Review of: Quantifying the buffering of oceanic oxygen isotopes at ancient midocean ridges
By: Yoshiki Kanzaki

Recommendation: Major revision.

Manuscript summary:
The author develops a 2D coupled model of hydrothermal circulation and oxygen isotope exchange in oceanic crust, and uses the model to address the apparent disagreement between d18O records in authigenic marine precipitates and altered oceanic crust sequences ("ophiolites"). The author validates the model against several observations and estimates of heat fluxes, water fluxes, d18O profiles in an ophiolite, etc. The author then uses the model to investigate the capacity of hydrothermal circulation and alteration of the oceanic crust to buffer the isotopic composition of seawater. The main finding is that the d18O profiles in the altered crust and the resulting net O isotope fluxes to/from the ocean are insensitive to seawater d18O, relative to suggestions in previous studies, suggesting that seawater d18O is very weakly buffered by hydrothermal alteration of oceanic crust. This weak feedback is suggested to arise from a combination of kinetically limited O isotope exchange in the cooler portion of the crust, and rock-dominated O isotope exchange in the deeper, hotter portion of the crust. The author explores the sensitivity of the feedback strength to several physical parameters and model design choices, and finds that the weak feedback is robust to these choices. The conclusion is that ophiolite d18O profiles that are invariant over Earth history cannot be used to infer constant seawater d18O through time.

Review summary:
This is a well-written and reasoned manuscript, which addresses an important and actively debated topic: the evolution of seawater O isotope ratios over Earth history. The approach of coupling 2D forward models of heat and water transport and of O isotope exchange is innovative, and it promises to bring constraints and insights of a different nature to this debate. I have only two major comments, which appear in several of my specific comments below.

Firstly, where the model is validated against ophiolite d18O profiles or estimates of 18O fluxes to/from the oceanic crust, these consistency tests only have meaning when the age (i.e., alteration duration) of the oceanic crust is known, and when the model results at that specific alteration duration are compared to the observations. The model needs to be validated against profiles with better-constrained duration of alteration, perhaps from ODP boreholes.

Secondly, all of the insights gained from the model are based on simulation of circulation and O isotope exchange out to a distance of 30 km from the ridge axis, and a more limited investigation of off-axis alteration out to 300 km. The claims made on the basis of these simulations have far-reaching implications. In my opinion, an effort should be made to show that the weak buffering intensity revealed by the model is not an outcome of this limited model spatial domain. In other words, if one considers sustained low-T alteration as the crust continues aging and until it is subducted, do the main findings of this study hold? Are O isotope fluxes still insensitive to seawater d18O? I urge the author to test this, which will provide confidence in the findings.

Finally, not a concern so much as a suggestion, related to my second major comment. If this detailed modeling reveals an insensitivity to seawater d18O even out to thousands of km from the ridge axis, but a dependence of subducted crust d18O on physical parameters such as the spreading rate and the thickness of sediment draped on the oceanic crust, then it may provide an explanation not only for the invariant d18O of ophiolites, but also for the long-term secular evolution of seawater d18O. Perhaps this is beyond the scope of the current study, but it would be a welcome and timely contribution.

On the basis of the volume of work required to validate the model against well-constrained targets and to model hydrothermal alteration out to larger distances from the ridge axis, I recommend major revision. Once revised, this study will be an important contribution to the outstanding debate about seawater O isotopes.

Below are my specific comments. Comments that are related to my main comments are in **bold**.
Itay Halevy

<u>Specific comments:</u>
1. L19-21: The sentence in these lines can be worded more clearly.

2. L26: It may be worth mentioning that by “authigenic sedimentary rocks” you mean d18O records in carbonate rocks, cherts, phosphorites, glauconites and shales, all of which show a pronounced increase in d18O over Earth history.

3. L32: Is the range 70–15°C correct? Shouldn’t the second number be larger than 70?

4. L38: Perhaps “weak” instead of “little”?

5. L38-42: The motivation for reconciling the sedimentary and ophiolite records is more than just being able to use sedimentary d18O records to reconstruct temperatures. The evolution of seawater d18O is driven by the same processes that govern the chemical fluxes to the ocean (e.g., from low-T continental weathering, from hydrothermal alteration of the oceanic crust at both high and low T), with implications for the evolution of ocean chemistry, the attendant productivity of the biosphere and the composition of the atmosphere.

