic lining on the inside of the test.

Answer: We acknowledge that foraminifera can have organic linings additional to the

primary organic sheet.

Changes: We added “Here, we use the term organic linings to refer collectively to the primary organic sheet and other organic linings in the shell wall.” to the discussion for clarity.

Comment RC2.11: 4.1 How could you check if fluorite of fluorapatite are the incorporation mechanism for fluorine in calcite? Has there been a discussion about this with regards to aragonite which is also higher in F?

Answer: Spectroscopic techniques such as synchrotron could potentially identify incorporation mode of F in foraminiferal calcite, hence, whether fluorite or fluorapatite may play a role here. This requires further investigations outside the scope of this study. The incorporation mechanism for F into aragonite can be attributed to ion exchange with carbonate ion (Ichikuni, Chemical Geology 1979) and to the best of our knowledge alternatives have not been discussed yet.

Changes: We have added text to the discussion to point towards future research options.

Comment RC2.12: Figure 5 What is new here compared with previous work? Needs appropriate referencing.

Answer: done.

Changes: References were added to the figure caption.

Comment RC2.13: Figure A1 SEM images are mirrored. Please change back!

Answer: The SEM images in Figure A1 are mirrored on purpose to represent the orientation of the nanoSIMS images. Mirroring them back would complicate visual comparison of the SEM images and nanoSIMS images. We therefore decided to leave the SEM images in their mirrored state.

Changes: we have flipped back the scale bar annotation for better readability and

added “SEM images are flipped horizontally to facilitate navigation in the NanoSIMS instrument, where the secondary ion images are horizontally mirrored.” to the caption of Figure A1.

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