

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

Anonymous Referee #2

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Review of manuscript HESS-2020-429 submitted to Hydrology and Earth System Sciences by Martin and colleagues: The evolution of stable silicon isotopes in a coastal carbonate aquifer, Rottneest Island, Western Australia

Martin et al present silicon isotope ratios (expressed as $\delta^{30}\text{Si}$) from fresh and saline groundwater samples from a carbonate island in Western Australia. They interpret variation in $\delta^{30}\text{Si}$ of the freshwater samples to be driven by sorption of Si to Fe/Al oxides, while the saline water samples are governed by mixing with a low [Si], high $\delta^{30}\text{Si}$ endmember. Given a recent focus on topics like e.g. boundary exchange, coastal filtering, SGD, etc. for the trace element and isotope budgets of the ocean, this paper

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has potential to be an interesting case study.

In general, the manuscript is well written and seems appropriately referenced. The topic is an interesting one, I think, though does seem to fall slightly outside the scope of HESS as I understand it. I have some methodological concerns (detailed below), and some comments about the interpretations, some more major than others. I list these below in order they appear in the manuscript.

Comments

L71: this suggestion of interaction with basement rocks is interesting but never returned to. If it can be relevant for Li, why not for Si?

L95: relevance?

L100, 103: spell out units here – TU = tritium units? pMC = percent modern carbon? G PES = ??

L104 vs. L98 – repetition, but with age expectations reversed. Not sure what's going on here.

L127: Some indication of precision and accuracy needed here.

L132: This column protocol works sufficiently well for samples with low anionic components in the matrix. But for the saline samples, anions like sulphate or chlorine would elute at the same time as the sample. This could cause matrix effects between bracketing NBS28 standards and samples. Previous work has shown that matrix effects, *sensu lato*, can induce large bias to silicon isotope ratios (e.g. Hughes et al. 2011 JAAS. What steps were taken to correct for this, or demonstrate that it is not a problem? Typically, a pre-concentration step like the so-called 'MAGIC' protocol is used for brackish and marine samples, since this also has the effect of removing much of the matrix.

L137: Drying to 'incipient' dryness is also slightly worrying. What does this mean, in

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practice? If silica precipitates because it becomes oversaturated in the solution, there is a danger that it will not redissolve in 2% HNO₃. And because the precipitation is likely associated with a fractionation, this may also induce bias. Did the authors demonstrate 100% Si yield at this stage of protocol?

L140 or around: Give details of procedural blanks, for column chemistry and for alkali fusion

L147: Give 'Si' for 28 and 29.

L148: $M/\Delta M = 2000$ is probably at the low end of resolution with which the polyatomic interferences can be avoided, and could induce some noise to the measurement if some of the interference peaks overlap onto the measurement plateau (though the three-isotope plot shows this isn't a large problem – uncertainties should be given in this plot).

L155: This implies only 1 bracket was measured – is this correct? Normally, 3-5 individual standard-sample brackets are analysed per sample. If this is correct, the stated ± 0.12 uncertainty may be too precise.

L158: There are more recent values for IRMM-018 – see e.g. Geilert et al. 2020 (Nat Comms); Baronas et al. 2018 (EPSL), etc.

L161: Not sure the uncertainties of ± 0.000 are required here.

Figure 2: Panel A and B – the colorbar scale seems to imply the concentrations are negative. Figure 2: It's not clear which data are included in this. There is a red line in Fig 1, but presumably the samples falling off this line have been incorporated somehow. More detail could be useful.

L172: I find the conclusion that T1 DSi is higher than fresh and T2 very hard to believe given Fig. 3A. I am also skeptical about the correlation on L171.

L191: extra ")”

C3

Results section: I can't see the Si concentration and $\delta^{30}\text{Si}$ for the seawater sample mentioned on L114. In e.g. Fig 4B, a literature value is used from Singh et al., but this is not sufficiently justified.

L262: I disagree that there is a threshold of Al concentration necessary for Si isotopes to fractionate – pure SiO₂ experiments also show fractionation (as noted elsewhere in this manuscript).

L264: If the interpretation for d7Li is the same as for $\delta^{30}\text{Si}$, why is there no relationship between the two? (L189)

L265: the evidence for Fe oxides playing an important role seems to be circumstantial. Is there any direct evidence they are present, with sufficient sorption capacity, to be important?

Section 5.2: There is no real explanation for the positive trend between Si concentration and isotope ratios – this is a bit counter-intuitive. One might expect a negative correlation between Si concentration and isotope ratio.

L305: missing word (divided?)

L312: See also above – this does not appear to be the case from Fig 3A.

Section 5.3.1. I struggle to follow the rationale for including 'T1' groundwaters as a separate case rather than just viewing them as intermediate between freshwaters and the marine/T2 samples.

L335 and around – the challenge seems to be to define the non-marine endmember. If this was more rigorously achieved, then the discussion might be more usefully structured in terms of deviations from conservative mixing as in e.g. estuary papers (Zhang et al. 2020 GCA). In general, it's also not clear where the marine endmember comes from. I don't think a value from the Bay of Bengal is necessarily very representative for waters bathing western Australia (see e.g. Holzer et al. 2015 GBC)

C4

L355: Could/should this not instead yield low $\delta^{30}\text{Si}$ values if there is a re-equilibration between solute and rock?

L372: I don't understand this – wouldn't these values be representative of the terrestrial component of SGD?

It is disappointing there is no attempt to calculate fluxes and place them in a global context. In general, the global implications section is rather weak and seems added on as an afterthought. It would be good to see a better discussion of how the lessons from this case study can (or cannot) be applied elsewhere, for example, and a more rigorous attempt at upscaling.

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