6. L52-54: The statement in this sentence is not entirely correct. Any mechanism to lower the T of oceanic crust alteration will result in greater enrichment of the altered crust in 18O (and greater removal of this 18O from the ocean, as the author mentions).

For a given amount of alteration, the resulting altered crust will be more strongly offset in d18O from the altering fluid (~seawater). In this case, more 18O-depleted seawater gives rise to correspondingly 18O-depleted authigenic minerals, as observed. This same 18O-depleted seawater could concurrently give rise to altered oceanic crust with d18O similar to modern altered oceanic crust, if the alteration T was lower and the mineral-water O isotope fractionation larger. So at least some of these mechanisms may also explain approximately invariant ophiolite d18O.

7. L67: "The present study has been undertaken to present…". Suggest rewording.

8. L95: Should be "length scale"? Also, perhaps "for an e-fold increase"?

9. L107: Why does the model grid extend to 12 km if the rocks are taken to be impermeable below 6 km?

10. L107: The choice of a domain length of 30 km from the ridge axis has implications for the timescale of the simulation. At the spreading rates investigated in this study (1e-2 to 30e-2 m/y), formation of 30 km (3e4 m) of new crust takes between 1e5 and 3e6 years. How long does it take to reach a steady state for the q-*P*-*T* fields over the domain? Presumably much less than the time that it takes newly produced crust to exit the model domain?

11: L112-113: When you refer to the bottom and right boundaries as insulating, do you mean that there is no temperature gradient across these boundaries? Do the results change if you relax this assumption (e.g., using Neumann boundary conditions with a non-zero flux)? You mention what happens when you relax the assumption of impermeability of these boundaries, and it would be good to also mention what happens when you don't assume the boundaries to be insulating.

12. L140-143: Could you please better substantiate the choice of a lower-than-lab kex? Is it only due to the smaller specific surface area in the field, or are there other factors, too? In the Supplementary Material, it would be good to show the sensitivity to kex up to the highest lab values (10^-6.6 mol/kg y). This would increase confidence in the low d18O buffering capacity of seafloor alteration suggested in this study.

13. L151-152: "The first term on the right-hand side…, while the second term represents the hydrodynamic dispersion.".

14. L158: Is the O isotope model insensitive to the assumption of impermeability, like the **q**-*P*-*T* model?

15. L163: The Results section contains a lot of discussion. It may be useful to combine the Results and Discussion sections.

16. L168 and elsewhere: "Ma" is usually reserved for millions of years ago. When referring to millions of years, "Myr" is more commonly used.

17. L170: The modeled water mass flux is not only within the range of Elderfield and Schultz (1996), it is quite close to their recommended value of 3(±1.5)e13 kg H2O/y.

18. L172-174: There is nothing special about the distance of 30 km from the midocean ridge - if alteration is a sustained process, then there will be some distance at which the model d18O profiles most closely resemble the observations. For a different spreading rate, "consistency with observations" could be reached at a different distance from the spreading center, as suggested by Fig. 8. Consistency can be assessed (or the model calibrated, alternatively) only with independent knowledge on the age of the profiled crust - how long was the sampled crust altered, and does the model resemble the d18O profile in that crust at a comparable duration of alteration. The model should be tested against d18O profiles in crust with a known duration of alteration (perhaps in ODP boreholes).

The above relates to a bigger issue, which is the somewhat arbitrary choice of 30 km as the edge of the model domain. Does alteration of the oceanic crust stop farther out from the spreading center? Again, Fig. 8 suggests that this is not the case. In panel (a) of that figure a lower spreading rate results in much more 18O-enriched altered crust than at higher spreading rates (Fig. 4, 8b, 8c). Would this degree of enrichment not be reached farther out from the spreading center at the higher spreading rates? Does the proposed insensitivity to seawater d18O hold if alteration continues over the lifetime of an oceanic plate?

