

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 ($> \sim 1$ m in horizontal). Therefore, it is not unreasonable to account for the presence of fractures/cracks by adopting correspondingly high permeability for the bulk rock. The permeability at the crust/ocean interface is assumed to be $\sim 10^{-12}$ m², which falls in the range of fractured rock permeability ($\geq 10^{-12}$ m²; Fisher, 1998). Also, the model that assumes a higher permeability ($\sim 10^{-11}$ m² 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 $\delta^{18}\text{O}$, 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ (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 $\delta^{18}\text{O}$. 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 $\delta^{18}\text{O}$, so couldn't it actually be used as a proxy for seawater $\delta^{18}\text{O}$?”

Response:

The sensitivity to seawater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ is still significantly smaller than previously assumed. Given the general weak coupling between oceanic crust and seawater $\delta^{18}\text{O}$, one has to evaluate the alteration conditions (e.g., spreading rate and permeability) more carefully because they might affect solid rock $\delta^{18}\text{O}$ distributions possibly more than seawater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ rather than a constant seawater $\delta^{18}\text{O}$. One can still use the model to reconstruct seawater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$.

I added a section to Supplementary material where I compared the model simulations that assume 0 ‰ of seawater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ (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 Archean 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 $\delta^{18}\text{O}$ from the Archean sediment. Their finding of the relatively high phosphate $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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).

Specific comment 3:

“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).

Specific comment 4:

“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., $10^{-8.5} \text{ mol}^{-1} \text{ kg yr}^{-1}$. 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ (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 km²) 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 $\delta^{18}\text{O}$. 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 $\delta^{18}\text{O}$ and tends to assume a relatively strong coupling between solid rock and seawater $\delta^{18}\text{O}$ 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 m² grid cell sizes in Cathles’s model (1983) vs. 320×200 grid with 1.1×0.17 to 330×82 m² grid cell sizes in the present model), the size of calculation domain (5×5 vs. 12×30 km²), 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 $\leq 3 \times 10^7$ 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 $\delta^{18}\text{O}$ in Cathles (1983). Thus, the importance of $\delta^{18}\text{O}$ buffering by transported oceanic rocks cannot be inferred from the work by Cathles (1983). Nonetheless, Cathles (1983) described that the positive and negative $\delta^{18}\text{O}$ anomaly relative to the fresh rock $\delta^{18}\text{O}$ is caused by non-equilibrium alteration and $\delta^{18}\text{O}$ 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).

Response to Referee #2 (Dr. Itay Halevy)

I express my gratitude to Dr. Itay Halevy 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.

Major comment 1:

“Firstly, where the model is validated against ophiolite $\delta^{18}\text{O}$ profiles or estimates of ^{18}O 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.”

Response:

Oxygen isotopic data from the modern oceanic crust with known ages including ODP boreholes has suggested that significant oxygen isotope exchange during oceanic crust alteration is completed within the first <10 million years from the ridge axis (Muehlenbachs, 1979) and not recognized afterwards (e.g., Muehlenbachs, 1979; Barrett and Friedrichsen, 1982; Alt and Bach, 2006). On the other hand, the simulations in the main text assume 30 km for the maximum reaction distance from the ridge axis with variable spreading rates from 1×10^{-2} to 30×10^{-2} m yr⁻¹, i.e., the time duration for significant oxygen isotope exchange is assumed to be in the range from 0.1 to 3 million years. The assumed range of the time duration (i.e., 0.1 to 3 million years) satisfies <10 million years and therefore is consistent with the constraint from the observations of the modern oceanic crust with known ages including ODP boreholes (Muehlenbachs, 1979). Also, the modern oceanic crustal $\delta^{18}\text{O}$ data cannot be used to further constrain or test the time duration for significant oxygen isotope exchange because it is derived from rocks whose ages are mostly > 3 million years (Muehlenbachs, 1979; please also see Table S1 in Supplementary material). Nonetheless, comparison of fluxes as well as oxygen isotope distributions between the simulations and observations is justifiable, given that observed ^{18}O fluxes and distributions reported in the literature have been obtained from systems where significant oxygen isotope exchange is completed (e.g., Holland, 1984; Muehlenbachs, 1998).

The mechanisms to explain why effective oxygen isotope exchange ceases at <10 million years from the ridge axis are important to consider the validity of the model, given that the only maximum time duration (i.e., 10 million years) has been derived from the observations (Muehlenbachs, 1979). Possible mechanisms can include a decline in the reaction rate with age often observed in natural systems (e.g., White and Brantley, 2003; Maher et al., 2004). To further assess the plausibility of the assumed time duration (0.1 to 3 million years), I ran an additional numerical experiment that assumes 300 km maximum reaction distance (or 10 million years with the standard spreading rate of 3×10^{-2} m

yr⁻¹) from the ridge axis, includes off-axis water flows and implements a decline in the kinetic constant for oxygen isotope exchange with age that is consistent with field and laboratory observations for mineral dissolution by Maher et al. (2004). The simulation indeed showed that significant changes in solid rock $\delta^{18}\text{O}$ (e.g., > 2 ‰) with age are no longer recognized at > ~0.1 to 1 million years from the ridge axis (Section S6 in Supplementary material), and thus further confirmed that the assumed time duration for oxygen isotope exchange in the simulations in the main text (0.1 to 3 million years) is reasonable. Please see Section S6 in Supplementary material for further details.

Even though the modern oceanic crustal $\delta^{18}\text{O}$ has given only the constraint of <10 million years for the time duration for oxygen isotope exchange (please see above), it can be compared with the present model simulations to further assess the validity of the model, especially regarding the effect of spreading rate on the distribution of oxygen isotopes. Accordingly, I added a section to Supplementary material (Section S2) where I compare the simulations that assume various spreading rates and 0 ‰ for seawater $\delta^{18}\text{O}$ with the $\delta^{18}\text{O}$ datasets from the modern oceanic crust (including ODP boreholes) and Phanerozoic ophiolites. The comparison suggests that the model can predict the relationships between oceanic rock $\delta^{18}\text{O}$ distributions and the spreading rate that are consistent with the observations and thus further supports the validity of the model. Only exceptions are the data by Barrett and Friedrichsen (1982) and Muehlenbachs et al. (2003). The data by Barrett and Friedrichsen (1982) is slightly smaller than the model prediction but can still be explained by the model if a smaller permeability or kinetic constant for oxygen isotope exchange than in the standard parameterization is assumed. The data by Muehlenbachs et al. (2003) from a Paleozoic ophiolite shows solid rock $\delta^{18}\text{O}$ that is smaller than the model prediction, which can be attributed to the lower contemporaneous seawater $\delta^{18}\text{O}$ (e.g., Galili et al., 2019) as well as a smaller permeability and/or rate constant for oxygen isotope exchange. Please see Section S2 in Supplementary material for the details.

Changes in manuscript (Page numbers/Line numbers):

I added Section S2 to Supplementary material where the model simulations are compared with more datasets of oceanic rock $\delta^{18}\text{O}$ available in the literature (P1/L6-P2/L62 in Supplementary material). The added section is referred to in the main text where relevant (P7/L195).

I added Section S6 to Supplementary material where I discuss the plausible range of the time duration for significant oxygen isotope exchange, showing results from an additional numerical experiment that assumes 300 km maximum reaction distance (or 10 million years) from the ridge axis, includes off-axis water flows and implements a decline in the kinetic constant for oxygen isotope exchange with age that is consistent with observations by Maher et al. (2004) (P5/L144-P6/L181 in Supplementary material).

I added more model explanations regarding the calculation domain width and the time duration for significant oxygen isotope exchange referring to the above sections of Supplementary material (P5/L125-128, P9/L276-278, P10/L287-289).

Major comment 2:

“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 $\delta^{18}\text{O}$? I urge the author to test this, which will provide confidence in the findings.”

Response:

As described in my response to major comment 1 by Referee #2, it has been observed that oceanic crust alteration has only limited influences on oxygen isotopes of oceanic rocks after <10 million years from the ridge axis (e.g., Muehlenbachs, 1979; Barrett and Friedrichsen, 1982; Alt and Bach, 2006). Thus, 30 km reaction distance (or 0.1 to 3 million years) from the ridge axis in the simulations in the main text is reasonable. In addition, simulations that assume 300 km reaction distance from the ridge axis show essentially the same results as those from the simulations with 30 km reaction distance from the ridge axis, with respect to the sensitivity of ^{18}O flux and oceanic rock $^{18}\text{O}/^{16}\text{O}$ fractionation to seawater $\delta^{18}\text{O}$ (Sections S5 and S6 in Supplementary material). Furthermore, an additional numerical experiment that assumes 300 km reaction distance from the ridge axis, includes off-axis water flows and implements the decline in reaction kinetics with age further supports that 30 km is wide enough to simulate oxygen isotope exchange during hydrothermal alteration (Section S6 in Supplementary material; please also see my response to major comment 1 by Referee #2). Therefore, the present study’s findings will remain valid even in a wider calculation domain.

The mechanisms to cause the weak buffering in the present simulations are already discussed; oxygen isotope exchange is kinetically prevented from reaching equilibrium in the low temperature sections and oxygen isotopes of deeper solid rocks are buffered by solid rocks transported via spreading rather than circulating seawater. The two mechanisms make oceanic rocks partially decoupled from seawater with respect to oxygen isotopes, resulting in a relatively weak seawater- $\delta^{18}\text{O}$ buffering. These mechanisms operate in systems where significant oxygen isotope exchange continue over longer time scales than assumed in the main text, as confirmed by supplementary simulations in Sections S5 and S6 of Supplementary material.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to major comment 1 by Referee #2.

I added more explanations of the mechanisms to cause the partial decoupling between oceanic crust and seawater $\delta^{18}\text{O}$ under different spreading rate conditions in Section 3 (P9/L276-279,

P10/L284-289).

Suggestion related to major comment 2:

“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.”

Response:

Please see my response to major comment 2 by Referee #2 on the issue about the time duration for oxygen isotope exchange or the calculation domain width. I do not consider that simulations with thousands of km from the ridge axis is necessary or reasonable, especially when the apparent cessation of significant oxygen isotope exchange at < 10 million years from the ridge axis has been observed and can be explained/simulated with a decline in efficiency of oxygen isotope exchange with age (Section S6 in Supplementary material).

I agree with the reviewer that revealing the long-term control on oxygen isotopic composition of seawater will make a timely contribution. However, the buffering from hydrothermal systems could have been weak as suggested in the present study and thus understanding oxygen isotope exchange through continental weathering could have been more important than previously assumed, which requires additional modeling work, as discussed in Section 4.2. In other words, it could lead to a false conclusion if one discusses the control of oxygen isotopic composition of ancient oceans only based on hydrothermal alteration of oceanic crust, whose contribution to the oceanic ¹⁸O budget might have been overwhelmed by that from continental weathering in the deep past.

Changes in manuscript (Page numbers/Line numbers):

I modified the relevant sentence in Section 4 to be clearer about the importance of modeling continental weathering to elucidate the control on oxygen isotopes in the ancient oceans (P11/L327-329).

Specific comment 1:

“L19-21: The sentence in these lines can be worded more clearly.”

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

I revised the sentence (P1/L19-21).

Specific comment 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.’

Response:

I could not find the literature which shows a pronounced increase of $\delta^{18}\text{O}$ in glauconites over Earth history. Otherwise I agree.

Changes in manuscript (Page numbers/Line numbers):

I added ‘(e.g., carbonates, cherts, phosphorites and shales)’ to the relevant sentence (P2/L26).

Specific comment 3:

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

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).

Specific comment 4:

‘L38: Perhaps “weak” instead of “little”?’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Corrected as suggested (P2/L39).

Specific comment 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.”

Response:

I agree with the reviewer that oxygen isotopic composition of seawater can be related to the relative magnitude of low- and high-temperature alteration processes, which can further be linked to the evolution of biosphere, atmosphere and hydrosphere, as well as tectonics (e.g., Verard and Veizer, 2019).

Changes in manuscript (Page numbers/Line numbers):

I revised the relevant sentence to be clearer (P2/L42).

Specific comment 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.”

Response:

The mechanisms to lower seawater $\delta^{18}\text{O}$ might have lowered the surface temperature, as inferred from the comment. However, one can still assume that the temperatures of deep sections of ophiolites were high and little affected by surface temperature variations. In such high temperature sections, fractionation factors are small and thus if porewater is equivalent to seawater with respect to oxygen isotopes, the deep sections could directly record seawater $\delta^{18}\text{O}$ (though not supported by this study; please see the next paragraph). Thus, ophiolite records, especially those from deep high-temperature sections, have been interpreted to suggest invariant seawater $\delta^{18}\text{O}$. This is well illustrated in Fig. 2 of Holmden and Muehlenbachs (1993). Therefore, the mechanisms to lower seawater $\delta^{18}\text{O}$ cannot explain age-invariant ophiolite $\delta^{18}\text{O}$ records especially those from deep sections.

Please find that the present simulations revealed that the isotopic equivalence between porewater and seawater mentioned above is unlikely in deep sections of oceanic crust because of significant $\delta^{18}\text{O}$ buffering via transported solid rocks. Combined with kinetic inhibition in shallower low-temperature sections, oceanic crust is partially decoupled from seawater $\delta^{18}\text{O}$. Thus age-invariant ophiolite $\delta^{18}\text{O}$ records may be alternatively interpreted to suggest the relative insensitivity of oceanic crust to seawater $\delta^{18}\text{O}$.

