

Interactive comment on “Impact of ambient conditions on the Si isotope fractionation in marine pore fluids during early diagenesis” by Sonja Geilert et al.

Anonymous Referee #1

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This paper presents new pore water and sediments data from the Guaymas Basin in the Pacific, focusing on silicon and stable silicon isotopes, early diagenetic processes, and implications for silicon cycling in the oceans. The authors present new and high-quality data, adding to a relatively sparse literature on the subject, and explore their interpretation with a model. The paper is very well-written and enjoyable to read. I have only a few comments and suggestions for where the methods and discussion could be expanded. As such, I am fully supportive of the publication of this manuscript with minor revisions.

1) I would like to see some more detail in the methods and supplementary information.

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Firstly, on page 6, line 182, the authors describe drying down the dissolved bSiO₂ samples prior to analysis. Could there have been any problems with loss of Si at this stage? Could the authors comment upon this and perhaps include yield data?

Secondly, I think that it would be incomplete not to mention the possibility of isotopic fractionation during dissolution of biogenic opal in section 4.1. I appreciate that this fractionation is poorly constrained, with very few studies that do not agree (Demarest et al., 2009; Egan et al., 2012, Wetzel et al., 2014). As such, I think that it's acceptable to say that we can assume that there is no appreciable fractionation, but the possibility should be included as a caveat.

Thirdly, I would like to see more information about the modelling in the supplementary information. Such models are highly sensitive to the assumed dissolution rates of the involved phases. If any other group wanted to reconstruct this model, it would be challenging to do so without knowing exactly how e.g. the terrigenous phase dissolution rate profile parameter was quantified. Could the authors please include the actual equations used, linking depth in the sediment column with kinetic constants (i.e. the equations used to produce Figure S2)?

I would like to know more about the sensitivity of the model to the assumed values of K/AI for the different phases. In particular, what is the sensitivity of the outputs to the ratio for the authigenic phase? It seems that the assumed value is for sediments from a very different environmental setting – can the authors justify the use of values from the Gulf of Mexico for modelling the Guaymas Basin? How does precipitation at a hydrothermal site impact this ratio (section 4.3.2.)? I would suggest that the authors include a sensitivity experiment, perhaps with a few different profile plots for different (reasonable) assumed K/AI values, in the supplementary information. It might also be interesting to investigate the sensitivity of the model to variations in other 'constants' too, especially those that are poorly constrained or found to be variable in natural systems (e.g. the solubility of biogenic opal). Lastly, the caveats of the model are buried in the supplementary information, and I would like to see them more integrated into main

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text.

2) I also think that there are aspects of the discussion that could be expanded upon to utilize the full range of data available.

Firstly, the XRD data is not referred to at all the discussion. How does the clay mineralogy inform on the discussion? Does it help with constraining reverse weathering reactions and/or, for example, the potential shifts in K/Al within the sediments (e.g. section 4.3.3.)?

Secondly, I also do not think that the pore water trace metals are used to their full potential. For example, are there any trends in the [Fe] data from the hydrothermal site to suggest that Fe-cycling could be impacting silicon isotope fractionation? (section 4.3.3.)

3) Other minor comments:

I'd suggest that the authors should be consistent and use either "pore fluids" or "pore waters" throughout the text.

Line 32: Please change "the only other marine setting where Si isotopes have been investigated to constrain early diagenetic processes" to "the only other OMZ marine setting where Si isotopes have been investigated to constrain early diagenetic processes", to acknowledge that other marine settings have been investigated (e.g. Ng et al., 2020).

Additional references:

Demarest, M. S., Brzezinski, M. A., & Beucher, C. P. (2009). Fractionation of silicon isotopes during biogenic silica dissolution. *Geochimica et Cosmochimica Acta*, 73(19), 5572-5583

Egan, K. E., Rickaby, R. E., Leng, M. J., Hendry, K. R., Hermoso, M., Sloane, H. J., ... & Halliday, A. N. (2012). Diatom silicon isotopes as a proxy for silicic acid utilisation: a

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Southern Ocean core top calibration. *Geochimica et Cosmochimica Acta*, 96, 174-192
Wetzel, F., De Souza, G. F., & Reynolds, B. C. (2014). What controls silicon isotope fractionation during dissolution of diatom opal?. *Geochimica et Cosmochimica Acta*, 131, 128-137

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