

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 manuscript presents new interesting silicon isotope data from sediment pore fluids ($\delta^{30}\text{Si}_{\text{pf}}$) in different marine environments from Guyamas Basin and Gulf of California. The data are of high quality and include $\delta^{30}\text{Si}_{\text{pf}}$ from sites located into Oxygen Minimum Zone or under the influence of hydrothermal vents both of which are particularly new in terms of Si isotopic system. This work certainly deserves publication in Biogeosciences after improvement / clarification of some parts of the discussion. I have compiled my concerns under the scope of the three main concerns below, which do not necessarily imply much work to be implemented.

C1

Dear Damien Cardinal, Thank you very much for your positive feedback and valuable comments to our manuscript. We are happy to discuss and incorporate the aspects you raised below in a revised version of this manuscript in case of a positive evaluation by the editor.

1) The role of bioturbation is never mentioned in the main text (e.g. 76-77) despite it is an important process in the upper cm (cf. e.g. Rabouille et al. 1997 for Si). It is however a parameter of the model. However, the model is used only for the OMZ site where we could expect null or negligible bioturbation because it is very low oxygen environments. How could bioturbation not affect the porefluid profiles of the other sites? In contrast why this has been considered at the OMZ site? Some discussion should be added in the main text.

2) We agree that bioturbation and bioirrigation and with that the mixing of upper sediments and pore fluids are important processes which were not mentioned in the main text of the manuscript. Bioturbation is expected to have the largest impact within the upper ~10 cm below seafloor (cmbsf) and bioirrigation within the upper ~20 cmbsf. However, the homogeneity of the pore fluid $\delta^{30}\text{Si}_{\text{pf}}$ values with depth (see original manuscript lines 421-423) suggests that the effects of bioturbation/bioirrigation on pore fluid composition are largely compensated by fast reactions inducing rapid isotope exchange. Unfortunately, we have no independent data to quantify rates of bioturbation and bioirrigation in our study area. Therefore, we limited the modelling to the OMZ site where the biogenic mixing proceeds at very low rates due to the absence of large benthic biota.

3) Nevertheless, we will briefly discuss the potential effects of bioturbation/bioirrigation at the hydrothermal and basin sites in section 4.2.

Identification of minerals under or over saturated in the pf is not sufficiently directly addressed in the discussion. See e.g.:

1) 457-459. It is unclear how “Si concentrations lower than amorphous Si and quartz

C2

solubilities, indicating precipitation of the respective mineral phase during pore fluid ascent". If the DSipf is lower than equilibrium concentration, then Si should rather dissolve than precipitate.

2+3) The sentence will be rephrased according to calculated saturation indices (see comment below).

1) What are the minerals which are actually oversaturated in pf? Why saturation indexes of primary and secondary minerals have not been calculated e.g. using data of Table 1S?

2) We will calculate saturation indices for pure silica phases (amorphous SiO₂, quartz) using the program and databases of PHREEQC (Parkhurst and Appelo, 1999). However, no saturation indices can be calculated for the most important precipitating phase discussed in this manuscript, namely authigenic aluminosilicates because we have no data on the dissolved Al concentrations and in-situ pH values of the pore fluids. For the hydrothermal site, saturation indices show that quartz is supersaturated and amorphous silica is close to saturation. Consequently, quartz can precipitate directly from pore fluids at present. However, due to the dynamics of hydrothermal systems, this can be subject to changes and supersaturation of amorphous silica is likely to be obtained occasionally, due to the ascent of Si enriched fluids from greater depth as indicated by the presence of amorphous silica cement in the hydrothermally affected sediments (see lines 459-462 in the original manuscript).

3) We will add a paragraph discussing saturation indices in section 4.3.2.

1) 480-481 and 499-512. Could dissolution of primary minerals (e.g. feldspars) supply DSi in pf? If not, justify why this can be ruled out. Even though primary minerals are less prone to dissolution than clays, they are likely to be undersaturated in the pf and may have some impact on DSi and d30Sipf.

2) It is true that reactive primary minerals like feldspars may dissolve in the pore fluids

C3

(e.g. Singer, 1980; Wilson, 2004). However, the $\delta^{30}\text{Si}$ values of feldspars are rather high compared to clays with an average of -0.17‰ (Georg et al., 2009; Savage et al., 2011) and their dissolution alone cannot be responsible for the shift to low $\delta^{30}\text{Si}_{\text{pf}}$ values in the OMZ (see also answer to comment #3 Modelling). During changing environmental conditions immature clays like e.g. chlorite can transform and dissolve (Singer, 1980), often accelerated by organic ligands and iron reduction in the clay structure (Anderson and Raiswell, 2004; and original manuscript lines 502-508). We agree, that primary mineral dissolution is likely to take place, however, superimposed by clay dissolution, shifting OMZ pore fluid $\delta^{30}\text{Si}_{\text{pf}}$ to the observed low values. We conducted a sensitivity test considering feldspar dissolution (see also answer to comment #3). Our results indicate that feldspar dissolution alone cannot create the low $\delta^{30}\text{Si}_{\text{pf}}$ values in the OMZ.