Changes in manuscript (Page numbers/Line numbers):

I revised the relevant sentence to be clearer (P2/L56).

Specific comment 7:

‘L67: “The present study has been undertaken to present...”. Suggest rewording.’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

I revised the sentence (P3/L69-70).

Specific comment 8:

‘L95: Should be “length scale”? Also, perhaps “for an e-fold increase”?’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Corrected as suggested (P4/L97).

Specific comment 9:

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

Response:

I adopted 12 km rather than 6 km to facilitate changes in the location of the crust/mantle boundary (although I did not change the crust/mantle boundary from 6 km in this study).

Changes in manuscript (Page numbers/Line numbers):

I added more explanations to the relevant sentences (P4/L98-99, P5/L124-125).

Specific comment 10 (related to major comments):

“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?”

Response:

The simulations of q - P - T and oxygen isotopes calculate only steady-state profiles. Therefore, time to reach steady states is not calculated, though within 30 million years for q - P - T simulations, and the values reported for q , P , T and $\delta^{18}O$ at any distance (or age) from the ridge axis and any depth from the crust/ocean interface do not change with time. Unless there are multiple steady states, simulating transient states will not affect the steady state results. Simulating only steady-state results is justifiable because oxygen isotopic composition of seawater can change only on a long time scale, e.g., $\sim 0.5 \times 10^8$ yr (Holland, 1984), where long-term buffering intensity should be important.

Please also see my response to major comment 2 by Referee #2 on the issue about the assumed calculation domain width.

Changes in manuscript (Page numbers/Line numbers):

I added more explanations on why only steady state is simulated in the present study (P5/L122-124).

Please also see my changes in manuscript in response to major comment 2 by Referee #2

Specific comment 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.”

Response:

Insulating at a given boundary means there is no temperature gradient and thus no heat flux across the boundary, which is reasonable at the right boundary of a wide calculation domain as in Iyer et al.

(2010). Relaxing this boundary condition (e.g. allowing free heat flow) will not significantly affect the results because a simulation with a wider calculation domain (300 km) yielded similar temperature distributions (cf. Fig. S10 in Supplementary material).

Changes in manuscript (Page numbers/Line numbers):

I added more explanations to the relevant sentence (P4/L112-113).

Specific comment 12:

“L140-143: Could you please better substantiate the choice of a lower-than-lab k_{ex} ? 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 k_{ex} 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.”

Response:

The reaction kinetic discrepancy between the laboratory and field has long been recognized and its cause has been discussed but not fully understood. Possible mechanisms include significant difference of reactive surface area and residence time of porewater and porewater chemistry between the field and laboratory (e.g., White and Brantley, 2003; Maher et al., 2009). I extended the range of examined k_{ex}^{ref} value to $10^{-6.5}$ – $10^{-10.5}$ mol⁻¹ kg yr⁻¹ in sensitivity analysis in Section S4 of Supplementary material, which covers the laboratory range ($10^{-6.6}$ – $10^{-7.2}$ mol⁻¹ kg yr⁻¹) as suggested by the reviewer. Variations of k_{ex}^{ref} within the above range do not affect the general results and conclusions (Please see Section S4 in Supplementary material for the details).

Changes in manuscript (Page numbers/Line numbers):

I added more explanation on how the standard k_{ex}^{ref} value is obtained in Section 2.2 (P5/L147-152), and in Section S4 of Supplementary material (P3/L83-91 in Supplementary material).

Also, the range of k_{ex}^{ref} value examined in Section S4 of Supplementary material was extended and associated figures were modified (P3/L92-P4/L102, P17, P18 in Supplementary material).

Specific comment 13:

“L151-152: “The first term on the right-hand side..., while the second term represents the hydrodynamic dispersion.”.”

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):
Corrected as suggested (P6/L163-164).

Specific comment 14:

“L158: Is the O isotope model insensitive to the assumption of impermeability, like the q-P-T model?”

Response:

When the calculation domain is wide enough, the right boundary can be reasonably assumed to be impermeable with respect to flux of oxygen isotopes via water, given the observation that significant oxygen isotope exchange is limited within < 10 million years from the ridge axis. Simulations with a wider calculation domain show essentially the same results regarding the sensitivity of ^{18}O distributions and flux to seawater $\delta^{18}\text{O}$ as those by simulations with 30 km calculation domain width (Sections S5 and S6 in Supplementary material). Thus, the calculation domain seems to be wide enough to assume no ^{18}O flux via water at the right boundary. Please also see my response to major comment 2 by Referee #2 on the issue about the assumed calculation domain width.

Changes in manuscript (Page numbers/Line numbers):

I referred to Section 2.1 in the relevant sentence where I state that calculation domain is wide enough that changing the right boundary will not have significant influences on the results (P6/L170).

Specific comment 15:

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

Response:

I intended to present the details of results and mechanisms to cause the results in the Results section. Implications of the results and mechanisms from the Results section are discussed in the Discussion section. I consider keeping these two sections separate will be useful to the reader.

Changes in manuscript (Page numbers/Line numbers):

I did not make any specific changes in response to the comment (please see my response above). Please note that I revised the manuscript substantially so that it is easier for the reader to understand the manuscript (please see my changes in manuscript in response to other specific comments by Referee #2).

Specific comment 16:

‘L168 and elsewhere: “Ma” is usually reserved for millions of years ago. When referring to millions of years, “Myr” is more commonly used.’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

I changed Ma to Myr where appropriate (P6/L180, P7/L186, P7/L192, P23).

Specific comment 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 $3(\pm 1.5) \times 10^{13}$ kg H₂O/y.’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

I added a description of the recommended value to the sentence (P7/L182-183).

Specific comment 18 (related to major comments):

‘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 $\delta^{18}\text{O}$. 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 ^{18}O -enriched crust, leaving the ocean ^{18}O -depleted (Galili et al., 2019).”

Response:

Please see my response to major comment 1 by Referee #2 on the issue about comparison with more recent oceanic crust data with known ages (including data from ODP boreholes).

Please see my response to major comment 2 by Referee #2 on the issue about the assumed calculation domain width. Please find that extending the calculation domain width to thousands of km is not reasonable given that observations suggest that significant oxygen isotope exchange is limited within <10 million years from the ridge axis. Instead I conducted an additional simulation to evaluate the reasonable time duration for significant oxygen isotope exchange, which supports that the assumed calculation domain width of 30 km is reasonable (please see Section S6 in Supplementary material and my response to major comment 2 by Referee #2 for the details). Also, simulations with 300 km calculation domain width show essentially the same results regarding the sensitivity of ^{18}O distributions and flux to seawater $\delta^{18}\text{O}$ as those in the simulations with 30 km calculation domain width, supporting that the present study’s findings are robust.

The spreading rate affects oxygen isotope exchange both at low and high temperatures, and the net flux is affected also by changes in total oxygen supply, as discussed in Section 3.3. The difference caused by changes in the spreading rate is not solely caused by the different time duration but also by different distributions of local water/rock ratio (Fig. 7). This can be confirmed from comparison of Fig. 4 with Figs. S13 and S16 in Supplementary material; the general feature of crustal $\delta^{18}\text{O}$, especially that in the deep high-temperature section, is not affected by changes in the calculation domain width if other parameters including the spreading rate are the same. Also, residence time of oceanic crust is not necessarily equivalent to the time duration for significant oxygen isotope exchange (e.g., Muehlenbachs, 1979; Section S6 in Supplementary material). Accordingly, it is not reasonable to discuss changes in the relative significance of low-temperature alteration against high-temperature

alteration only based on the residence time of oceanic crust. Please also see my response to suggestion related to major comment 2 by Referee #2 where I discuss the importance of continental weathering in the oceanic ^{18}O budget.

There is an uncertainty in the spreading rate during the Precambrian and values can be different between models (e.g., Phipps Morgan, 1998; Korenaga et al., 2017). The present study conducted simulations with a range of spreading rate possible during the Precambrian, and all simulation results show the relative insensitivity of oceanic rocks to seawater $\delta^{18}\text{O}$ (Section 3.3). Therefore, the main conclusions in the present study are not affected by the uncertainty in the spreading rate during the Precambrian.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to major comments 1 and 2 and suggestion related to major comment 2 by Referee #2.

I added more explanations to descriptions of the calculation results with different spreading rates in Section 3.3 (P9/L276-279, P10/L284-289).

Specific comment 19:

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

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

I revised the sentence (P7/L190-192).

Specific comment 20 (related to major comments):

“L180-189: The model $d^{18}\text{O}$ profiles in the bulk rock and the ^{18}O 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 ^{18}O fluxes and previous estimates has meaning only if the estimates were made on the basis of altered crust of a comparable age.”

Response:

Please see my response to major comment 1 by Referee #2 where I addressed the issue.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to major comment 1 by Referee #2.

Specific comment 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.”

Response:

Please see my response to specific comments 18 and 20 by Referee #2.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to specific comments 18 and 20 by Referee #2.

Specific comment 22 (related to major comments):

“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 $\delta^{18}\text{O}$?”

Response:

Please see my response to major comments 1 and 2 by Referee #2 where I addressed the issue.

The distance from equilibrium decreases past 30 km if efficiency of oxygen isotope exchange does not decrease with age (Section S5 in Supplementary material). Observations of oceanic crustal $\delta^{18}\text{O}$ with known ages as well as a simulation on a wide calculation domain (300 km) with implementing off-axis flows and decline in efficiency of oxygen isotope exchange with age show apparent cessation of the decrease in the distance from equilibrium around 3-30 km from the ridge axis (Section S6 in Supplementary material).

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to major comments 1 and 2 by Referee #2.

I added explanations that enhancement of oxygen isotope exchange in a wide calculation domain in Section S5 of Supplementary material disappears when implementing the decrease of the reaction efficiency with age (Section S6 in Supplementary material) to Section S5 in Supplementary material (P5/L139-142 in Supplementary material).

Specific comment 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.”

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Revised as suggested (P8/L226).

Specific comment 24:

‘L238: Perhaps change “not inconsistent with” to “consistent with”?’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Revised as suggested (P9/L255).

Specific comment 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.”

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

I revised the sentence to be clearer (P9/L254-257).

Specific comment 26:

‘L252: “spreading” and “weaker” are misspelled.’

Response:

I thank the reviewer for pointing out the misspelled words.

Changes in manuscript (Page numbers/Line numbers):

I corrected the misspelled words (P9/L271).

Specific comment 27:

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

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

I revised the two paragraphs to be clearer (P9/L273-P10/L304).

Specific comment 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.”

Response:

Water properties calculated as functions of temperature and pressure are comparable to those by Kasting et al. (2006). Therefore, the different conclusion of this study regarding the effect of water depth stems from the difference in the model configuration. The significant difference of this study's model from Kasting et al. (2006) model includes that the permeability and water properties can change two-dimensionally. Also, Kasting et al. (2006) assume that hydrothermal circulation is represented only by water close to the critical pressures and temperatures to maximize the heat transport and they mentioned the need to verify this assumption in two-dimensional simulations.

Changes in manuscript (Page numbers/Line numbers):

I revised the relevant sentence to be clearer (P10/L302-304).

Specific comment 29 (related to major comments):

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

Response:

Please see my response to specific comments 18, 20, 21 and 22 by Referee #2.

I confirmed that the statement still holds by conducting an additional experiment where plausible time duration for significant oxygen isotope exchange was examined (Section S6 in Supplementary material).

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to specific comments 18, 20, 21 and 22 by Referee #2.

Specific comment 30:

‘L283-286: This sentence is awkwardly worded. Suggest “By comparison, the simulated solid rock $\delta^{18}\text{O}$ values fall within this range for seawater $\delta^{18}\text{O}$ values ≥ -10 , -8 and -2% at a spreading rate of $1\text{e-}2$, $3\text{e-}2$ and $\geq 9\text{e-}2$ 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 ^{18}O -buffering strength of hydrothermal alteration of oceanic crust over Earth history?’

Response:

I agree to revise the sentence.

Average spreading rates over the Earth history, especially during the Precambrian, are not fully known and diverse values have been suggested (e.g., Phipps Morgan, 1998; Korenaga et al., 2017). This is the reason why I adopted a range of spreading rate that covers the suggested diverse average values. Unless we can constrain the evolution of tectonics, it remains uncertain how ^{18}O buffering intensity evolved. Despite this uncertainty, the buffering intensity should have been weaker than previously assumed and continental weathering contribution is likely to have been more significant than previously assumed.

Changes in manuscript (Page numbers/Line numbers):

I revised the sentence as suggested (P10/L309-311).

Also, more explanations were added to the sentences on the spreading rates in the Precambrian (P9/L251-253).

Specific comment 31:

‘L286-288: There are values of seawater $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ mostly at low spreading rates. It is

worth mentioning that estimated Precambrian seafloor spreading rates were slower than Phanerozoic rates.”

Response:

I consider describing the seawater $\delta^{18}\text{O}$ values that are either consistent or inconsistent with ophiolite data is sufficient. I described only the consistent values but not inconsistent values.

