Ocean Science Discussions

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Comment on os-2021-78

Anonymous Referee #1

Referee comment on "Occurrence of structural aluminium (Al) in marine diatom biological silica: visible evidence from microscopic analysis" by Qian Tian et al., Ocean Sci. Discuss., https://doi.org/10.5194/os-2021-78-RC1, 2021

General comments

This study grew a common cultured centric diatom in low- and high-Al media. Cells from the high-Al media were analyzed for their Al and Si content with focused ion beam scanning EM and energy dispersive x-ray spectroscopy. This is an interesting and novel dataset that addresses an open question regarding the mechanism through which Al is associated with or incorporated into diatoms in the ocean. The data suggest that Al is contained within the frustule material. However, I have several concerns with this manuscript. First, few details are provided about the analyses to allow the reader to gauge the quality and consistency of the data. Relatively little of the collected data is actually shown. Additionally, the cells analyzed were grown in media with Al concentrations far exceeding that seen in the ocean, so I think efforts to apply measured Al/Si ratios to the ocean are unwarranted. I expand on these below.

While the analytical tools may be well-established, I feel more information is needed about sample preparation and the sequence of analyses for the ocean science reader. For example, the cultures were grown in artificial seawater but no information is given about the composition of this. Supplemental table shows the composition of f/2 media (f/2 ref could be cited and table removed) but nothing about the salt composition of media. Additionally, as shown in Fig 3 both 14-day cultures were senescent and not actively growing. In fact, the Al-free culture was actively degrading, although this isn't relevant for the Al measurements, which were done on Al-added cells. Still, the use of senscent cultures raises questions about whether Al is incorporated during normal growth and cell division, or as a feature of cell degradation.

FIB was used to remove the outer layer of the frustule. I am not familiar with this technique and would like to see more detail provided. How much material is ablated by the beam? Is it 1/10 of the frustule layer? 1/2? How thin is the slice? It isn't clear to me what the 'non-structural elements' are referred to in line 156. Is the only difference between the FIB-EDS sample and the BSi sample whether it was milled? It isn't clear to me where in fig 4a the 4b and 4c insets are taken from. What part of the frustule? The valve? The scale bars in figs 4a, b and c must not all be correct. 4b and 4c look much more zoomed in. The EDS spectra used to produce figs 4e-h should be shown, at least one in the paper and the rest in supplemental info.

Section 3.3 then presents quantification of Al and Si in the frustules. How were spots on the diatoms and BSi differentiated? BSi samples were milled first? How far do EDS electrons penetrate into diatom frustule and cell? I'm doubtful the electrons penetrate fully through the cell (for example, see Table 1 in (Twining et al. 2008), allowing accurate measures of Al/Si in the non-frustule parts of the diatom cell. How was Al and Si signal quantified? Was sample self-absorption accounted for? What support is there the statement on line 174 that Al occurs in the organic component of diatom? The higher Al/Si value for the non-bSi sample could readily be caused by the lower Si concentration of this fraction. This would be clarified by presenting the actual Al and Si concentration data and not just the ratios.

The paper presents an average Al/Si ratio of ~0.011 measured for the cultured diatoms and equates this to the Al content of marine diatoms in the ocean (line 211). I think the use of 2 uM Al solution (about 100-fold higher than Al in ocean surface waters) makes it problematic to conclude that the resulting Al content of the diatom opal is representative of ocean diatoms. This needs to be addressed in the manuscript.

Other specific comments

Line 187: refers to Zhou et al. but cites Liu et al. Please cite the correct reference.

Line 192: please provide a reference for this statement.

Lines 197-200: I find the short sections on the Al tolerance of the diatom out-of-place in this paper. It is not a paper about Al tolerance, and this aspect is not treated rigorously (for example, there is no discussion or consideration of Al speciation, and no other species were tested); I suggest removing these sections.

Line 210: What is the evidence for homogeneous distribution of Al in BSi? Figs 4e and g? Fig 4g doesn't show particularly homogeneous Al distribution, in my opinion, nor does the image provide a scale (it appears to be binary). This statement would be strengthened by showing more data.

Line 211: Given the small amount of data provided and the use of 2uM Al in the culture media (approx. 100-fold over ambient concentrations), I do not feel it is justified to present the measured Al/Si ratio is representative of marine diatoms. Additionally, diatoms vary significantly in their level of silicification (Baines et al. 2010), which could well also affect this ratio.

L218: what is meant by 'biological behaviors'? What evidence is provided of this?

L219: what evidence is provided that Al content of organic components is higher than that of BSi?

L222: how is it calculated that organic components account for 75% of Al in diatoms?

L224: This statement about sediments as an Al sink would be strengthened by a comparison of Al/Si in sediments and diatoms. How much sedimentary Al might be attributed to diatoms?

References

Baines, S. B., B. S. Twining, M. A. Brzezinski, D. M. Nelson, and N. S. Fisher. 2010. Causes and biogeochemical implications of regional differences in silicification of marine diatoms. Global Biogeochemical Cycles **24:** doi:10.1029/2010GB003856.

Twining, B. S., S. B. Baines, S. Vogt, and M. D. De Jonge. 2008. Exploring ocean biogeochemistry by single-cell microprobe analysis of protist elemental composition. Journal of Eukaryotic Microbiology **55:** 151-162.