Review of Quantifying the buffering of oceanic oxygen isotopes at ancient mid-ocean ridges: Yoshiki Kanzaki

*General Comments*. The author uses a coupled hydrothermal alteration-reactive transport model to investigate how oxygen isotopes are buffered during alteration of ocean crust. There was been a renewed interest in the controls on and history of the oxygen isotope composition of seawater, and this is a timely manuscript. The main conclusion from the work is that the buffering capacity is lower than previously expected, primarily due to slow kinetics of isotope exchange at low temperatures and shallow crustal depths. This was tested over a range of seawater  $\delta^{18}$ O values, and the work indicates that patterns of alteration in ocean crust are similar across this range. The author suggests, then, that the apparent constancy of ophiolite  $\delta^{18}$ O through time does not, in fact, require constant seawater  $\delta^{18}$ O through time. Rather, this crustal record is not a good reflection of seawater  $\delta^{18}$ O.

Thank you for the opportunity to read this paper! I think it's a valuable contribution, but I do have some comments below. Primarily, I'm interested in how you setup your model and some implications:

- What is the importance of pore-water exchange vs fluid in cracks? My impression was that more water is transported through cracks than pores?
- Would you expect this relationship if seawater had a positive  $\delta^{18}$ O, as has been suggested in previous and recent work? (Johnson and Wing, 2020, *Nature Geoscience*, Pope et al., 2012, *PNAS*).
- In your Figure 4, it looks like the measurements from Oman most closely match your simulation from a 0% ocean. The upper part of the crust, from your model, does change quite a bit under different ocean  $\delta^{18}$ O. There are older ophiolites that you could compare here, such as the one from Holmden and Muehlenbachs (1993), or Muehlenbachs et al. (2003). This figure makes it seem like the upper part of the crust is in fact sensitive to changing seawater  $\delta^{18}$ O, so couldn't it actually be used as a proxy for seawater  $\delta^{18}$ O?

## Specific Comments.

- Paragraph lines 26-42: In addition, lower temperatures are supported by O-isotopes in phosphates (Blake et al., 2010 Phosphate oxygen isotopic evidence for a temperate and biologically active Archaean ocean), so it's not just sporadic glacial activity. There are also GCM studies that support non-super hot conditions (Wolf and Toon, 2014, Controls on the Archean Climate System investigated with a global climate model)
- In this same paragraph, it's important to note that the samples from the new Galili et al. study are all from the Proterozoic and younger, and do not give additional information on the Archean.
- Line 105-106: is 10<sup>4</sup> years sufficient? Many low-temperature systems last much longer than this, with additional water circulation
- Equation 7: This seems to be a key part of your conclusions, that slow kinetics limit Oisotope buffering. Your constant, 10<sup>-8.5</sup>, is lower than previous estimates. This value needs a bit more justification. What is the reasoning that field kinetics are slower? Is it just harder to measure?
- In addition, the related material in the supplement (Fig. S7), appears to show a pretty different pattern of  $\delta^{18}$ O in the crust depending on  $k_{ex}$ . Can you provide some additional justification?

- I grant that your model fits the Oman ophiolite data well, but we know that the  $\delta^{18}$ O of seawater at the time this formed is not different than today, so perhaps testing your model in a system that we **know** has a different  $\delta^{18}$ O value, such as a freshwater system, might be insightful.
- Equation 8: why use this equation for andesite? You say it's similar to Cole et al. for basalt, so what is the advantage?
- Why is permeability set to 0 below 6km?
- Depaolo (2006), which you do cite, found that equilibrium exchange is a good approximation as long as fractures are ~1-4 m apart, as in MOR. Why does your work differ here?
- Another study using a similar approach is Cathles, L. M. in *The Kuroko and Related Volcanogenic Massive Sulfide Deposits* Vol. 5 (eds Ohmoto, H. & Skinner, B. J.) 439–487 (Economic Geology Publishing, 1983). How does your work compare to theirs, which is very similar in approach?

Technical Comments.

Typo in line 33? Should this be 70-85 degrees C?