Please see my response to specific comment 30 on the issue about the spreading rate. Precambrian spreading rates can be either higher or lower than Phanerozoic spreading rates depending on the model (e.g., Phipps Morgan, 1998; Korenaga et al., 2017).

Changes in manuscript (Page numbers/Line numbers):

No specific changes were made in response to the comment on the inconsistent seawater $\delta^{18}\text{O}$ values (please see my response above).

Please see my changes in manuscript in response to specific comment 30 by Referee #2.

Specific comment 32:

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

Response:

I agree to revise.

Changes in manuscript (Page numbers/Line numbers):

I revised Section 4.3 to be clearer (P11/L341-P12/L363).

Specific comment 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.”

Response:

I agree to revise the figure.

Changes in manuscript (Page numbers/Line numbers):

Corrected as suggested (P20).

Specific comment 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).”

Response:

Fine horizontal and vertical lines do not appear in my computers (both laptop and desktop). I guess they might appear depending on the settings in the pdf reading software, but not when printed.

Changes in manuscript (Page numbers/Line numbers):

No specific changes were made in response to the comment.

Specific comment 35:

‘Fig. 2: Suggest changing “0, –6 and –12 ‰ of seawater d18O” to “at seawater d18O values of 0, –6 and –12 ‰”.’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Corrected as suggested (P21).

Specific comment 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).’

Response:

Agreed.

Please see my response to major comment 1 by Referee #2 on the issue about comparison with crust with various ages.

Changes in manuscript (Page numbers/Line numbers):

Corrected as suggested (P23).

Please see my changes in manuscript in response to major comment 1 by Referee #2.

Specific comment 37:

‘Fig. 5 caption: “0 ‰ of seawater d18O” -> “a seawater d18O value of 0 ‰”.’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Corrected as suggested (P24).

Specific comment 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 $k_{ex} = 10^{-6.5}$. If the results are indeed insensitive to the value of k_{ex} , this will not matter much for the buffering intensity, and it would provide confidence in the proposed insensitivity of seafloor alteration to seawater d18O.”

Response:

Please see my response to specific comment 12 by Referee #2.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to specific comment 12 by Referee #2.

Specific comment 39:

‘Fig. 7 caption: The sentence starting with “Spreading rate” is awkward. Suggest rewording.’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

I revised the sentence (P26).

Specific comment 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 ‰”.’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Revised as suggested (P27).

Specific comment 41:

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

Response:

The buffering intensity is determined by the sensitivity of solid rock and porewater $\delta^{18}\text{O}$ to seawater $\delta^{18}\text{O}$. Although the absolute values are different with different reference rate constants for oxygen isotope exchange, the sensitivity is little affected, as can be seen from the limited ranges of changes in solid rock $\delta^{18}\text{O}$ compared to the imposed range of seawater $\delta^{18}\text{O}$. The mechanisms to accomplish weak buffering are described in the main text (kinetic inhibition and ^{18}O supply via spreading solid rocks in the shallow and deep sections of oceanic crust, respectively) and the same mechanisms can be applied to the simulations in Section S4. Please find that the section number has been changed from S3 in the previous SM to S4 in the revised SM.

Changes in manuscript (Page numbers/Line numbers):

I added more explanations to Section S4 in Supplementary material (P3/L97-P4/L102 in Supplementary material).

Specific comment 42 (related to major comments):

“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.”

Response:

As in my response to major comment 2 by Referee #2, the modern observations of oceanic crust with known ages suggest that significant oxygen isotope exchange is limited within less than 10 million years from the ridge axis and thus the assumed calculation domain width is reasonable. Supplementary experiments in Supplementary material (e.g., experiments in Sections S5 and S6 of Supplementary material) were conducted only to confirm that the assumed time duration for significant oxygen isotope

exchange is reasonable. Moving these supplementary simulations to the main text will distract the reader from the point of this study and thus was avoided for clarity.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to major comment 2 by Referee #2.

Specific comment 43 (related to major comments):

“SM Section S4: Is a distance of 300 km from the ridge axis sufficient? Does the model d_{18O} 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.”

Response:

Please see my response to major comments 1 and 2 by Referee #2 where I addressed the issue.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to major comments 1 and 2 by Referee #2.

Specific comment 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 ^{18}O . Fig. S13 clearly shows that despite similar buffering intensities, the cases with off-axis circulation differ substantially in the net ^{18}O 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 d_{18O} suggested on the basis of the O isotope record in authigenic minerals. Perhaps this is beyond the scope of the current contribution.”

Response:

Simulations in Section S5 (S4 in the previous SM) ignore a mechanism that can explain the apparent cessation of oxygen isotope exchange at < 10 million years (Muehlenbachs, 1979) because the specific section only focuses on the effect of off-axis water flows on oxygen isotopic composition of oceanic crust. An additional simulation which further implements a decline in efficiency of oxygen isotope exchange with age in a wide calculation domain (300 km) is closer to the standard simulation where

contributions from the low- and high-temperature alteration are comparable. Accordingly, one should not discuss the control of oxygen isotopes in the ancient ocean by changing the calculation domain width, unless the mechanisms of apparent cessation of oxygen isotope exchange during oceanic crust alteration are fully known, which should be studied in the future work. Please find that the results and conclusions remain valid even with assuming a wide calculation domain (i.e., 300 km) (Sections S5 and S6 in Supplementary material). Please also see my response to suggestion related to major comment 2 by Referee #2 where I discuss the importance of continental weathering in the oceanic ^{18}O budget.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to specific comment 22 and suggestion related to major comment 2 by Referee #2.

Specific comment 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.”

Response:

Please see my response to specific comment 44 by Referee #2 where I addressed the issue.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to specific comment 44 by Referee #2.

I added explanations on why simulations in Section S5 of Supplementary material show the enhancement of oxygen isotope exchange at low temperature (P5/L136-139 in Supplementary material).

Specific comment 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 $\leq 1\text{-}3 \text{ MPa}$, 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?”

Response:

As stated in Section S5 of Supplementary material, imposed pressures and sediment burden intervals are larger than suggested by Fisher and Becker (2000) because of limited resolution in the wider calculation domain. One may resolve the problem by adopting finer grid cells, but it will not be practically possible as it can require the calculation time as long as weeks even to months.

Sediment thickness to cause an additional pressure of 10 MPa can be calculated to be ~1200 m, with a sediment grain density of 2700 kg m^{-3} and a porosity of 0.5. Please note that pressure caused by water need be excluded from the calculation of additional pressure because water pressure is already included in the default hydrostatic pressure of 25 MPa at the crust/ocean interface.

The sediment thickness to cause the additional pressure of 10 MPa (e.g., 1200 m) is close to the maximum value within 10 million years from the crust formation: sediment thickness can be as thick as ~1 km on crust that is <10 million years old depending on the latitude (Fig. S4 in Müller et al., 2008, Science 319, 1357).

As long as off-axis flows are numerically implemented, sediment thickness does not have to be so realistic because the purpose of the specific section is not to mechanistically explain the off-axis flows as in Fisher and Becker (2000) but to examine the effect of off-axis flows on oxygen isotopes of oceanic crust. Indeed, the implemented off-axis flows satisfy the constraint on the total off-axis water flux from observations as described in Section S5 of Supplementary material. Therefore, even if the model can be improved with respect to off-axis flow simulation, the results and conclusions will remain the same.

Changes in manuscript (Page numbers/Line numbers):

I added more explanations to Section S5 in Supplementary material (P4/L111-117, P4/L127 in Supplementary material).

Specific comment 47:

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

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Revised as suggested (P4/L135 in Supplementary material).

Specific comment 48:

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

Response:

Please see my response to specific comment 44 by Referee #2 where I addressed the issue.

Changes in manuscript (Page numbers/Line numbers):

Please see my changes in manuscript in response to specific comment 44 by Referee #2.

Specific comment 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.’

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Revised as suggested (P11 in Supplementary material).

Specific comment 50:

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

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Revised as suggested (P12, P16, P17, P20, P21 in Supplementary material).

Specific comment 51:

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

Response:

Agreed.

Changes in manuscript (Page numbers/Line numbers):

Revised as suggested (P14, P16, P17, P18, P21, P22 in Supplementary material).

Quantifying the buffering of oceanic oxygen isotopes at ancient midocean ridges

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Abstract. To quantify the intensity of oceanic oxygen-isotope buffering through hydrothermal alteration of oceanic crust, a two-dimensional hydrothermal circulation model was coupled with a two-dimensional reactive transport model of oxygen isotopes. The coupled model calculates steady-state distributions of temperature, water flow and oxygen isotopes of solid rock and porewater given physicochemical conditions of oceanic crust alteration and seawater $\delta^{18}\text{O}$. Using the present-day seawater $\delta^{18}\text{O}$ under plausible modern alteration conditions, the model yields $\delta^{18}\text{O}$ profiles for solid rock and porewater and fluxes of heat, water and ^{18}O that are consistent with modern observations, confirming the model's validity. The model was then run with different assumed seawater $\delta^{18}\text{O}$ values to evaluate oxygen isotopic buffering at the midocean ridges. The buffering intensity shown by the model is significantly weaker than previously assumed and, consistently, calculated $\delta^{18}\text{O}$ profiles of oceanic crust are relatively insensitive to seawater $\delta^{18}\text{O}$. These results are attributed to the fact that isotope exchange at shallow depths does not reach equilibrium due to the relatively low temperatures, and ^{18}O supply via spreading solid rocks overwhelms that through water flow at deeper depths. Further model simulations under plausible alteration conditions during the Precambrian showed essentially the same results. Therefore, $\delta^{18}\text{O}$ records of ophiolites that are invariant at different Earth's ages can be explained by the relative insensitivity of oceanic rocks to seawater $\delta^{18}\text{O}$ and do not require constant seawater $\delta^{18}\text{O}$ through time.

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1 Introduction

Hydrothermal alteration of oceanic crust at midocean ridges works as the dominant source/sink of several elements/isotopes in the ocean (e.g., Wolery and Sleep, 1976; Elderfield and Schultz, 1996). Notably, oxygen isotopes have been considered to be primarily controlled by isotope exchange at midocean ridges. The observation of oceanic crustal $\delta^{18}\text{O}$ has revealed that oceanic rocks gain and lose ^{18}O ~~is added to and depleted from the oceanic crust through low- and high-temperature hydrothermal alteration~~ at shallow and deeper depths, respectively, ~~relative to the isotope amount of pristine crust.~~ The close balance between the addition and removal of the heavy isotope, together with the huge oxygen supply from the mantle, has led to a hypothesis that the water-rock interactions at midocean ridges have buffered oceanic $\delta^{18}\text{O}$ at the present-day value (0 ‰

relative to standard mean ocean water, SMOW) throughout Earth's history (e.g., Muehlenbachs and Clayton, 1976; Gregory
25 and Taylor, 1981; Holland, 1984; Muehlenbachs, 1998). Age-invariant $\delta^{18}\text{O}$ records of ophiolites (ancient oceanic crust) have
been argued to support the hypothesis (e.g., Holmden and Muehlenbachs, 1993).

In contrast to ophiolites, ~~authigenic-sedimentary rocks~~ sedimentary rocks (e.g., carbonates, cherts, phosphorites and shales)
have shown secular $\delta^{18}\text{O}$ increases with the Earth's age; sedimentary rocks in the Precambrian are depleted in ^{18}O by as much
as 10 ‰ compared to those in the modern (e.g., Shemesh et al., 1983; Karhu and Epstein, 1986; Bindeman et al., 2016),
30 and the exception to this has rarely been reported (e.g., Blake et al., 2010). In theory, if constituting minerals of sedimentary
rocks were formed in equilibrium with seawater and if the later diagenetic/metamorphic modification of $\delta^{18}\text{O}$ was negligible,
 $\delta^{18}\text{O}$ records of ~~authigenic~~ sedimentary rocks can be utilized to infer surface temperatures in the past, using temperature-
dependent isotope fractionation factors and assuming the $\delta^{18}\text{O}$ value of seawater from which the constituting minerals formed.
Indeed, several authors have suggested hot climates in the Precambrian from ^{18}O -depleted sedimentary records assuming the
35 present-day seawater $\delta^{18}\text{O}$ (e.g., 70 ± 15 °C at 3.2–3.5 Ga and 50–60 °C through the later Precambrian; Knauth and Lowe,
2003; Knauth, 2005). Such high temperatures are apparently at odds with glacial records observed through the Precambrian
(e.g., Catling and Kasting, 2017, Ch. 11). If one excludes hot climates based on the glacial records, one must conclude that
sedimentary $\delta^{18}\text{O}$ records do not reflect seawater $\delta^{18}\text{O}$ (e.g., instead reflecting diagenetic/metamorphic overprints) and/or
that seawater $\delta^{18}\text{O}$ has changed through time (e.g., Walker and Lohmann, 1989). The latter conclusion has recently been
40 supported by Proterozoic-Phanerozoic marine iron (oxyhydr)oxides, whose $\delta^{18}\text{O}$ shows a similar secular evolution to those in
sedimentary rocks despite its little-weak temperature dependence (Galili et al., 2019). On the other hand, the secular change
in ~~seawater~~ seawater $\delta^{18}\text{O}$ apparently conflicts with the result derived from ophiolites: an invariant seawater $\delta^{18}\text{O}$ resulting
from strong oceanic- $\delta^{18}\text{O}$ buffering at midocean ridges. Overall, one cannot rely on sedimentary $\delta^{18}\text{O}$ to reconstruct ancient
surface temperatures and discuss associated climate forcings unless $\delta^{18}\text{O}$ records of sedimentary rocks and ophiolites can be
45 explained at the same time (cf. Godderis and Veizer, 2000; V  rard and Veizer, 2019).

