

Ocean Sci. Discuss., referee comment RC2  
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## **Comment on os-2021-78**

Anonymous Referee #2

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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-RC2>, 2021

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Occurrence of structural aluminium (Al) in biological silica: Visible evidence from microscopic analysis.

By Qian Tian

The present article deals with the occurrence of Al in diatoms frustules. Data are presented that show that Al is also found in the inner parts of diatoms frustules. This underlines that Al is taken up and incorporated in the frustules and excludes that Al is from other sources like detrital aluminium silicates. These data are a valuable addition to our knowledge of Al in BSi and should be published.

However, the authors state that the "occurrence mechanism of Al in marine diatoms is unclear. In particular, whether or not Al is incorporated in the structure of BSi." This is in my view not correct: Gehlen et al. (2002, cited by the authors) already gave evidence that Al is incorporated in frustules. They also showed that Al is present in the Si structure of cultured diatoms exclusively is in a four-fold coordination. Additional work by Beck et al. (2002, not cited by the authors) show that Ca is present in proportion to Al(3+) further supporting the structural incorporation of Al in the SiO<sub>2</sub> network of frustules.

In my view, this work has to be acknowledged and the research question of the paper should be adapted to this.

Further comments:

L20: "occurrence mechanism" should be replaced by a more clearer wording

L37: Given the global perspective of the paper, the range of Al concentrations can be specified ranging from below 1 nM in the Southern Ocean (e.g. van Beusekom et al., 1997) to well above 100 nM in the Mediterranean (e.g. Chou & Wollast, 1997).

L55: Here, the work by Gehlen et al. (2002) and Beck et al. (2002) showing that Al is a structural part of the BSi should be cited. Note that Gehlen et al. acknowledge that Al bearing minerals may interfere when analyzing field material, but they also report on cultured diatoms grown in mediums well below the concentrations used in the present study.

L65 ff: These statements need to be precised regarding the work by Beck et al. and Gehlen et al. who actually showed (not proposed) the coordination of Al in BSi (and the compensation of charge by inclusion of Ca).

L74-75: This is an unclear sentence, that needs rewording.

L90. Figure 1: misspelling of "isolate"

L94 Light intensity of 100  $\mu\text{mol}$  photons..... (isn't the unit in  $\mu\text{mol}$ ?)

L95: F/2 was used. This contains Fe-EDTA. A large part of the Fe may be released and precipitate, impacting the Al concentrations. Given the very high concentrations used (2000 nM (10-fold of max concentrations in the ocean) precipitates may occur. Please comment on this.

L101: Please indicate the Al concentration of the medium without Al. These concentrations can be substantial.

L130: Are the authors referring to their own studies? This should be cited.

L225: Here, the work by van Cappellen et al. ( ) on the effect of Al on the dissolution rate would be appropriate.

L236: The conclusion that 2000 nM Al is not toxic should be discussed in the light of the possibility that part of the Al is co-precipitated with Fe from the F2 Trace metal mix. Furthermore, it has to be clarified whether EDTA is able to build a complex with EDTA. This is also relevant for the cleaning procedure where EDTA is used to desorb impurities.

L237: The statement that structural Al in BSi is demonstrated for the first time is in my view not valid, as Gehlen et al. and Beck et al. this already demonstrated. The observation that Al is present throughout the BSi is a good addition to our knowledge of Al in BSi.

#### Literature

Beck, L., M. Gehlen, A. M. Flank, A. J. van Bennekom, and J. E. E. van Beusekom. 2002. The relation between Al and Si in biogenic silica as determined by PEXE and XAS. Nuclear Instruments & Methods in Physics Research Section B - Beam Interactions with Materials and Atoms **189**:180-184.

van Beusekom, J. E. E., A. J. van Bennekom, P. Tréguer, and J. Morvan. 1997. Aluminium and silicic acid in water and sediments of the Enderby and Crozet Basins. Deep-Sea Research II **40**:987-1003.

van Cappellen, P., S. Dixit, and J. E. E. van Beusekom. 2002. Biogenic silica dissolution in the oceans: Reconciling experimental and field-based dissolution rates. Global Biogeochemical Cycles **16**.