Response to Referee #1 (Dr. Benjamin Johnson)

I express my gratitude to Dr. Benjamin Johnson for his useful comments. My response to the reviewer's comments and the corresponding revision are described in detail below. The numbers of pages, lines, equations, tables and figures are those in the revised manuscript unless otherwise described.

General comment 1:
"What is the importance of pore-water exchange vs fluid in cracks? My impression was that more water is transported through cracks than pores?"

Response:
As long as fractures/cracks occur on smaller spatial scales than the control volume in the calculation domain, their effects can be accounted for by adopting corresponding bulk-rock permeability (cf. Cathles, 1983; DePaolo, 2006). DePaolo (2006) suggested 1-4 m for the fracture spacing, which is generally smaller than the grid cells of the calculation domain (>~1 m in horizontal). Therefore, it is not unreasonable to account for the presence of factures/cracks by adopting correspondingly high permeability for the bulk rock. The permeability at the crust/ocean interface is assumed to be $\sim 10^{-12}$ m^2, which falls in the range of fractured rock permeability ($\geq 10^{-12}$ m^2; Fisher, 1998). Also, the model that assumes a higher permeability ($\sim 10^{-11}$ m^2 at the ocean/crust interface) yields essentially the same results as those in the standard simulation (Supplementary material). Therefore, the present results and conclusions will remain valid in systems that include fractures/cracks.

Changes in manuscript (Page numbers/Line numbers):
Description of fractured rock permeability is added to Section S3 in Supplementary material where I compare the permeability adopted for this study and observations by Fisher (1998) (P3/L72-73 in Supplementary material).

General comment 2:
"Would you expect this relationship if seawater had a positive δ18O, as has been suggested in previous and recent work? (Johnson and Wing, 2020, Nature Geoscience, Pope et al., 2012, PNAS)."

Response:
I ran additional experiments that assume positive seawater $\delta^{18}O$ up to 6 ‰ and confirmed that the results and conclusions in the manuscript remain valid.

Changes in manuscript (Page numbers/Line numbers):
I modified figures to include the results from simulations that assume positive seawater $\delta^{18}O$ (P23, P25, P27, P28) and included the reference of Johnson and Wing (2020) in the revised manuscript (P9/L252-253).

General comment 3:
"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 δ18O. 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 δ18O, so couldn't it actually be used as a proxy for seawater δ18O?"

Response:
The sensitivity to seawater $\delta^{18}O$ is higher at shallow depths of oceanic crust compared to that in the deeper sections as suggested by the reviewer. However, the sensitivity to seawater $\delta^{18}O$ is still significantly smaller than previously assumed. Given the general weak coupling between oceanic crust and seawater $\delta^{18}O$, one has to evaluate the alteration conditions (e.g., spreading rate and permeability) more carefully because they might affect solid rock $\delta^{18}O$ distributions possibly more than seawater $\delta^{18}O$ as discussed in Section 4.1. As a conclusion, I suggested that ophiolites may be interpreted to indicate the insensitivity of oceanic rocks to seawater $\delta^{18}O$ rather than a constant seawater $\delta^{18}O$. One can still use the model to reconstruct seawater $\delta^{18}O$ but the uncertainty would be larger compared to those when using other models in the previous studies that assume strong coupling between oceanic crust and seawater $\delta^{18}O$.

I added a section to Supplementary material where I compared the model simulations that assume 0 ‰ of seawater $\delta^{18}O$ with the modern oceanic crust and Phanerozoic ophiolites including the ophiolite that is studied by Muehlenbachs et al. (2003) to further assess the validity of the present model (Section S2 in Supplementary material). Most of data are comparable to the present simulations. However, the data by Muehlenbachs et al. (2003) is an exception, i.e., their data is significantly smaller than the model prediction. This discrepancy may be attributed to the lower seawater $\delta^{18}O$ during the Paleozoic (Galili et al., 2019) but could also be caused by changes in the permeability and/or rate constant for oxygen isotope exchange (also related to reactive surface area). Please see Section S2 in Supplementary material for more details about the model-data comparison.