Several hypotheses have been put forward to reconcile apparently conflicting invariant and variant $\delta^{18}\text{O}$ records of respective
ophiolites and sedimentary rocks. Perry et al. (1978) pointed out that oceanic rocks in the Precambrian were more mafic than
those in the modern and this could have resulted in more intense low-temperature alteration of oceanic crust, removing more
 ^{18}O from seawater than today. Walker and Lohmann (1989) argued that the midocean ridges could have been above sea level
50 in shallower Precambrian oceans. Resultant subaerial water-rock interactions at low temperatures then could have removed
a large amount of ^{18}O from the Precambrian oceans. Even if midocean ridges were below the sea level, lower pressures
on the seafloor in the shallow oceans could have brought less water into the oceanic crust, and water-rock interactions at
midocean ridges could have been dominated by those at low temperatures at shallower depths, again resulting in lower oceanic
 $\delta^{18}\text{O}$ in the Precambrian (Kasting et al., 2006). Absence of biogenic sediment cover during the Precambrian could have also
55 contributed to more significant low-temperature seafloor alteration and a lower seawater $\delta^{18}\text{O}$ (e.g., Jaffr  s et al., 2007). The
above arguments, however, give possible explanations only for low oceanic $\delta^{18}\text{O}$ during the Precambrian; they do not explain
age-invariant ophiolite $\delta^{18}\text{O}$ records. Wallmann and colleagues have indicated that the invariant $\delta^{18}\text{O}$ records of ophiolites can
be explained by decoupling ancient oceanic crust from the contemporaneous seawater $\delta^{18}\text{O}$ (e.g., Wallmann, 2001; Jaffr  s et

al., 2007). However, the simple box models considered by these authors cannot explain whether and/or how this decoupling could have been made possible (Jaffrés et al., 2007).

To resolve the issue, a process-based approach that simulates oxygen isotope behavior during oceanic crust alteration is indispensable. Lécuyer and Allemand (1999) have developed an oxygen-isotope exchange model which utilizes prescribed distributions of temperature and water/rock ratio within oceanic crust and an equation for half-closed systems (e.g., Gregory et al., 1989), and thus is not entirely process-based. Using this model, Lécuyer and Allemand (1999) concluded that oceanic $\delta^{18}\text{O}$ cannot change from the present-day value by more than 2 ‰ due to the strong buffering exhibited by their modelled isotope-exchange at midocean ridges. This conclusion contrasts with that by Wallmann (2001), who adopted a box model to argue that the buffering must have been weak and that the oxygen-isotopic composition of the ocean has evolved through the Phanerozoic. These conflicting conclusions from different models emphasize that a mechanistic understanding of oxygen isotope behavior during oceanic crust alteration is lacking.

The present study ~~has been undertaken to present~~ develops a process-based model to simulate oxygen isotope behavior during hydrothermal alteration of oceanic crust and presents its application to the Precambrian. A two-dimensional (2D) hydrothermal circulation model presented in the literature is combined with a 2D reactive transport model of oxygen isotopes. The coupled model can thus yield 2D distributions of solid-rock and porewater $\delta^{18}\text{O}$ reflecting alteration conditions including seawater $\delta^{18}\text{O}$ and hydrothermal fluid circulation. After confirming the model's validity by comparing the model results that assume the present-day seawater $\delta^{18}\text{O}$ with modern observations, we examine the intensity of oceanic- $\delta^{18}\text{O}$ buffering by hydrothermal alteration of oceanic crust at midocean ridges by changing seawater $\delta^{18}\text{O}$. The buffering quantification is then conducted under different physicochemical conditions that could have been the case during the Precambrian, to give insights into how oceanic $\delta^{18}\text{O}$ could have been affected by water-rock interactions at midocean ridges during the Earth's early eons.

2 Methods

2.1 Hydrothermal circulation model

Hydrothermal flow circulating around midocean ridges is simulated two-dimensionally based on conservations of energy, mass and momentum (Steeffel and Lasaga, 1994; Cherkaoui et al., 2003; Iyer et al., 2010). Assuming steady state, the mass conservation of fluid is represented by

$$\nabla \cdot \mathbf{q} = 0, \tag{1}$$

where ∇ is the vector differential operator ($\nabla = (\partial/\partial x, \partial/\partial y)$) and \mathbf{q} is the mass flux vector ($\text{kg m}^{-2} \text{yr}^{-1}$). Conservation of momentum is realized by adopting Darcy's law (e.g., Steeffel and Lasaga, 1994):

$$\mathbf{q} = -\frac{k}{\nu} (\nabla P - \rho_f \mathbf{g}), \tag{2}$$

where k is the permeability of oceanic bulk rock (m^2), ν is the kinematic viscosity of water ($\text{m}^2 \text{yr}^{-1}$), P is the fluid pressure (Pa), ρ_f is the fluid density (kg m^{-3}) and \mathbf{g} is the gravity vector given by $\mathbf{g} = (0, -g)$ where g represents the acceleration by

90 gravity (m yr^{-2}) (e.g., Steefel and Lasaga, 1994). The energy conservation is represented by

$$\left\{ \phi \rho_f c_p^f + (1 - \phi) \rho_m c_p^m \right\} \frac{\partial T}{\partial t} = \nabla \cdot (-\mathbf{q} c_p^f T + \kappa \nabla T), \quad (3)$$

where t is time (yr), ϕ is the porosity, ρ_m is the density of oceanic rock (kg m^{-3}), c_p^f and c_p^m are the specific heat capacity of water and oceanic rock, respectively ($\text{J kg}^{-1} \text{K}^{-1}$), T is the temperature (K) and κ is the thermal conductivity of oceanic rock ($\text{J yr}^{-1} \text{m}^{-1} \text{K}^{-1}$). The thermodynamic and transport properties of water (c_p^f , ρ_f and ν) are obtained through a FORTRAN90
95 library STEAM which is based on the NBS steam table package (Meyer et al., 1983; Haar et al., 1984). As in Iyer et al. (2010), we assume pure water for hydrothermal fluid. The petrophysical parameters except for the permeability (i.e., κ , ϕ , ρ_m and c_p^m) are assumed to be the same as those in Iyer et al. (2010). We assume that $\log k$ exponentially decreases from -11.8 to -16.8 with a [scale-length-length scale](#) of 300 m for [the an](#) e-fold decrease, which is consistent with observations (Fisher, 1998; Supplementary material). Following Cherkaoui et al. (2003), oceanic rocks below [the crust/mantle interface](#) (6 km depth from
100 the ocean/crust interface) and with temperatures above the critical temperature for rock cracking (600°C) are impermeable. As long as the model is consistent with observations, changing the assumptions about permeability does not affect the general conclusions given in the present study (Supplementary material).

[The boundary conditions adopted in the present study follow those by Iyer et al. \(2010\) and/or Cherkaoui et al. \(2003\). Pressure at the ocean/crust interface is assumed as constant at 25 MPa, corresponding to the assumption of 2.5 km water
105 depth. This assumption is modified when we explore the Precambrian hydrothermal circulation in Section 3.3. The right and bottom sides of the calculation domain are assumed to be insulating. The ocean above the top boundary is assumed to have a constant temperature of \$2^\circ\text{C}\$. The ridge axis on the left-hand boundary is assumed to supply a boundary heat flux \$J_b\$ \(\$\text{J m}^{-2} \text{yr}^{-1}\$ \):](#)

$$J_b = \rho_m w (T_m - T) c_p^m, \quad (4)$$

[where \$w\$ is the spreading rate \(\$\text{m yr}^{-1}\$ \) and \$T_m\$ is the temperature of the intrusion \(\$1200^\circ\text{C}\$ \). As a standard value, we assume \$3 \times 10^{-2} \text{m yr}^{-1}\$ for \$w\$, and this assumption is again changed in Section 3.3 where we consider the Precambrian hydrothermal
110 circulation. Free flow is allowed at the top boundary, and the other boundaries are assumed to be impermeable \(Iyer et al., 2010\). The calculation domain is wide enough \(see below\) that making the right-hand boundary permeable with respect to heat and water will change the results only negligibly \(cf. Supplementary material; Cherkaoui et al., 2003\). See Table 1 for the
115 definitions and values of the parameters used in the present study.](#)

A finite difference approach is taken to solve Eqs. (1)–(3) for \mathbf{q} , P and T using the second-order central differencing scheme for the second-order differential terms and the first-order upwind and forward differencing schemes for the first-order spatial and temporal differential terms, respectively (e.g., Steefel and Lasaga, 1994). The calculation procedure follows that by Iyer et al. (2010). First, we obtain P by solving Eqs. (1) and (2). Then, \mathbf{q} is obtained from the calculated P and Eq. (2). Finally, the
120 calculated \mathbf{q} is used in Eq. (3) which is solved to obtain T for the same time step. The calculated P and T are used to update the thermodynamic and transport properties of water for the next calculation step. The above procedure is repeated with a time step of $3 \times 10^4 \text{ yr}$ until steady states are reached, which is accomplished within 10^3 time steps [or \$3 \times 10^7\$ model years](#) (cf.

Cherkaoui et al., 2003). Note that only steady states are considered in this study because of the long time scale over which oceanic oxygen-isotopic composition can change ($> \sim 5 \times 10^7$ yr; e.g., Holland, 1984; Walker and Lohmann, 1989; Wallmann, 2001). The model grid extends to as deep as 12 km depth from the ocean/crust interface and allowing changes in the location of the crust/mantle interface (though not varied in this study); and it extends to 30 km distance from the ridge axis, wide enough to simulate major changes in oxygen isotopic composition of oceanic crust which have been observed to be completed within less than 10 million years from the rock formation at midocean ridges (Muehlenbachs, 1979) (see Supplementary material for more details). The calculation domain ($12 \times 30 \text{ km}^2$) is divided into a 320×200 irregular grid, with the grid-cell size horizontally increasing from the ridge axis (1.1 to 330 m) and vertically from the ocean/crust interface (0.17 to 82 m) (cf. Cathles, 1983; Cherkaoui et al., 2003).

~~The boundary conditions adopted in the present study follow those by and/or . Pressure at the ocean/crust interface is assumed as constant at 25 , corresponding to the assumption of 2.5 water depth. This assumption is modified when we explore the Precambrian hydrothermal circulation in Section 3.3. The right and bottom sides of the calculation domain are assumed to be insulating. The ocean above the top boundary is assumed to have a constant temperature of 2 . The ridge axis on the left-hand boundary is assumed to supply a boundary heat flux J_b ($-2 -1$):-~~

$$J_b = \rho_m w (T_m - T) c_p^m,$$

~~where w is the spreading rate (-1) and T_m is the temperature of the intrusion (1200). As a standard value, we assume $3 \times 10^{-2} -1$ for w , and this assumption is again changed in Section 3.3 where we consider the Precambrian hydrothermal circulation. Free flow is allowed at the top boundary, and the other boundaries are assumed to be impermeable . The calculation domain is wide enough that making the right-hand boundary permeable Cherkaoui03 changes the results only negligibly.-~~