To address this, the author should perform simulations out to much greater distances from the spreading center and identify the distance from the ridge at which the isotopic composition no longer changes. I presume this distance will depend on the model parameters, and this may affect the sensitivity of the ultimate isotopic composition of the crust on seawater d18O. I don't know if this request is practical, given the computational cost of extending the simulation out to thousands of km from the ridge. If not, a way to parameterize the behavior farther away from the ridge with continued water-rock interaction and O isotope exchange should be developed.

As an aside, constraints on the distance to which water-rock interactions continue to change the isotopic composition of oceanic crust have implications for the effect of oceanic crust alteration on the isotopic composition of seawater. For example, if alteration continues over much of the lifetime of an oceanic plate, then slower seafloor spreading in the Precambrian, as suggested in several recent studies (several papers from Korenaga over the past decade; Fuentes et al., 2019), would lead to subduction of older, more 18O-enriched crust, leaving the ocean 18O-depleted (Galili et al., 2019).

19. L178-179: The sentence in these lines is difficult to understand. Suggest rephrasing.

20. L180-189: The model d18O profiles in the bulk rock and the 18O fluxes from high- and low-T alteration are reported in these lines and compared with available

observations and previous estimates. As in comment #18, consistency with the observed profiles has meaning only if the model and observed profiles are of an equivalent age (i.e., alteration duration). Likewise, the consistency between model 18O fluxes and previous estimates has meaning only if the estimates were made on the basis of altered crust of a comparable age.

21. Sections 3.2, 3.3 and onwards: The results, interpretations and implications in the rest of the manuscript should be consistent with the tests performed in response to comments #18 and 20 above.

22. L207-212: As in comments #18 and 20, does the distance from equilibrium keep decreasing past 30 km? If it keeps decreasing, does this affect the proposed insensitivity to seawater d18O?

23. L213: Perhaps it would be useful to mention that the reason for the near-equilibrium in the deeper parts of the section are due to the higher T.

24. L238: Perhaps change "not inconsistent with" to "consistent with"?

25. L235-238: The way these results are reported is very hard to take in, with all of the numbers and parentheses within parentheses. Suggest rewording.

26. L252: "spreading" and "weaker" are misspelled.

27. L255-278: The two paragraphs in these lines are less well-written than the previous text. Suggest editing for grammar, language and clarity.

28. L273-278: The model of Kasting et al. (2006) included the effect of overburden (ocean depth) on the depth in the crust at which water reached the critical point, leading to changes in the capacity of hydrothermal systems to transport heat and, consequently, on the temperature profile of water-rock interactions. Are such water phase changes considered in the present model, and if not, could that be an additional reason for disagreement with the results of Kasting et al. (2006)? Please discuss.

29. L281-282: This statement needs to be reevaluated following the tests requested in comments #18, 20, 21, 22. Hopefully, it still holds.

30. L283-286: This sentence is awkwardly worded. Suggest "By comparison, the simulated solid rock d18O values fall within this range for seawater d18O values ≥–10, –8 and –2‰ at a spreading rate of 1e-2, 3e-2 and ≥9e-2 m yr^-1, respectively (Figs. 4, 8)." Related to the above, what are the average Archean/Proterozoic/Phanerozoic seafloor spreading rates suggested in previous studies, and what are the implications for the evolution of the 18O-buffering strength of hydrothermal alteration of oceanic crust over Earth history?

31. L286-288: There are values of seawater d18O that are inconsistent with the range observed in ophiolites, right? Perhaps mention those values? Related to this, it appears

that the model reproduces the range observed in ophiolites irrespective of seawater d18O mostly at low spreading rates. It is worth mentioning that estimated Precambrian seafloor spreading rates were slower than Phanerozoic rates.

32. Section 4.3: This section could also benefit from editing for grammar, language and clarity.

33. Fig. 1: The labels on contours in panels b and d can be moved and spread out so that they are more easily seen. In panel b, orienting the text sub-parallel to the contours near the bottom and right domain boundaries would work nicely. In panel d, orienting the text sub-parallel to the contours near the left boundary would work.

34. Maybe it's just on my laptop, but there are fine horizontal and vertical lines on the filled contour plots with a continuous color scale (Fig. 1, 5, 7).