In the above comparison with datasets (Section S2 in Supplementary material), I excluded Precambrian ophiolites (including the ophiolite studied by Holmden and Muehlenbachs, 1993) because seawater $\delta^{18}O$ in the Precambrian could have been more significantly deviated from the present-day value (e.g., Galili et al., 2019; Johnson and Wing, 2020) and thus Precambrian ophiolites are not suited for assessing the validity of the model. Also, Holmden and Muehlenbachs (1993) did not provide explicit depth information of rock samples and thus their data cannot be directly compared with the simulation results.

Changes in manuscript (Page numbers/Line numbers):
I added Section S2 to Supplementary material where I compare the model simulations with more $\delta^{18}O$ datasets from the modern oceanic crust and Phanerozoic ophiolites (P1/L6-P2/L62 in Supplementary material). The added section is referred to in the main text where relevant (P7/L195).

More explanations were added to Section 4 regarding the uncertainty in reconstruction of ancient seawater $\delta^{18}O$ (P12/L361-363).

Specific comment 1:
"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)"

Response:
Blake et al. (2010) suggested temperate climate based on phosphate $\delta^{18}O$ from the Archean sediment. Their finding of the relatively high phosphate $\delta^{18}O$ is in contrast to the trend of phosphate oxygen isotopes reported by Karhu and Epstein (1986, Geochim. Cosmochim. Acta 50, 1745), which should be mentioned when introducing the general sedimentary $\delta^{18}O$ trend (Section 1).

Wolf and Toon (2014) simulated Archean climate under various CH_4 and CO_2 conditions. However, one cannot conclude whether hot conditions could have been possible or not in the Archean only with the study by Wolf and Toon (2014) because it depends on the constraints on atmospheric CO_2 and CH_4. More recently, Charnay et al. (2017, Earth Planet Sci. Lett. 474, 97) showed that hot climate in the Archean can be realized in a GCM if weathering feedback is not effective.

Changes in manuscript (Page numbers/Line numbers):
I included the reference of Blake et al. (2010) in the revised manuscript (P2/L28-29), but did not refer to climate models (please see my response above).

Specific comment 2:
"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.”

Response:
Agreed.

Changes in manuscript (Page numbers/Line numbers):
I revised the relevant sentence to be clearer (P2/L38).

<u>Specific comment 3</u>:
“Line 105-106: is 104 years sufficient? Many low-temperature systems last much longer than this, with additional water circulation”

Response:
3×10^4 yr is the duration of time in each iteration, but not the total time duration of hydrothermal simulations. Iterations are repeated 10^3 times so the total duration of hydrothermal simulation is 3×10^7 years. This time scale is sufficient to reach the system’s steady state as reported in other studies (e.g., Cherkaoui et al., 2003).

Changes in manuscript (Page numbers/Line numbers):
I added more explanations (P4/L121).

<u>Specific comment 4</u>:
“Equation 7: This seems to be a key part of your conclusions, that slow kinetics limit Oisotope buffering. Your constant, 10-8.5, 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?”

Response:
The slower reaction kinetics in the field than in the laboratory has long been recognized and discussed especially regarding mineral dissolution/precipitation (e.g., Pačes, 1983, Geochim. Cosmochim. Acta 47, 1855; Velbel, 1993, Chem. Geol. 105, 89; White and Brantley, 2003; Maher et al., 2004, 2009). However, the cause of the kinetic discrepancy has not been fully understood. Suggested mechanisms include a decline in the reactive surface area with rock age and significantly different porewater residence time and porewater chemistry in the field (e.g., White and Brantley, 2003; Maher et al., 2009). Thus, it is appropriate to account for the kinetic discrepancy in a reactive transport model, as done in other models (e.g., Fantle and DePaolo, 2006, Geochim. Cosmochim. Acta 70, 3883; Moore et al., 2012, Geochim. Cosmochim. Acta 93, 235; Yokota et al., 2013,

Geochim. Cosmochim. Acta 117, 332). Cathles (1983) also used a factor to lower the kinetic rate constant for oxygen isotope exchange down to 10^{-4}. He indicated that such a factor is necessary to better explain observed oxygen isotope profiles, which is not inconsistent with the present study.