2.2 Reactive transport model of oxygen isotopes

Oxygen isotopes of solid rock are assumed to be transported by the spreading of oceanic rocks, while those of porewater are transported by water flow and molecular diffusion (cf. Norton and Taylor, 1979; Lécuyer and Allemand, 1999). At the same time, isotope exchange reactions transfer ^{18}O between the two phases (e.g., Norton and Taylor, 1979; Lécuyer and Allemand, 1999). Then, from the mass conservation of ^{18}O in the two phases, the time rates of change of the ^{18}O /total O mole ratios of solid rock and porewater (F_r and F_p , respectively) can be represented by

$$(1 - \phi) \rho_m m_s \frac{\partial F_r}{\partial t} = - (1 - \phi) \rho_m m_s w \frac{\partial F_r}{\partial x} - \rho_b m_s m_f k_{\text{ex}} \{ F_r (1 - F_p) - \alpha (1 - F_r) F_p \}, \text{ and} \quad (5)$$

$$\phi \rho_f m_f \frac{\partial F_p}{\partial t} = \nabla \cdot (-m_f \mathbf{q} F_p + \phi \rho_f m_f D \nabla F_p) + \rho_b m_s m_f k_{\text{ex}} \{ F_r (1 - F_p) - \alpha (1 - F_r) F_p \}, \quad (6)$$

where m_s and m_f are the oxygen concentrations of solid rock and porewater, respectively (mol kg^{-1}), ρ_b is the density of bulk rock given by $\rho_b = \phi \rho_f + (1 - \phi) \rho_m$, k_{ex} is the rate constant for oxygen isotope exchange ($\text{mol}^{-1} \text{kg yr}^{-1}$), α is the oxygen isotope fractionation factor and D is the effective diffusion coefficient for ^{18}O ($\text{m}^2 \text{yr}^{-1}$), determined by molecular diffusion and hydrodynamic dispersion. The first and second terms on the right-hand sides of Eqs. (5) and (6) represent oxygen isotope

transport and oxygen isotope exchange, respectively. The kinetic expression of oxygen isotope exchange in Eqs. (5) and (6) is formulated based on Cole et al. (1983, 1987) and the rate constant is given by an Arrhenius equation:

$$k_{\text{ex}} = 10^{-8.5} \exp \left\{ -\frac{E}{R_g} \left(\frac{1}{T} - \frac{1}{278} \right) \right\}, \quad (7)$$

where E is the apparent activation energy (5×10^4 J mol⁻¹) and R_g is the gas constant (8.314 J mol⁻¹ K⁻¹). The value of $10^{-8.5}$ mol⁻¹ kg yr⁻¹ at reference temperature 278 K (5 °C) is ~~comparable to the~~ obtained by reducing the range $10^{-7.2}$ – $10^{-6.6}$ mol⁻¹ kg yr⁻¹ at 5 °C extrapolated from $10^{-2.1}$ – $10^{-1.5}$ mol m⁻² yr⁻¹ at 300 °C (Cole et al., 1987) with $E = 5 \times 10^4$ J mol⁻¹ (cf. Cole et al., 1987) and 10^3 m² kg⁻¹ specific surface area of marine basalt (cf. Nielsen and Fisk, 2010) ~~given by a factor of~~ $10^{1.3}$ – $10^{1.9}$. The reducing factor ($10^{1.3}$ – $10^{1.9}$) accounts for the fact that the reaction rate in the field is generally slower than in the laboratory by a factor of up to 10^3 (e.g., Wallmann et al., 2008) ~~(see Supplementary material for the details). A similar factor (up to 10^4) has been adopted by~~ Cathles (1983) for the formulation of oxygen isotope exchange kinetics. Note that the general results and conclusions in the present study are not affected by changes in the reference k_{ex} value within a plausible range (Supplementary material). The oxygen isotope fractionation factor for andesite by Zhao and Zheng (2003) is adopted in the present study:

$$10^3 \ln \alpha = \beta \left(\frac{6.673 \times 10^6}{T^2} + \frac{10.398 \times 10^3}{T} - 4.78 \right) \exp \left(\frac{1 - \beta}{R_g T} \right) - \frac{2.194 \times 10^6}{T^2} - \frac{15.163 \times 10^3}{T} + 4.72 + 1.767(2\beta - 1), \quad (8)$$

where $\beta = 0.876$ (Zhao and Zheng, 2003), because Eq. (8) with $\beta = 0.876$ yields comparable α values to experimental results for basalt by Cole et al. (1987) at 300–500 °C while applicable over the ~~wide~~ wider range of temperature considered for the present study (~~0–1200~~ 2–1200 °C). The effective diffusion coefficient D considers both molecular diffusion and hydrodynamic dispersion; the former is obtained from the modified Stokes-Einstein relation for H₂¹⁶O diffusion by Krynicki et al. (1978) and the isotope effect from Harris and Woolf (1980) and a homogeneous dispersivity of 10 m is assumed for the latter (Frind, 1982; Gelhar et al., 1992):

$$D = \tau 6.9 \times 10^{-15} \frac{T}{\rho_f \nu} \sqrt{\frac{18}{20}} + 10 \frac{|\mathbf{q}|}{\phi \rho_f}. \quad (9)$$

The first term ~~in on~~ the right-hand side of Eq. (9) represents the molecular diffusion including the tortuosity factor $\tau = \phi^{1.4}$ (Aachib et al., 2004), while the second term represents the hydrodynamic dispersion. The petrophysical parameters are assumed to be the same as those in the hydrothermal circulation model (Section 2.1, Table 1). The thermodynamic and transport properties of water are obtained through the hydrothermal circulation model (Section 2.1).

The steady-state values of F_r and F_p are obtained by solving $\partial F_r / \partial t = \partial F_p / \partial t = 0$ in Eqs. (5) and (6). The intrusion on the left-hand boundary is assumed to have a ¹⁸O/total O mole ratio of fresh crust (F_m) that corresponds to 5.7 ‰ relative to SMOW (e.g., Holmden and Muehlenbachs, 1993), and the ocean above the top boundary is assumed to have a constant ¹⁸O/total O mole ratio of seawater (F_{sw}). The other boundaries are impermeable for ¹⁸O fluxes via water ~~(cf. Section 2.1)~~. A finite difference method is used for equation discretization (first-order upwind and second-order central differencing schemes for the first-order

and second-order spatial differential terms, respectively) and Newton's method is adopted to solve the difference equations. The calculation is conducted on the grid described earlier for the hydrothermal circulation model (Section 2.1). The ^{18}O mole ratios are all reported in δ notation relative to SMOW, using 2.0052×10^{-3} as the $^{18}\text{O}/^{16}\text{O}$ mole ratio of SMOW (Fry, 2006).

3 Results

3.1 Application to the present day and model validation

The calculated flow geometry and temperature distribution (Fig. 1; note that Figs. 1c and d are plots of Figs. 1a and b, respectively, on logarithmic scales) are similar to those in previous studies (e.g., Cherkaoui et al., 2003). The 2D model results can be converted to associated mass and heat fluxes, assuming 10^8 m ridge length (cf. Wolery and Sleep, 1976). The total heat flux from the system is 0.74×10^{12} W, comparable to the observed cumulative heat flux within 1 Myr (corresponding to 30 km with 3×10^{-2} m yr^{-1} spreading rate) from the ridge axis, $0.4(\pm 0.3) \times 10^{12}$ W (Stein and Stein, 1994). The total mass of water exchange is 1.2×10^{13} kg yr^{-1} , falling within the constrained range ~~by~~ (3×10^{12} to 1.6×10^{14} kg yr^{-1}) and close to the recommended value ($3(\pm 1.5) \times 10^{13}$ kg yr^{-1}) by Elderfield and Schultz (1996), and also comparable to the prediction from other hydrothermal circulation models (e.g., Norton and Knight, 1977; Fehn et al., 1983; Cherkaoui et al., 2003). The calculated 2D distributions of solid-rock and porewater $\delta^{18}\text{O}$ (Figs. 2a, 2d, 3a and 3d; note that Fig 3 is a plot of Fig. 2 on logarithmic scales) are consistent with observations, especially at 30 km (1 Myr) from the ridge axis (black solid curves in Fig. 4; see Section 3.2 for paler curves). Where flow rate and temperature are highest near the ridge axis and close to the ocean/crust interface (at $< \sim 200$ m depths), porewater $\delta^{18}\text{O}$ is in the range between 0 and 2 ‰ (Fig. 3d), which is comparable to the observed $\delta^{18}\text{O}$ ranges for high-temperature hydrothermal fluids, e.g., 0.49–2.3 ‰ by Jean-Baptiste et al. (1997) and 0.3–1.4 ‰ by James et al. (2014). Away from the ridge axis, porewater $\delta^{18}\text{O}$ ~~at the ocean/crust interface~~ is equivalent to the seawater value at the ocean/crust interface, but drops down to -4 to -14 ‰ within ~ 200 m depths, again not inconsistent with ~~those receiving small water exchange, observed porewater $\delta^{18}\text{O}$ values~~ (down to -8 ‰ ~~within~~) at < 500 m depths where water exchange is limited (e.g., Lawrence and Gieskes, 1981). Solid rock $\delta^{18}\text{O}$ at 1 Myr (i.e., 30 km from the ridge axis) is characterized by high (< 16 ‰) and low (> 3 ‰) values at shallow ($\geq \sim 2 \leq \sim 2$ km) and deeper ($\leq \sim 2 \geq \sim 2$ km) depths, respectively, consistent with observations of modern oceanic crust (e.g., Alt et al., 1986) and ophiolites (e.g., Gregory and Taylor, 1981; crosses in Fig. 4) ~~-(Fig. S3 in Supplementary material)~~. The ^{18}O fluxes to the ocean from high- and low-temperature alteration are 3.0×10^9 and -2.8×10^9 mol yr^{-1} , respectively, well balanced, resulting in a net ^{18}O flux of 0.2×10^9 mol yr^{-1} , consistent with the suggestion of zero net-flux by Gregory and Taylor (1981). Individual ^{18}O -flux values are also comparable to those suggested in the previous studies. As examples, ^{18}O fluxes through high-temperature alteration have been suggested to be 4.5×10^9 (Holland, 1984), 3.2×10^9 (Muehlenbachs, 1998) and 2.8×10^9 mol yr^{-1} (Wallmann, 2001), and those through low-temperature alteration $< -2.3 \times 10^9$ mol yr^{-1} (Lawrence and Gieskes, 1981), -1.1×10^9 (Holland, 1984), -1.0×10^9 (Muehlenbachs, 1998) and -0.9×10^9 mol yr^{-1} (Wallmann, 2001). The consistency between the model calculation and observations described above supports the validity of the model.

3.2 Evaluation of oceanic- $\delta^{18}\text{O}$ buffering capacity

As both the source and sink of oceanic ^{18}O , hydrothermal systems can buffer oceanic $\delta^{18}\text{O}$ but the strength of the buffering depends on the sensitivity of isotope exchange between oceanic crust and porewater to seawater $\delta^{18}\text{O}$ (cf. Wallmann, 2001). As an extreme example, if the oxygen isotope fractionation between solid rock and porewater is independent of seawater $\delta^{18}\text{O}$, there should not be any feedbacks from the hydrothermal systems on changes in seawater $\delta^{18}\text{O}$, i.e., no oceanic- $\delta^{18}\text{O}$ buffering. The previous studies that support the strong oceanic- $\delta^{18}\text{O}$ buffering at midocean ridges assume linear relationships between oxygen isotope fractionation and seawater $\delta^{18}\text{O}$ (e.g., Gregory and Taylor, 1981; Holland, 1984; Muehlenbachs, 1998). This assumption regarding the sensitivity to seawater $\delta^{18}\text{O}$ is difficult to confirm through observations of geological records because seawater $\delta^{18}\text{O}$ is not known. We can examine the response of rocks to seawater $\delta^{18}\text{O}$ with the present model by adopting different values for seawater $\delta^{18}\text{O}$. We can then measure the buffering capacity of the system by plotting net ^{18}O flux against seawater $\delta^{18}\text{O}$ and calculating the slope value, i.e., $\partial(\text{net } ^{18}\text{O flux})/\partial(\text{seawater } \delta^{18}\text{O})$, as in, e.g., Muehlenbachs and Clayton (1976). For example, a hydrothermal system with a large negative slope value should exhibit a strong buffering of oceanic $\delta^{18}\text{O}$, because a slight change in seawater $\delta^{18}\text{O}$ makes the system introduce a large net ^{18}O flux to the ocean that restores the change in seawater $\delta^{18}\text{O}$ (e.g., Muehlenbachs and Clayton, 1976; Muehlenbachs, 1998).

Most features of 2D distributions of solid-rock and porewater $\delta^{18}\text{O}$ are not significantly affected by decreasing-changing seawater $\delta^{18}\text{O}$ from 0-6 to -12‰ (Figs. 2–4). Although the porewaters close to the ocean have $\delta^{18}\text{O}$ compositions close to those of seawater (e.g., Fig. 3), $\delta^{18}\text{O}$ signatures of solid rocks are not linearly proportional to seawater $\delta^{18}\text{O}$ (e.g., Fig. 4). The relative insensitivity at shallow depths ($\leq \sim 2\text{ km}$; Figs. 2–4) can be explained by the kinetics of oxygen isotope exchange. The distance from isotope exchange equilibrium can be measured by $\Omega = F_r(1 - F_p)/\{\alpha(1 - F_r)F_p\}$ (Eqs. (5) and (6); Figs. 5b and d; note that Figs. 5c and d are plots of Figs. 5a and b, respectively, on logarithmic scales), and the shallow regions show non-equilibrium states ($\Omega \neq 1$) because of their relatively low temperatures (Figs. 1b and d). Therefore, despite the approximate isotopic equivalence between porewater and seawater (Figs. 2 and 3), solid rocks do not directly reflect seawater $\delta^{18}\text{O}$ in their oxygen-isotopic compositions. In deeper sections of oceanic crust, on the other hand, solid rocks attain isotope exchange equilibrium with porewater because of the relatively high temperatures and the correspondingly fast rates of isotope exchange (e.g., Figs. 5b and d). These deep regions, however, receive less water exchange than the shallow regions, as can be seen from the distribution of local water/rock oxygen-mole ratio $\eta (\equiv m_f|\mathbf{q}|/\{(1 - \phi)\rho_m m_s w\})$ (Figs. 5a and c). Accordingly, deep oceanic rocks and porewaters are oxygen-isotopically buffered by spreading solid-rocks rather than by seawater, and $\delta^{18}\text{O}$ values of deep porewaters are almost independent of seawater $\delta^{18}\text{O}$ (Figs. 2d–f and 3d–f). Consequently, despite the isotope exchange equilibrium, deep oceanic rocks are almost completely insensitive to seawater $\delta^{18}\text{O}$. The combination of the above two factors (isotope exchange kinetics and ^{18}O supply from spreading solid-rocks) explains the insensitivity of midocean ridge systems to seawater $\delta^{18}\text{O}$ (Figs. 2–4). Note that the kinetics of oxygen isotope exchange and ^{18}O supply from rocks have been invoked to explain the positive and negative $\delta^{18}\text{O}$ anomalies, respectively, relative to the pristine crustal $\delta^{18}\text{O}$ value by Cathles (1983), not inconsisteint with the two factors causing the partial decoupling between oceanic crust and seawater $\delta^{18}\text{O}$ in the present model.

