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Discussions

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Interactive comment

Interactive comment on "The evolution of stable silicon isotopes in a coastal carbonate aquifer, Rottnest Island, Western Australia" *by* Ashley N. Martin et al.

Anonymous Referee #3

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The manuscript is well written, providing a critical dataset in an understudied system. I enjoyed reading it. The figures are generally clear. I have suggested some minor revisions and have some suggestions for the discussion. There were some few grammatical errors. I don't anticipate the revisions would take the authors very long to incorporate.

Suggested changes throughout the paper: I prefer "bSi" to "BSi" as the capital "B" in "BSi" can be mistaken for the symbol for Boron. Similarly, I suggest changing "DSi" to "dSi" so that the capital D won't be mistaken for Deuterium. For readers versed in the biogenic silica literature, the capital letters may not pose a problem. However, for new

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readers it may contribute to some confusion.

Well written introduction. Clear reasoning, concise review, and compelling set-up and motivation for the project to fill a known data gap. I suggest adding Ehlert et al, 2016 (Ehlert, C., Reckhardt, A., Greskowiak, J., Liguori, B.T., Böning, P., Paffrath, R., Brumsack, H.J. and Pahnke, K., 2016. Transformation of silicon in a sandy beach ecosystem: Insights from stable silicon isotopes from fresh and saline groundwaters. Chemical Geology, 440, pp.207-218) to the 2nd paragraph (lines 42-54). That data was not included in Frings et al 2016.

2. Study Area The last paragraph is confusing w.r.t. description of "fresh" mixing type. One set of parameters is given for this zone in lines 99-101, and another set is given later in the paragraph (lines 103-105), with some repeated conditions (e.g., above 1m AHD). Also would it be possible to add a salinity or [Cl-] range to the three mixing zones? 3. Methods: No salt corrections or formation of a brucite precipitate was conducted to account for matric effects prior to purification on via Biorad AG 50W-X8? 4.Results Do the authors have a surface coastal water/open ocean value for dSi? I think the manuscript would be improved by adding a comparison of d30Si found in fresh-T2 to Ehlert et al 2016 in the second paragraph (lines 176-186). Incidentally, have the authors seen Mayfield et al., 2021 (Nature Communications)? Line 190: missing punctuation at end of sentence Line 191: extraneous parenthetical after "respectively" Fig. 2: So cool! Regarding the legend for TDS and dSi: are those negative values? Fig. 4: Can authors add a regression line to 4a as this is discussed in results and discussion? Also, in 4b, there are 2 green dashed lines and only description of 1 green dashed line in the caption.

5.1 Evidence for the source of DSi. . . Lines 223-226: referring to a figure here would be helpful Would you expect lower d30Si if RI was behaving like a closed system which could be described via Rayleigh distillation model? To clarify, if almost all the dSi supplied by quartz dissolution formed a secondary clay mineral, would the subsequent dissolution of that secondary mineral would impart a dissolved d30Si signature more like the primary mineral? This scenario could be added to the discussion of secondary mineral dissolution in lines 230-235), unless the authors have other evidence this is not likely. Line 237: regarding bSi solubility, coastal settings can actually make for recalcitrant diatom frustules: proximity to dissolved Al and metals can help preserve frustules (e.g., solubility studies by Van Cappellen, Van Bennekom, and Loucaides et al 2012). I suggest authors clarify this sentence with specific conditions of their study site or leave out the last phrase about preservation in coastal sediments. Could the authors add some site specific data w.r.t. to dissolved Fe concentrations in their discussion of adsorption being the likely mechanism that takes up light isotope of dSi. What were the concentrations of Fe in the 0.5M HCl leachate? Are there dissolved Fe or O2 profiles at the sites? Are these sediments oxic? The more positive d30Si of dSi observed in groundwater in Ehlert et al 2016 was due to secondary mineral formation. Can the authors provide more evidence of why that's not occurring here? PHREEQC doesn't encompass the solubilities of all the amorphous-type alumino-silicates that can form. Line 286: refer to a figure Line 305: missing a word or phrase here "...can be into two water types..." Line 325-328: This three end-member mixing concept is important: could it be highlighted in one of the figures and accompanied by a reference to that figure at the end of this sentence? Or is this in Figure 4b?

Conclusions highlight broad impacts, well written.

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