35. Fig. 2: Suggest changing "0, –6 and –12 ‰ of seawater d18O" to "at seawater d18O values of 0, –6 and –12 ‰".

36. Fig. 4 caption: "Ma" -> "Myr". Suggest changing "0, –2, …, –12 ‰ of seawater d18O" to "at seawater d18O values of 0, –2, …, –12 ‰". Note that this comparison is meaningful only for crust of a similar alteration duration (see comments #18, 20, 21, 22).

37. Fig. 5 caption: "0 ‰ of seawater d18O" -> "a seawater d18O value of 0 ‰".

38. SM L33: As mentioned in comment #12, the choice of a factor of 10 for the uncertainty is arbitrary. It would be good to perform an additional simulation at kex = 10^-6.5. If the results are indeed insensitive to the value of kex, this will not matter much for the buffering intensity, and it would provide confidence in the proposed insensitivity of seafloor alteration to seawater d18O.

39. Fig. 7 caption: The sentence starting with "Spreading rate" is awkward. Suggest rewording.

40. Fig. 8: Suggest decreasing font size of axis tick labels. Also, "0, –2, …, –12 ‰ of seawater d18O" -> "at seawater d18O values of 0, –2, …, –12 ‰".

41. SM Section S3, Figs. S7, S8: Looking at Fig. S7, there are significant differences between the profiles at a different value of kex. Please explain mechanistically why the buffering intensity ends up being so similar.

42. SM Section S4: A major concern of any clued reader will be that the current model only extends out to an oceanic crust age of 1e5 to 3e6 years (see many of my comments above). As such, I suggest moving some of this section to the main text, perhaps in the discussion.

43. SM Section S4: Is a distance of 300 km from the ridge axis sufficient? Does the model d18O of the crust stop evolving after this distance? As with many of

my comments above, it is important to constrain the change in the profiles as the crust ages and run the simulations out to a distance beyond which the additional change is negligible.

44. SM Section S4: The finding that the buffering intensity is no different from the standard case when off-axis alteration is included is very important, and it is understandable that the author focuses on this aspect, given the focus of the paper. However, there is a missed opportunity here, in my opinion, which is an exploration of ways in which changes through Earth history in seafloor spreading rates and oceanic plate lifetimes affect the net budget of 18O. Fig. S13 clearly shows that despite similar buffering intensities, the cases with off-axis circulation differ substantially in the net 18O flux from the standard case. If the proportion of off-axis alteration out of the total alteration has changed through time (e.g., changing spreading rate, changing sediment cover, changing crustal thickness), the current model can help to explain the change in seawater d18O suggested on the basis of the O isotope record in authigenic minerals. Perhaps this is beyond the scope of the current contribution.

45. SM L44-46: Please elaborate on the basis for the notion that the oceanic crust is altered within 10 Myr of its formation. The author's off-axis simulations suggest continued low-T alteration for much longer durations.

46. SM L51: What is the approximate sediment thickness required for this additional 10 MPa? With a density of 2700 kg/m^3 and an assumed porosity of 0.5, about 550 m of sediment are required. Please comment on the plausibility of this at 300 km from the spreading center (given, e.g., Straume et al., 2019) - to me this seems high. Fisher and Becker applied pressures ≤1-3 MPa, up to an order of magnitude less than here. Is it possible to overcome the numerical issues and perform the off-axis simulations with less of an overburden and lower imposed pressures?

47. SM Section 4 and elsewhere: Please replace "Ma" with "Myr", as necessary (see comment #16).

48. SM L74-78: See comment #44. There is a missed opportunity here.

49. SM Fig. S1 caption: "0, –6 and –12 ‰ of seawater d18O" is grammatically awkward. I suggest changing this (in two places in the caption) to "at seawater d18O values of 0, –6 and –12 ‰". Likewise, suggest "adopt a spreading rate of R1, R2 and R3, respectively." instead of the current text.

50. SM Fig. S2 caption: Same as comment #49. This wording appears also in several of the other SM figures. Suggest changing.

51. SM Fig. S3, S5, S6, S7, S8, S12, S13: Suggest smaller font size on axis tick labels.