250 Consistent with the insensitivity of oceanic rocks to seawater $\delta^{18}\text{O}$ (Figs. 2–4), the net ^{18}O flux from the midocean ridge systems is a very weak function of seawater $\delta^{18}\text{O}$ (Fig. 6). Compared to the large buffering capacity suggested in the previous studies, which can be recognized from large negative slopes in Fig. 6, the intensity of oceanic- $\delta^{18}\text{O}$ buffering exhibited by the present model is weak; the magnitude of slope ($-0.4 \times 10^9 \text{ mol yr}^{-1} \text{‰}^{-1}$) is smaller than those previously assumed by a factor of up to >7 . The reason why the previous studies suggested strong buffering is because these studies assume isotope
255 exchange equilibrium between porewaters and oceanic rocks and equivalence between porewater and seawater at the same time. These assumptions are ~~generally not applicable to~~ not satisfied simultaneously in midocean ridge systems in general, as can be anticipated from Figs. 2–5. The exception to the previous studies is Wallmann (2001), which shows relatively small negative slope value (Fig. 6). Note, however, that Wallmann (2001) simulated weak buffering in a different way, i.e., by adopting low and temperature-independent rate constants for oxygen isotope exchange.

260 3.3 Application to the Precambrian

As the tectonics of the Earth likely evolved through time, the midocean ridge systems in the Precambrian could have been quite different from those in the present day. Indeed, differences in ocean volume and the spreading rate of oceanic crust have been discussed (e.g., Kasting et al., 2006; Korenaga et al., 2017). Here, we examine the ~~system responses to changes in the spreading rate~~ oceanic- $\delta^{18}\text{O}$ buffering during the Precambrian by utilizing possible ranges of the spreading rate (1×10^{-2} to
265 $30 \times 10^{-2} \text{ m yr}^{-1}$) and ocean volume ~~regarding oceanic~~ (1 to 5 km of water depth at the ocean/crust interface) as well as seawater $\delta^{18}\text{O}$ buffering (-12 to 6‰) suggested in the literature (e.g., Phipps Morgan, 1998; Kasting et al., 2006; Jaffres et al., 2007; Korenaga et al., 2017; Galili et al., 2019; Johnson and Wing, 2020).

Increasing the spreading rate ~~from 1×10^{-2} to $30 \times 10^{-2} \text{ m yr}^{-1}$~~ results in increases in the heat flux (~~0.50×10^{12} , 0.99×10^{12} and $1.25 \times 10^{12} \text{ W}$ at 1×10^{-2} , 9×10^{-2} and $30 \times 10^{-2} \text{ m yr}^{-1}$, respectively; Eq. (4)) and associated water exchange between the
270 crust and ocean (consistent with modern observations (e.g., Baker et al., 1996; Bach and Humphris, 1999): 0.50×10^{12} , 0.99×10^{12} and $1.25 \times 10^{12} \text{ W}$ of heat flux and 2.4×10^{12} , 4.9×10^{13} and $8.5 \times 10^{13} \text{ kg yr}^{-1}$ at of water exchange at spreading rates of 1×10^{-2} , 9×10^{-2} and $30 \times 10^{-2} \text{ m yr}^{-1}$, respectively) (Figs. 7a–f), ~~not inconsistent with modern observations Baker96, Bach99~~. On the other hand, differences in temperature and water-flow distributions caused by those in ocean depth (from 1 to 5 km) are relatively minor ($0.74 \times 10^{12} \text{ W}$ and $(1.2\text{--}1.3) \times 10^{13} \text{ kg yr}^{-1}$; Figs. 7g–j). The distributions of solid-
275 rock and porewater $\delta^{18}\text{O}$ predicted under these different alteration conditions are correspondingly modified but show features common to those shown in the previous sections with the standard parameterization. Porewater $\delta^{18}\text{O}$ is close to seawater $\delta^{18}\text{O}$ only along the ocean/crust interface and becomes quite different from seawater $\delta^{18}\text{O}$ at deep depths (Supplementary material). Solid rock $\delta^{18}\text{O}$ is relatively insensitive to seawater $\delta^{18}\text{O}$ in general, showing relative addition and removal of ^{18}O at shallow and deeper depths, respectively (Fig. 8). The buffering capacity exhibited by models that reflect changes in the spreading rate
280 and ocean depth is different from that in the standard case (Fig. 9), but still weaker than any of those assumed in the previous studies (cf. Fig. 6). Note that in the previous studies, the buffering capacity is assumed to increase linearly with the spreading rate (Gregory and Taylor, 1981; Holland, 1984; Muehlenbachs, 1998; Wallmann, 2001) and thus the slope values in Fig. 9 need be compared with those in the literature (Fig. 6) ~~multiplied~~ multiplied by a factor that accounts for changes in the spreading~~

rate. As an example, the slope value of $-1.9 \times 10^9 \text{ mol yr}^{-1} \text{‰}^{-1}$ with a spreading rate $30 \times 10^{-2} \text{ m yr}^{-1}$ in Fig. 9 should be
285 compared with -6×10^9 (Wallmann, 2001), $-(14-27) \times 10^9$ (Gregory and Taylor, 1981), -24×10^9 (Muehlenbachs, 1998)
and $-31 \times 10^9 \text{ mol yr}^{-1} \text{‰}^{-1}$ (Holland, 1984) (cf. Fig. 6); thus the buffering with the present model assuming 30×10^{-2}
 m yr^{-1} of ~~spreading~~ spreading rate is much ~~weaker~~ weaker than those assumed in the previous ~~studies~~ studies. More details of
changes in the system behavior are described below.

When spreading is slower, ~~the resultant flow geometry shows less intense but more homogenized mixing seawater penetrates~~
290 ~~deeper into the crust because of a weaker boundary heat flux (Eq. (4)) and thus hydrothermal flows are more homogenized~~
~~but less intense, compared to those in the standard case (Fig. 7a) and.~~ Although the changes of crustal $\delta^{18}\text{O}$ from the pristine
 $\delta^{18}\text{O}$ value (5.7 ‰) become larger over the whole crust (Fig. 8a). ~~The,~~ the sensitivity of solid-rock to seawater $\delta^{18}\text{O}$ ~~is~~
~~remains~~ small (Fig. 8a) ~~because of low water/rock ratios resulting from the less intense water mixing (Fig. 7a) overwhelming~~
~~the smaller supply of ^{18}O via spreading rocks. The small sensitivity combined with the.~~ The small sensitivity is caused because
295 oxygen isotope exchange at shallow depths of oceanic crust is still kinetically limited despite the elongated time duration for
oxygen isotope exchange (3 Myr; cf. Figs. S13 and S16 in Supplementary material) and because the deeper section is buffered
by spreading rocks rather than circulating seawater, given the simultaneous decreases in the amount of water exchange and
the spreading rate. The lower O supply from the mantle combined with the small sensitivity makes the buffering intensity
weaker than that ~~in the standard case with the standard spreading rate~~ (Fig. 9). With the spreading rate high, on the other
300 hand, ~~hydrothermal~~ the hydrothermal penetration depth becomes shallower as a result of enhanced boundary heat flux (Eq.
(4)) and hydrothermal flows are more intense ~~but and~~ more localized close to the ocean and the ridge axis (Figs. 7c and e).
Accordingly, ^{18}O depletion from solid rocks near the ridge axis at relatively high temperatures and water/rock ratios is not
recovered even after continued reactions at low temperatures. ~~making the system more sensitive.~~ Nonetheless, the sensitivity
of solid-rock to seawater $\delta^{18}\text{O}$ does not significantly differ from that in the other spreading-rate cases (Figs. 8b and c) ~~With~~
305 ~~the higher~~ because the kinetics of oxygen isotope exchange and ^{18}O buffering by spreading oceanic rocks remain effective to
decouple the shallow and deeper oceanic crust from seawater $\delta^{18}\text{O}$, respectively. Note that the time duration for oxygen isotope
exchange is reduced with the higher spreading rate ($> 0.1 \text{ Myr}$) but can still be long enough to complete major changes in
the oxygen-isotopic composition of oceanic crust (cf. Fig. S15 in Supplementary material). Despite the weak rock sensitivity
to seawater $\delta^{18}\text{O}$, ~~combined with~~ the larger O supply from the mantle ~~, makes~~ the buffering capacity is larger with the higher
310 spreading rate than larger than that with the standard spreading rate (Fig. 9). Overall, the system as a whole exhibits non-linear
and reduced sensitivity to changes in the spreading rate as recognized from the relationship between the spreading rate and
buffering capacity in Fig. 9 (cf. Gregory and Taylor, 1981; Holland, 1984; Muehlenbachs, 1998; Wallmann, 2001).

When assuming ~~shallow ocean and thus water depth (a shallow ocean with the ocean/crust interface at 1 km), water mixing~~
~~water depth, hydrothermal circulation~~ becomes slightly stronger and ~~localized occurs~~ slightly closer to the ocean (Fig. 7g)
315 (cf. Kasting et al., 2006). ~~Otherwise, changes are negligible compared to our standard case and the resultant oxygen-isotope~~
~~behavior is relatively similar to that in the standard case (Figs. 4 and 8d). The situation is almost the same when we consider~~
~~deeper ocean with a water depth~~ In contrast, in a deep ocean with the ocean/crust interface at 5 km, except that the mixing
localization shifts slightly deeper and the mixing is slightly weaker compared to shallower ocean cases depth from the sea

surface, the mixing of water becomes slightly weaker and occurs slightly deeper (Fig. 7i). In both cases, the above changes in the flow geometry and intensity are relatively minor. The resultant oxygen-isotope behaviors are thus similar to the standard case (Figs. 4, 8d and correspondingly $\delta^{18}\text{O}$ distributions are slightly modified (Fig. 8e). In both shallow- and deep-ocean cases, and the oceanic- $\delta^{18}\text{O}$ buffering becomes only slightly weaker in the shallow- and deep-ocean cases than in the standard case (Fig. 9), attributable to slight changes in the flow geometry and intensity. Because of the slight shifts in water-mixing localization, isotope exchange at low temperature. Notably, oxygen isotope exchange through low-temperature hydrothermal alteration is relatively enhanced in shallow oceans the shallow ocean case (Fig. 9), which is not inconsistent with the prediction by Kasting et al. (2006). On the other hand However, the magnitude of the ocean-depth effect is much smaller than anticipated by Kasting et al. (2006), probably because of the settings in the hydrothermal circulation model (Section 2.1) where permeability distribution dominantly controls the amount of water exchange (e. g., Cherkaoui et al., 2003; two-dimensional distributions of permeability as well as boundary heat flux associated with the spreading rate (Eq. (4)) may exert a more significant control over the hydrothermal penetration depth (cf. Fig. 7 and Supplementary material).

4 Discussion

4.1 Interpretation of ophiolites

Simulations conducted in the present study suggest that oceanic rocks are not significantly affected by changes in seawater $\delta^{18}\text{O}$ under any plausible alteration conditions (Figs. 4 and 8). Reported $\delta^{18}\text{O}$ values of ophiolites and/or oceanic crust range from ~ 1 to 16 ‰ (dashed lines in Fig. 8). By comparison, the simulated solid-rock $\delta^{18}\text{O}$ values fall within this range at $\geq \sim -8$ ‰ for seawater $\delta^{18}\text{O}$ with $3 \times 10^{-2} - 1$ of spreading rate (Figs. 4, 8d values $\leq \sim -10$, ~ -8 to 0 , $\geq \sim -2$ and 8e), at $\leq \sim -10$ ‰ seawater $\delta^{18}\text{O}$ with $1 \times 10^{-2} - 1$ of spreading rate (Fig. 8a), at $\geq \sim -2$ ‰ seawater $\delta^{18}\text{O}$ with at a spreading rate of 1×10^{-2} , 3×10^{-2} , $9 \times 10^{-2} - 1$ of spreading rate (Fig. 8b) and at $\geq \sim -2$ ‰ seawater $\delta^{18}\text{O}$ with and $30 \times 10^{-2} \text{ m yr}^{-1}$ of spreading rate (Fig. 8e, respectively (Figs. 4 and 8). Accordingly, we conclude that the constant seawater $\delta^{18}\text{O}$ at 0 ‰ is neither a necessary nor a sufficient condition for explaining the relatively invariant $\delta^{18}\text{O}$ records of ophiolites. As ophiolite $\delta^{18}\text{O}$ profiles can be affected more by alteration conditions (e.g., the spreading rate and permeability; Section 3.3 and Supplementary material) with the control by seawater $\delta^{18}\text{O}$ remaining relatively weak, feedbacks between the alteration parameters (e.g., spreading rate and permeability) could be more important in reproducing ophiolite records. Therefore, ophiolites may be interpreted to indicate the insensitivity of oceanic rocks to seawater $\delta^{18}\text{O}$, realized by the feedbacks between alteration parameters, and not necessarily a constant seawater $\delta^{18}\text{O}$. The weak buffering (Figs. 6 and 9) accompanying the partial decoupling between the oceanic crust and seawater $\delta^{18}\text{O}$ (e.g., Fig. 8) shows that this interpretation is more plausible than the constant seawater $\delta^{18}\text{O}$.