In addition, sensitivity analysis where the rate constant for oxygen isotope exchange at reference temperature (5 °C) is varied from the laboratory value to the reduced value by a factor of 10^4 (Section S4 in Supplementary material) suggests that the general results and conclusions are not affected by the variations in the rate constant, although the model reproduces the observations best with the standard value, i.e., $10^{-8.5}$ mol^{-1} kg yr^{-1}. Please also find that the standard value is not a random number but the geometric mean of the range that could be observed in the field, i.e., from the laboratory value to the reduced value by a factor of 10^4 that accounts for the field-laboratory discrepancy (a factor of up to 10^3; e.g., White and Brantley, 2003) and the uncertainty in reactive surface area (a factor of up to 10; Nielson and Fisk, 2010).

Changes in manuscript (Page numbers/Line numbers):
I added explanations on how the standard value of the rate constant for oxygen isotope exchange at reference temperature (5 °C) is determined in Section 2.2 (P5/L147-151), and in Section S4 of Supplementary material (P3/L83-91 in Supplementary material).

I added a section to Supplementary material (Section S6) where I explain the kinetic discrepancy between the laboratory and field and its potential mechanisms in more detail (P5/L144-P6/L181 in Supplementary material).

Specific comment 5:
"In addition, the related material in the supplement (Fig. S7), appears to show a pretty different pattern of δ18O in the crust depending on kex. Can you provide some additional justification?"

Response:
Please see my response to specific comment 4 by Referee #1 where I addressed the issue.

Changes in manuscript (Page numbers/Line numbers):
Please see my changes in manuscript in response to specific comment 4 by Referee #1.

Specific comment 6:
"I grant that your model fits the Oman ophiolite data well, but we know that the δ18O 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 δ18O value, such as a freshwater system, might be insightful."

Response:

Freshwater systems can be characterized by a relatively-short-term intrusion and later cooling, i.e., little effect of solid rock transport via spreading (e.g., Norton and Taylor, 1979). In such a case without solid rock transport, transient simulation is necessary (e.g., DePaolo, 2006), which cannot be conducted by the present reactive transport model of oxygen isotopes, which simulates only steady state distributions of solid-rock and porewater δ^{18}O (Section 2.2). Therefore, the present model cannot be applied to freshwater systems. Please also see my response to specific comment 10 by Referee #1 on the related issue.

Instead, in response to the comment, I compared the model simulations with more datasets of the modern oceanic crust and Phanerozoic ophiolites (Section S2 in Supplementary material) to further assess the validity of the model. The model and data are mostly comparable and effects of spreading rate are well predicted by the present model, and the validity of the model is further supported.

Changes in manuscript (Page numbers/Line numbers):

I added Section S2 to Supplementary material where the present simulations are compared with more datasets of oceanic crust and ophiolites (P1/L6-P2/L62 in Supplementary material). This specific section is referred to in the main text where relevant (P7/L195).

Specific comment 7:

"Equation 8: why use this equation for andesite? You say it's similar to Cole et al. for basalt, so what is the advantage?"

Response:

Data by Cole et al. (1987) is limited to the temperature range of their experiments (i.e., 300 to 500 °C). To extrapolate the data by Cole et al. (1987) over the wider temperature range considered in the present study (from 2 to 1200 °C), theoretical models are useful. I adopted the model by Zhao and Zheng (2003) because their model can be applied to the above wide range of temperature and their model for andesite also predicts fractionation factors that are similar to those reported by Cole et al. (1987).

Changes in manuscript (Page numbers/Line numbers):

I revised the relevant sentence to be clearer (P6/L157).

Specific comment 8:

"Why is permeability set to 0 below 6km?"

Response:
6 km depth from the crust/ocean interface is assumed to be the location of the boundary between the oceanic crust and mantle, below which the permeability can be assumed to be significantly reduced as in Cherkaoui et al. (2003). The assumption is also consistent with no water flux at the lower boundary (at 5 km depth) for a smaller calculation domain (5×5 km^2) by Cathles (1983) (please also see my response to specific comment 10 by Referee #1).

