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

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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.

Dear Reviewer, Thank you very much for your positive feedback and the appreciation of our work. We mainly agree with the comments and suggestions you have raised and we will incorporate the requested changes in the manuscript, in case of a positive evaluation by the editor. Please find below our answers to your comments.

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

1) 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?

2) The described process of bSiO2 digestion is a standard procedure following Reynolds et al. (2008) and Ehlert et al. (2012). Drying of the samples was shown by Ehlert et al. (2012) to have no effect on the Si isotopic composition of the samples. Additionally, Si is not volatile during evaporation and therefore fractionation affects not likely to occur.

3) We will comment on this and include the method references in the method section of the main text.

1) 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.

2) As the referee mentions, we exclude significant effects on pore fluid δ30Sipf values, given the highly unconstrained and diverging results of former studies (Demarest et al., 2009; Egan et al., 2012; Wetzel et al., 2014). Nevertheless, the discussion of possible Si isotope fractionation in dependence of bSiO2 dissolution is an important aspect.

3) We will add a short paragraph in section 4.1 to address this caveat.

1) 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/Al 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/Al 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 text.

2) The assumed K/Al ratio is taken from sediments in the Amazon River delta, which are considered as the end product of reverse weathering reactions, given the complete conversion of the diatom frustule to authigenic aluminosilicates (Michalopoulos et al., 2000). The complete conversion of the diatom frustule is due to the input of highly reactive terrigenous minerals in the Amazon deltaic setting (Michalopoulos and Aller, 2004). The state of conversion of the diatom assemblage in the Guaymas Basin is difficult to assess, but similar K/Al ratios compared to the Amazon setting indicate a comparable high maturity state. At the hydrothermal site, the K/Al ratio is similar to the basin sites and indicates a similar state of conversion of the diatom frustule. Lower K/Al ratios and with that a lower maturity state of the diatom frustule were found in

experiments by Loucaides et al. (2010). We agree that sensitivity tests will benefit the modelling outcomes and interpretation. For the modelling itself not K/Al but K/Si ratios from the same literature were used (see supplement) and modelling outcomes were recalculated for K/Al ratios. Therefore we conducted sensitivity tests with varying K/Si ratios and also sensitivity tests concerning the solubility constant of biogenic opal. The sensitivity tests showed that lower K/Si ratios (and with that lower K/Al ratios) could not reproduce the measured K/Al ratios in the OMZ. Therefore, we conclude that the assumed K/Al ratios of Michalopoulos et al. (2000) are valid also for authigenic minerals in the Guaymas OMZ.

3) We will incorporate the sensitivity tests and the outcomes in the supplement. Also, we will move the caveats of the model, which are currently discussed in the supplement, to the main text. Additional sensitivity tests regarding the solubility of biogenic opal, the δ30Si values of the dissolving terrigenous phase and the Si isotope fractionation during authigenic clay formation were conducted following also the recommendations by reviewer #3.

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

1) 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.)?

2) In section 4.3.2 of the original manuscript we actually used the XRD data on amorphous SiO2 in the discussion of hydrothermal processes (lines 459-465). However, we made no attempt to use XRD data for the detection of reverse weathering reactions because it is difficult to distinguish authigenic clays formed during these reactions from terrigenous clays that are very abundant in our study area. For this reason, we did in fact not analyze the OMZ sediments with XRD so that we are unfortunately not able to

follow this reviewer recommendation.

1) 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.)

2) Unfortunately, the available data set is too scarce to identify possible Si isotope fractionation induced by Fe. Experimental results by Zheng et al. (2016) indicate that δ30Sipf values should increase with the Fe/Si ratio in the solids and pore fluids. We see a similar trend in our data from the basin sites and hydrothermal site indicating a possible Fe-induced fractionation (see figure below). Data from the OMZ site, in contrast, deviate from this apparent trend (however, only based on two data points) and show lower δ30Sipf values as what would be expected regarding the Fe/Si ratio. This could be related to the likely one step fractionation during Fe-Si co-precipitation at the hydrothermal site and the existence of multiple Fe redox cycles inducing Si dissolution and re-precipitation and with that multiple fractionation steps at the OMZ site (see original manuscript lines 483-497). Furthermore, any Fe-induced Si isotope fractionation is likely superimposed by the dissolution of terrigenous clays as shown by the reactive transport model. Natural Fe-induced Si isotope fractionation needs further investigation in future studies in order to be able to identify magnitudes of fractionation if other fractionating processes take place simultaneously.

3) We will add the figure below and a short discussion on Fe-induced fractionation to the supplementary information in order to address the reviewer's comment.

Other minor comments:

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

3) We will use “pore fluids” throughout the text.

1) 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).

3) We will add ‘OMZ’ to the sentence and refer to the previous work conducted in other marine settings (e.g. Ng et al., 2020).

References

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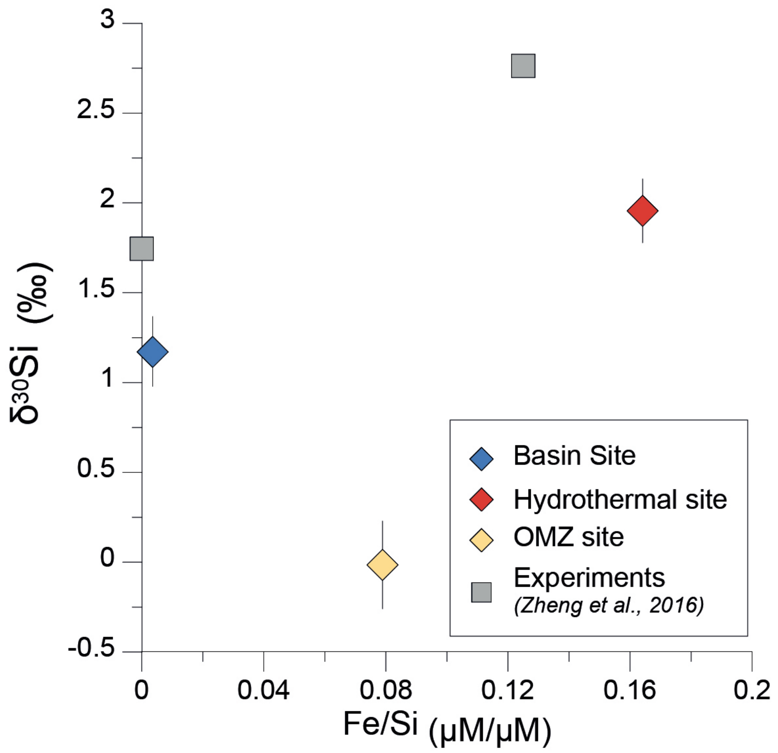

Fig. 1. Additional figure to reviewer comment 2-2. Si isotope fractionation in dependence of the Fe/Si ratio in the fluids. Experimental data from Zheng et al. (2016) are shown for comparison.