4.2 Controls of $\delta^{18}\text{O}$ in the Precambrian oceans

Although the buffering of oxygen isotopes through hydrothermal alteration of oceanic rocks is weaker than previously assumed under any alteration conditions (Section 3.3), it could have been relatively strong when the spreading rate is $\geq \sim 30 \times 10^{-2} \text{ m}$

350 yr^{-1} (Figs. 6 and 9). Such high-spreading rate conditions could have been possible only during the earliest period of Earth's history (> 3.5 Ga; Phipps Morgan, 1998) or even impossible according to Korenaga (2006). Excluding this earliest period, the buffering must have been weak despite the uncertainties in alteration conditions (Figs. 6 and 9). The weak buffering must have allowed variations of seawater $\delta^{18}\text{O}$ through other surficial processes that exchange ^{18}O with seawater, most likely through continental weathering (e.g., Walker and Lohmann, 1989). As surface environments likely have significantly changed through
355 the eons (cf. Introduction), ^{18}O fluxes from continental weathering could have correspondingly varied ~~throughout and might have contributed to the oceanic ^{18}O budget more significantly than those from hydrothermal alteration of oceanic crust during certain periods in~~ Earth's history.

Previous studies examining oceanic- $\delta^{18}\text{O}$ evolution on geological time scales have utilized box-modeling approaches to account for oxygen isotope exchange from both continental weathering and hydrothermal alteration of oceanic crust (Godderis
360 and Veizer, 2000; Godd ris et al., 2001; Wallmann, 2001; Kasting et al., 2006; Jaffr s et al., 2007). Among them, the studies that assume strong buffering at midocean ridges have had difficulty in modifying oceanic ^{18}O budget through other surficial processes including continental weathering (Godderis and Veizer, 2000; Godd ris et al., 2001). Other studies that assume weak buffering instead have shown the possibility of significant oceanic- $\delta^{18}\text{O}$ changes through modification of simplified continental-weathering parameters with the Earth's age (Wallmann, 2001; Kasting et al., 2006; Jaffr s et al., 2007). Revisiting
365 these previous box-model studies with the weak buffering suggested here (e.g., Figs. 6 and 9) and constructing a process-based model for continental weathering to be coupled with the present model will lead to a better understanding of controls on oceanic $\delta^{18}\text{O}$ during the Precambrian.

4.3 Comparison with other models

~~Our model results contrast with the results~~ The results in the present study differ significantly from those by L cuyer and Alle-
370 mand (1999), who utilized prescribed distributions of temperature and water/rock ratio ~~and along with~~ an isotope-fractionation equation for a half-closed system (a system that is open ~~for water phase to the water reservoir,~~ but not ~~for solid phase to the rock reservoir;~~ Gregory et al., 1989) (Introduction). The assumed range for water/rock ratio (≤ 10) by these authors is comparable to the simulated range in the present study ($\eta \leq 164$; Figs. 5a and c). ~~Also, because the Arrhenius equation adopted for kinetics of oxygen isotope exchange by is based on the dataset by,~~ the kinetic expression in the present study (Eq. (7);
375 ~~based on Cole et al., 1983, 1987) should not be significantly different from that by.~~ States of equilibrium and non-equilibrium in the bulk-rock-based ~~isotope exchange formulation~~ formulation of isotopes in the present study correspond to transport- and reaction-limited alteration states, respectively, in the mineral-based isotope ~~exchange~~ formulation in L cuyer and Allemand (1999); ~~this formulation difference~~ the difference in the formulation of isotopic composition of bulk rock should not cause any significant differences in oxygen isotope behavior ~~for bulk rock and porewater. Additional simulations with~~ of bulk rock (cf.
380 Bindeman et al., 2019). The temperature dependence of kinetic constant for oxygen isotope exchange is described with the Arrhenius equation, based on the datasets by Cole and Ohmoto (1986) in L cuyer and Allemand (1999) and by Cole et al. (1983, 1987) in the present study, and thus there should be little difference in the temperature dependence of isotope exchange kinetics between the two studies. The size difference in the calculation domain cannot explain the difference between the

present study and Lécuyer and Allemand (1999) as additional numerical experiments on a wider calculation domain (300
385 km ~~(cf. 30 in the standard simulation) and~~) with artificially imposing off-axis water exchange (up to 5.3×10^{15} kg yr⁻¹) ~~do~~
~~not show significant differences from the results presented above (yield essentially the same results as those with the standard~~
calculation domain width (30 km) (Supplementary material); ~~the size difference in the calculation domain cannot explain the~~
~~difference between the present study and~~. Although a thorough comparison cannot be made between the two studies because
Lécuyer and Allemand (1999) have not provided detailed model results ~~to be compared with those presented here~~, it is likely
390 that the isotopic effect of spreading crust has not been explicitly considered by Lécuyer and Allemand (1999). Should this
be the case, the sensitivity of oceanic rocks to seawater $\delta^{18}\text{O}$ and the buffering capacity at midocean ridges could be over-
estimated ~~in~~ by the model of Lécuyer and Allemand (1999). ~~This overestimation could also be applicable to other models,~~
~~e.g., by , , , and , who did not explicitly consider~~ More generally, the models that do not explicitly account for the transport
of solid rocks ~~, either~~ (e.g., Taylor, 1977; Norton and Taylor, 1979; Criss et al., 1987; Gregory et al., 1989; DePaolo, 2006)
395 could overestimate the coupling strength between oceanic crust and seawater $\delta^{18}\text{O}$ and the oceanic- ^{18}O buffering capacity
of hydrothermal systems. Application of these models to ophiolites may also underestimate the uncertainty in reconstructed
ancient seawater $\delta^{18}\text{O}$ that is caused by the partial decoupling between oceanic crust and seawater $\delta^{18}\text{O}$ (cf. Section 4.1 and
Supplementary material).

5 Conclusions

400 The 2D reactive transport model of oxygen isotopes combined with 2D hydrothermal circulation simulations enables us to
predict distributions of temperature, water flow and oxygen isotopes of solid rocks and porewaters within oceanic crust based on
mass, momentum and energy conservations. The model assuming the present-day seawater $\delta^{18}\text{O}$ reproduced those distributions
consistent with modern observations, supporting the model's validity. The intensity of seawater- $\delta^{18}\text{O}$ buffering at midocean
ridges was evaluated by calculating the net ^{18}O flux as a function of seawater $\delta^{18}\text{O}$. The buffering intensity predicted by the
405 model is significantly weaker than those previously assumed under any plausible alteration conditions during the Precambrian.
The weak buffering is realized because isotope exchange equilibrium is not reached in shallow sections of oceanic crust with
low temperatures, and because ^{18}O supply via spreading solid rocks exceeds that through hydrothermal circulation in deeper
high-temperature sections. Consistently with the weak buffering, oceanic rocks are insensitive to seawater with respect to
oxygen isotopes. Thus, ophiolites can alternatively be explained by the insensitivity of oceanic rocks to seawater $\delta^{18}\text{O}$ that
410 could have evolved through the Precambrian because of the weak buffering at midocean ridges.

Code availability. The source codes of the model are available upon request to the author.

Appendix A: Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/xxxxxx>.

Author contributions. YK conducted the whole research.

415 *Competing interests.* I declare no competing interests.

Acknowledgements. I thank Jim Kasting and Lee Kump for helpful discussions ~~and~~ Laurence Coogan and an anonymous reviewer ~~of~~ for their useful comments on earlier version of manuscript ~~provided helpful comments~~. I am grateful to Benjamin Johnson and Itay Halevy for their useful comments on the current manuscript and to Patrice Rey for editorial handling.

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Table 1. Symbols and their definitions and values.

Symbol	Definition	Value
c_p^f	Specific heat capacity of water ($\text{J kg}^{-1} \text{K}^{-1}$)	
c_p^m	Specific heat capacity of oceanic rock ($\text{J kg}^{-1} \text{K}^{-1}$)	10^3
D	Effective diffusion coefficient for ^{18}O ($\text{m}^2 \text{yr}^{-1}$)	
E	Apparent activation energy of oxygen isotope exchange (J mol^{-1})	5×10^4
F_m	Mole ratio of ^{18}O to total O (^{18}O plus ^{16}O) of pristine crust (dimensionless)	2.0126×10^{-3}
F_p	Mole ratio of ^{18}O to total O (^{18}O plus ^{16}O) of porewater (dimensionless)	
F_r	Mole ratio of ^{18}O to total O (^{18}O plus ^{16}O) of solid rock (dimensionless)	
F_{sw}	Mole ratio of ^{18}O to total O (^{18}O plus ^{16}O) of seawater (dimensionless)	
g	Gravity acceleration (m yr^{-2})	9.76×10^{15}
\mathbf{g}	Gravity vector (m yr^{-2})	
J_b	Boundary heat flux from the intrusion ($\text{J m}^{-2} \text{yr}^{-1}$)	
k	Permeability of oceanic rock (m^2)	
k_{ex}	Rate constant for oxygen isotope exchange between solid rock and porewater ($\text{mol}^{-1} \text{kg yr}^{-1}$)	
m_f	Mole concentration of oxygen per unit water mass (mol kg^{-1})	55.56
m_s	Mole concentration of oxygen per unit solid mass (mol kg^{-1})	31.25
P	Fluid pressure (Pa)	
\mathbf{q}	Water mass flux vector ($\text{kg m}^{-2} \text{yr}^{-1}$)	
R_g	Gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)	8.314
t	Time (yr)	
T	Temperature (K)	
T_m	Temperature of the intrusion (K)	1.473×10^3
w	Spreading rate of oceanic crust (m yr^{-1})	
x	Distance from ridge axis (m)	
y	Depth from ocean/crust interface (m)	
α	Oxygen isotope fractionation factor (dimensionless)	
β	Parameter relevant to the temperature dependence of α (dimensionless)	0.876
η	Water/rock oxygen-mole ratio (dimensionless)	
κ	Thermal conductivity of oceanic rock ($\text{J yr}^{-1} \text{m}^{-1} \text{K}^{-1}$)	9.47×10^7
μ	Kinematic viscosity of water ($\text{m}^2 \text{yr}^{-1}$)	
ρ_b	Density of bulk rock (kg m^{-3})	
ρ_f	Density of water (kg m^{-3})	
ρ_m	Density of solid rock (kg m^{-3})	3×10^3
τ	Tortuosity factor (dimensionless)	
ϕ	Porosity of crust (dimensionless)	5×10^{-2}
Ω	Degree of oxygen isotope exchange (dimensionless)	
∇	Vector differential operator (m^{-1})	

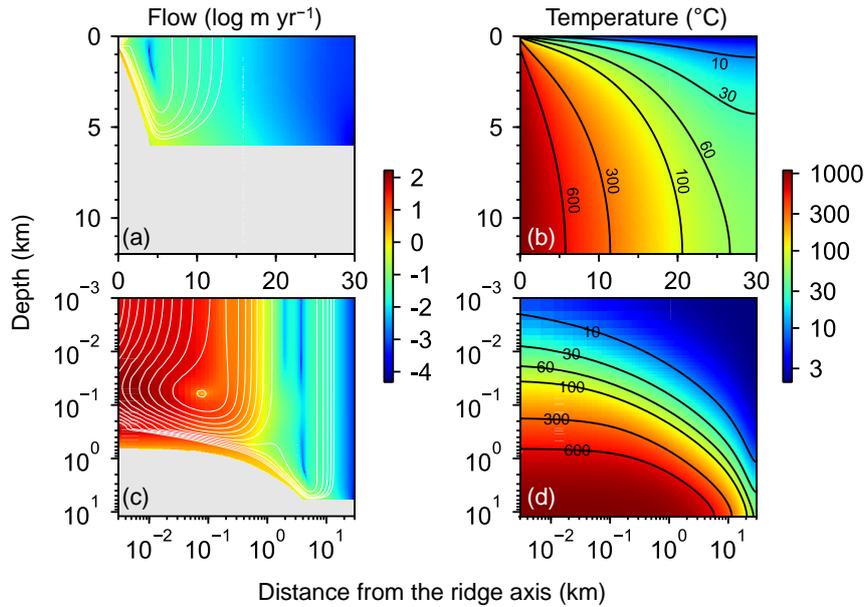


Figure 1. Two-dimensional distributions of hydrothermal fluid flow (a and c) and temperature (b and d). Shown in a and c are logarithms of fluid velocity (m yr^{-1}) together with mass-based stream lines that are depicted with white curves. The same data as in a and b are **plotted** on logarithmic scales in c and d, respectively. Gray zones in a and c represent where rocks are impermeable below 6 km depth and/or with temperatures above the rock-cracking threshold ($600\text{ }^{\circ}\text{C}$).