Changes in manuscript (Page numbers/Line numbers):
I added more explanations to the relevant sentence (P4/L98-99).

Specific comment 9:
"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?"

Response:
DePaolo (2006) adopted a dual porosity model where fractures and rock matrix between fractures are separately treated and argued that isotopic composition of pore fluid can change depending on the reaction length in the rock matrix and fracture spacing. In turn, applying the model to pore fluid data for O and Sr isotopes, DePaolo (2006) suggested fracture spacing can be 1-4 m, although the author also indicated that this estimate may change once the effect of solid rock transport is included. In the above fracture spacing estimate, the temperature of pore fluid and thus the reaction rate are assumed. In other words, equilibrium exchange is not a consequence of 1-4 m fracture spacing, but just an assumption. Thus, fracture spacing of 1-4 m does not necessarily mean that the system must be in equilibrium.

Please also find that I do not argue that isotope exchange equilibrium is not achieved in MOR; in contrary, sections where temperatures are high are characterized by isotope exchange equilibrium (e.g., Fig. 5). The differences of my model from DePaolo's model (2006) include that my model explicitly includes the effect of solid rock transport, which supplies significant O isotopes to the system and buffers porewater $\delta^{18}O$. As discussed in Section 4.3, because of the lack of solid rock transport, DePaolo's model (2006) might overestimate the contribution of seawater to formation of porewater $\delta^{18}O$ and tends to assume a relatively strong coupling between solid rock and seawater $\delta^{18}O$ as in other models (e.g., Taylor, 1977; Criss et al., 1987; Gregory et al., 1989).

Please also see my response to general comment 1 by Referee #1 on the issue about fracture/crack treatment in the model.

Changes in manuscript (Page numbers/Line numbers):

I revised the manuscript so that it becomes clearer that equilibrium can be achieved in high-temperature sections (P8/L226-227, P8/L242, P8/L243).

Specific comment 10:
"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?"

Response:
The hydrothermal circulation model by Cathles (1983) is similar to my model in that both models are based on energy, mass and momentum conservation. However, Cathles's model is more limited with respect to spatial resolution (39×29 grid with 35×20 to 520×260 m^2 grid cell sizes in Cathles's model (1983) vs. 320×200 grid with 1.1×0.17 to 330×82 m^2 grid cell sizes in the present model), the size of calculation domain (5×5 vs. 12×30 km^2), permeability distribution (assumed permeability that changes with temperature vs. constrained permeability based on observations by Fisher, 1998) and the time scale (< 50000 years vs. steady state (reached by $\leq 3\times10^7$ years simulations)). Accordingly, experimental setup by Cathles (1983) is suited to simulate effects of local and short-term episodic intrusion and later cooling of oceanic crust while the present model is suited to describing a hydrothermal system that operates on long term.

Oxygen isotope modeling for porewater is similar to that in this study, but not clear for the simulation of oxygen isotopes in solid rock as I could not find the governing equation for solid-rock $\delta^{18}O$ in Cathles (1983). Thus, the importance of $\delta^{18}O$ buffering by transported oceanic rocks cannot be inferred from the work by Cathles (1983). Nonetheless, Cathles (1983) described that the positive and negative $\delta^{18}O$ anomaly relative to the fresh rock $\delta^{18}O$ is caused by non-equilibrium alteration and $\delta^{18}O$ supply from solid rock, respectively, which is consistent with the present simulations (e.g., Fig. 5).

Changes in manuscript (Page numbers/Line numbers):
I added the reference of Cathles (1983) to the revised manuscript and added more explanations to description of the present model (P5/L130, P5/L151-152, P8/L233-236).

Technical comment 1:
"Typo in line 33? Should this be 70-85 degrees C?"

Response:
I thank the reviewer for pointing out the typo. It meant 70±15 °C.

Changes in manuscript (Page numbers/Line numbers):
I corrected the typo (P2/L34).