3) We will add the results of this sensitivity test to the supplement and address the results and a discussion on primary silicate dissolution in the main text.

1) Why there is no mineral data on the OMZ core (Table 2S) despite this is the site for which the discussion is the most developed?

2) We agree that XRD data for the OMZ site would be helpful and could add another argument for clay dissolution and/ or authigenic mineral precipitation. Unfortunately, by the time when the XRD analyses were conducted, the focus of the study was not on the OMZ site. Only in the course of the manuscript writing and handling, the focus shifted to the OMZ site. However, we also think that the recognition of authigenic mineral formation is rather difficult to decipher based on XRD data (see comment to reviewer #1, point 2-1) and would not have supported the discussion to a large degree because the clay mineralogy of the OMZ site is probably dominated by riverine clays that are very abundant in our study area and complicate the detection of authigenic clay formation. We show, that we can fully explain the observed low $\delta^{30}\text{Si}_{\text{pf}}$ values by clay dissolution. The interpretation is additionally supported by our modeling and K/Al data.

C4

1) Fig.3. What is the uncertainty we have on Si concentration for dissolved bSi to build the mixing line that has been taken at equilibrium (900 μM)? The equilibrium concentration is theoretical however why would the dissolution of bSiO₂ be at equilibrium and give Sipf at 900 μM for the end-member chosen in Fig. 3?

2) The assumed bSiO₂ equilibrium concentration of 900 μM is an experimentally determined value for siliceous sediment (Van Cappellen and Qiu, 1997; see also lines 390-392). This concentration value takes into account early diagenetic reactions like the incorporation of Al in the diatom frustule. This diagenesis-affected concentration value is lower than equilibrium concentrations of acid-cleaned bSiO₂ (see Van Cappellen and Qiu, 1997 and references therein). We agree, however, that equilibrium concentrations might vary from site to site depending on the maturity of the diatom frustules.

3) Therefore we will add an uncertainty of $\pm 150 \mu\text{M}$ Si to the assumed concentration (c.f. Van Cappellen and Qiu, 1997) and add a range in Fig. 3 and a comment in the caption. Note that the uncertainty of the equilibrium solubility of bSiO₂ has only minor impact on the calculated mixing curves.

Model set up from line 524 and in the Supplement. The sensitivity of the model to its main hypotheses is not sufficiently discussed in the main text and there is a lack of justification for some of its core parameters.

1) The average value of clay used in the model is -2 pmil and reference to Frings et al. (2016) is given for this. However, average clays in Frings et al. is not at -2 pmil. I'm not sure it is actually calculated, but from the figure, it should be more between -1.5 and -1 pmil. This would be also consistent with the review of Sutton et al. (2018) in which the world average value of secondary minerals is at -1.08 pmil. Similarly, in Bayon et al. (2018) the average clay $\delta^{30}\text{Si}$ from river sediment fluctuate from -1.5 to -0.32 pmil depending on climatic regimes. How does it affect model outputs when using a more realistic $\delta^{30}\text{Si}$ of clay (i.e. -1.5 or -1 pmil) and/or propagate the uncertainty of this

C5

value? In any case, the use of -2 pmil as average clay value is not properly justified.

2) The terrigenous clays brought to the basin by river discharge are likely phyllosilicates like kaolinites (e.g. Georg et al., 2006; Frings et al., 2014) which are associated with lower $\delta^{30}\text{Si}$ values caused by the larger Si isotope fractionation factor associated with single layer phyllosilicates (Opfergelt et al., 2012). Therefore, it is valid to assume a clay $\delta^{30}\text{Si}$ value of -2‰. However, we agree that the reference to Frings et al. (2016) is not sufficiently explaining this assumption and we agree that a sensitive test of the model taking into account various clay $\delta^{30}\text{Si}$ values will improve the manuscript and the significance of the model results. Therefore, we conducted sensitivity tests for clay $\delta^{30}\text{Si}$ values covering a range of -2 to -1 ‰ and for primary mineral dissolution with $\delta^{30}\text{Si}$ values close to zero. Results of the sensitivity tests show that dissolution of terrigenous material with higher $\delta^{30}\text{Si}$ values than -2‰ cannot reproduce the measured $\delta^{30}\text{Si}$ values in the OMZ pore fluids. Only if the fractionation factor is lowered to -1‰ terrigenous material with $\delta^{30}\text{Si}$ values of -1.7‰ can produce the observed values (see also comment below). In conclusion, the dissolving terrigenous phase is strongly depleted in $\delta^{30}\text{Si}$ and only clay dissolution can produce the low pore fluid $\delta^{30}\text{Si}$ values in the OMZ.

3) We will add these sensitivity tests to the supplement and refer to the results in the main text.

1) Similarly uncertainty on the -2 pmil for the isotopic fractionation during precipitation of authigenic clay should be discussed and taken into account

2) We agree that the model will benefit from sensitivity tests concerning the Si isotope fractionation factor. We conducted sensitivity tests applying $\Delta^{30}\text{Si}$ values of -1‰ and 0‰ following Opfergelt et al. (2012). A fractionation factor of -1 ‰ reproduces the measured pore fluid $\delta^{30}\text{Si}$ values in the OMZ if a terrigenous phase with slightly higher $\delta^{30}\text{Si}$ values (-1.7‰ compared to -2‰) dissolves.

3) We will include the outcomes of this sensitivity test in the supplement and refer to

C6

the results in the main text.

1) Role of bioturbation in the model for the OMZ (cf. first comment)

2) Bioturbation is of minor importance for the OMZ given the absence of large benthic biota under anoxic conditions. The model incorporates a small bioturbation coefficient. However, the depth of the bioturbated layer is limited to 1 cm considering the absence of burrowing organisms.

1) Could the model be applied to the other sites, e.g. basin?

2) In contrast to the OMZ, the other sites are likely influenced by bioturbation and bioirrigation even if the impact on pore fluid $\delta^{30}\text{Si}$ values appears to be compensated by fast reactions (see answer to comment #1). Unfortunately, we have no independent data to quantify rates of bioturbation and bioirrigation in our study area. Therefore, we limited the modelling to the OMZ site where the biogenic mixing proceeds at very low rates due to the absence of large benthic biota.

Minor comments

1) Throughout the ms, better use heavier / lighter than higher / lower when reference is made to isotopic composition.

2) In the original manuscript we used the expression higher and lower when referring to $\delta^{30}\text{Si}$ values, as a value by its nature cannot be light or heavy. We used the expression lighter and heavier when referring to isotopic compositions (e.g. in lines 28 and 402 in the original manuscript).

1) 176 : The bSiO₂ samples were stored in Milli-Q water. Does it mean that once separated by Morley et al. (2004) method, the bSiO₂ samples were kept in water ? For how long? Dissolution could have occurred with some isotopic fractionation?

2) The cleaned diatom samples were stored in MQ-water for several days. Dissolution of bSiO₂ is unlikely given that the pH of the MQ-water (~ 5) is not favoring bSiO₂

C7

dissolution. Dissolution rates increase quickly between pH 9 to 10.7 (Iler, 1979) and that is also the reason why digestion of the bSiO₂ samples is conducted in an alkaline medium. Additionally, the water-bSiO₂ mixture was transferred to a Teflon vial for further handling, so in the unlikely case of fractionation effects during dissolution, the bulk would have been further processed and no isotopic signal was lost.

1) 238. Typo, 2 times 'and' and 'and'

2+3) We will remove the second 'and'.

1) 301 Is it worth keeping MUC-22-04 whose bottom SW has been contaminated? (likely by surface SW)

2) Because of completeness of the results section, we prefer to leave the sample MUC-22-04 in and report the Si concentration and $\delta^{30}\text{Si}$ values.

1) 366: the kinetics of reverse weathering is poorly known, especially in situ and is certainly not immediate. So do not to use such wording 'as soon as Si is released (...), it reprecipitates'. Moreover not all Si reprecipitates, otherwise there won't be more DSi in pore fluids than in bottom water (indeed in their previous work, Elhert et al. 2016 have quantified that only 24% of dissolved bSi reprecipitates). This sentence needs to be corrected.

3) We will correct the sentence accordingly.

1) 371-372 From the three references cited here, only Elhert et al. 2016 has estimated fractionation factors for reverse weathering, the other two refer to continental weathering (Georg et al., 2006 and Opfegerl et al., 2013). Remove them or specify it since this sentence is misleading.

3) We will remove the references Georg et al., 2009 and Opfegerl et al., 2013.

1) 395-398. Sentence unclear / grammatically incorrect

3) We will rewrite the sentence.

C8

1) 397. At least one reference should be cited for Si isotope fractionation during bSi dissolution (e.g. DeMarest et al., 2009).

2+3) We will discuss the potential impact on Si isotope fractionation during dissolution and add the following references: Demarest et al., 2009, Egan et al., 2012, Wetzel et al., 2014 (see also comment to reviewer #1).

1) 440-441. This sentence is too affirmative given the level of discussion at this stage of the ms. It could be changed to e.g. "Thus, at Basin sites both K/Al ratios of sediments and the heavier $d_{30}Si$ are in agreement to recognise bSi dissolution followed by authigenic clay formation as significant processes taking place".

3) We will rephrase the sentence accordingly.

1) 527: typo in isotope

3) We will correct the typo.

1) Table S5 Typo Æñ auf Åž

3) We will correct the typo.

1) Fig. 5. It should be mentioned in the caption that Fig. 5b is from another study (Ehlert et al. 2016?)

3) We will include the reference Ehlert et al., 2016 in the caption of Fig. 5.

1) Fig. 6. Need to define red and black dashed line in the caption without having to go through the text in the ms.

3) We will include the definitions of the red and black dashed lines in the caption.

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