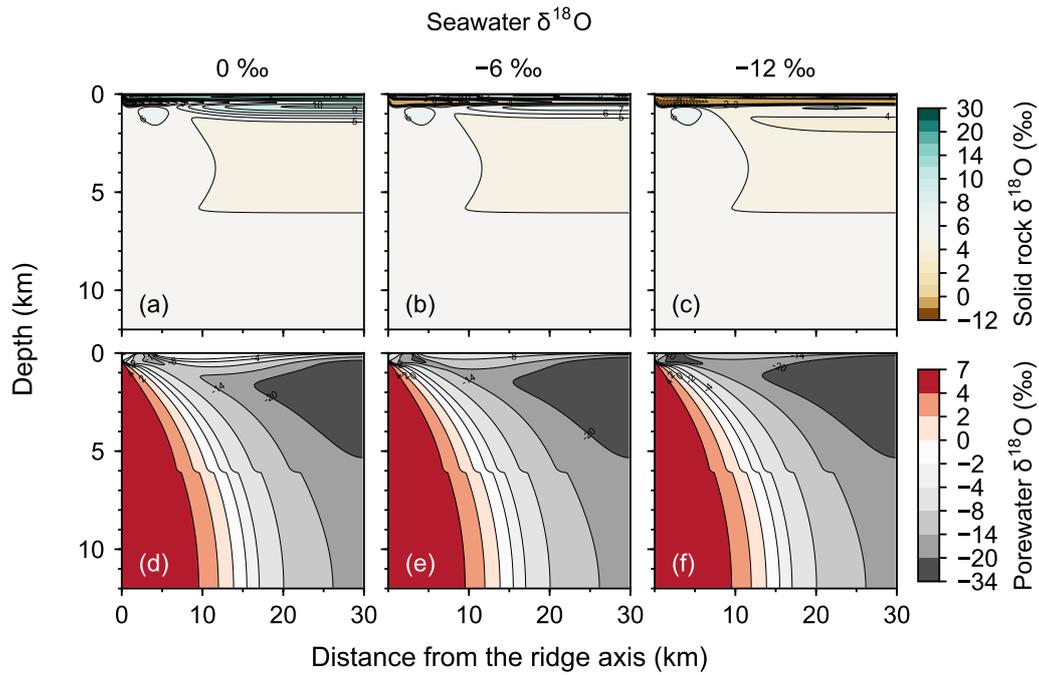


Figure 2. Two-dimensional distributions of solid-rock and porewater $\delta^{18}\text{O}$ (a–c and d–f, respectively) at seawater $\delta^{18}\text{O}$ values of 0, –6 and –12 ‰ of seawater $\delta^{18}\text{O}$ (a and d, b and e, and c and f, respectively).

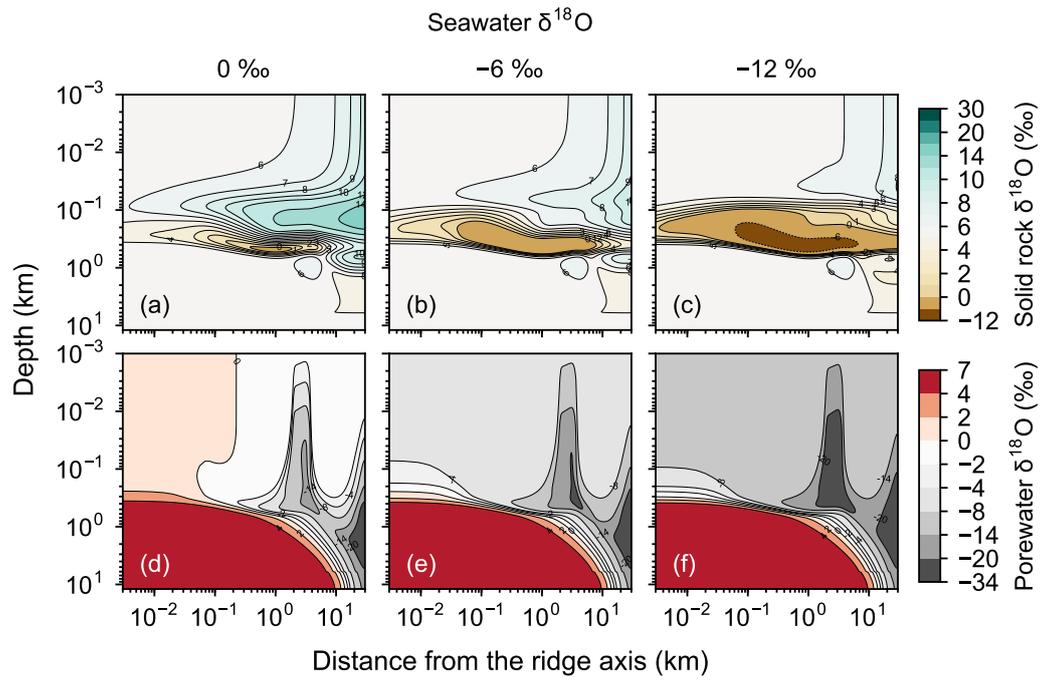


Figure 3. As for Fig. 2, except plotted on logarithmic scales.

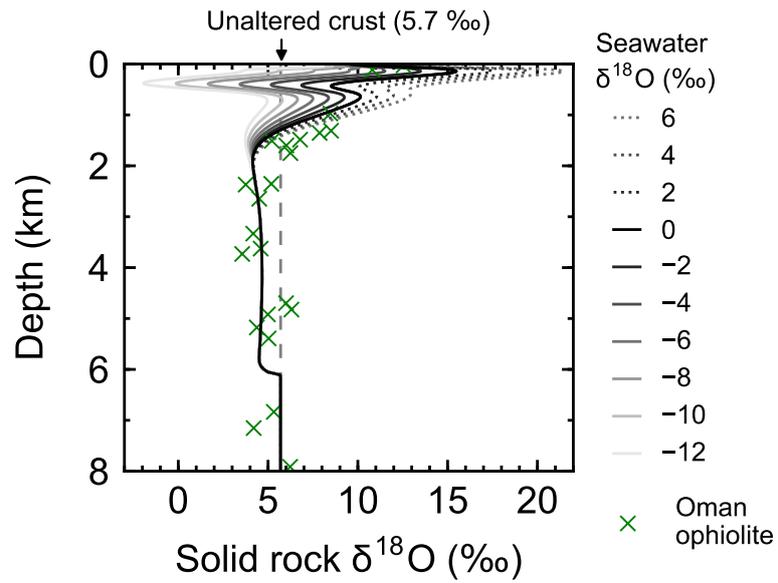


Figure 4. Solid rock $\delta^{18}\text{O}$ as function of depth at 1 Myr (30 km) from the ridge axis with 0, -2 at seawater $\delta^{18}\text{O}$ values of 6, 4, ..., -12 ‰ of seawater $\delta^{18}\text{O}$. Also plotted are Oman ophiolite data from Gregory and Taylor (1981) (crosses) converting their reported depth y' (km) to $(7.4 - y')$ (km) to facilitate comparison.

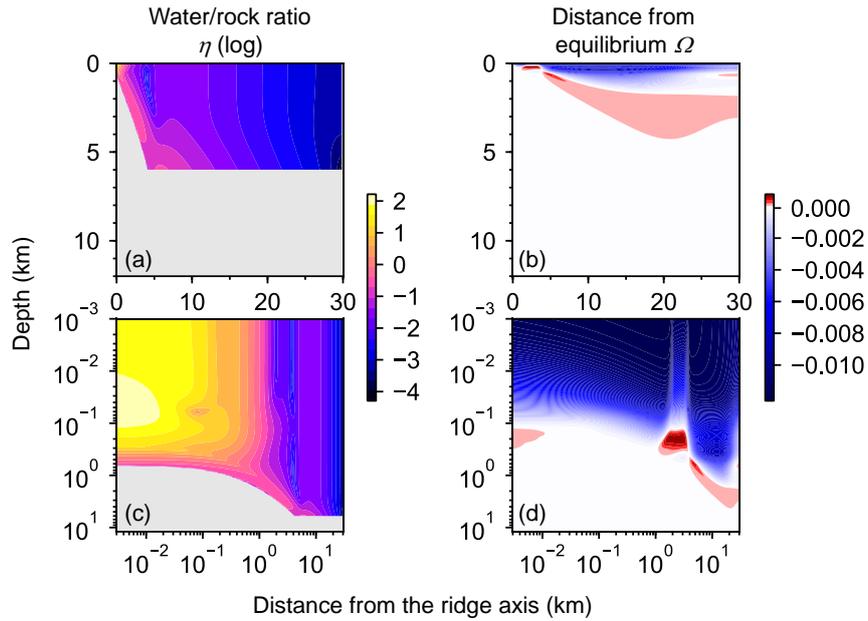


Figure 5. Two-dimensional distributions of local water/rock oxygen-mole ratio (a and c) and degree of oxygen isotope exchange at 0% of a seawater $\delta^{18}\text{O}$ value of 0% (b and d). The same data as in a and b are plotted on logarithmic scales in c and d, respectively. See the caption of Fig. 1 for the explanation of gray zones in a and c.

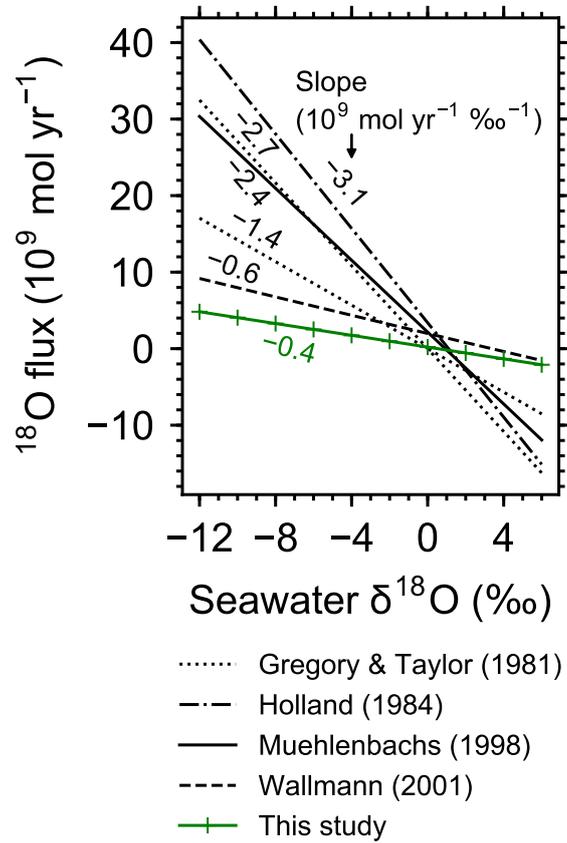


Figure 6. Net ^{18}O flux to the ocean from hydrothermal systems as function of seawater $\delta^{18}\text{O}$. Slope values are denoted near the lines from previous studies and the standard simulation in this study.

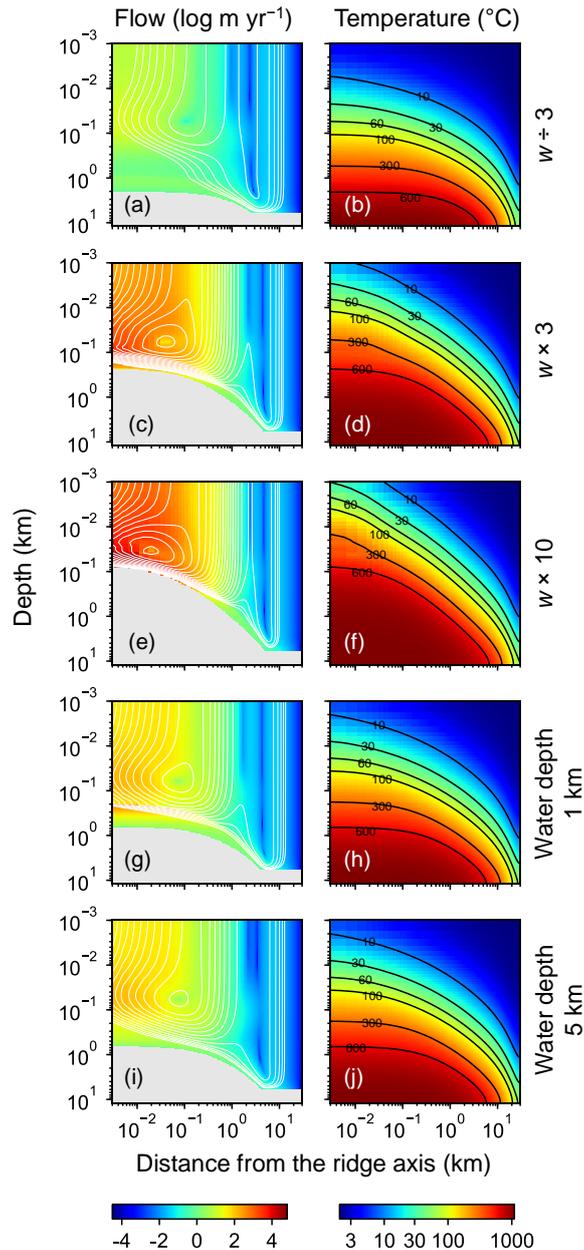


Figure 7. Two-dimensional distributions of hydrothermal fluid flow (a, c, e, g and i) and temperature (b, d, f, h and j) from simulations with different spreading rates and ocean depths. Logarithms of fluid velocity and mass-based stream lines are depicted in a, c, e, g and i.

Spreading rate is changed at The panels in the first three rows assume different spreading rates ($1 \times 10^{-2} \text{ m yr}^{-1}$ in a and b, $9 \times 10^{-2} \text{ m yr}^{-1}$ in c and d, and $30 \times 10^{-2} \text{ m yr}^{-1}$ in e and f, while ocean depth is changed at), while those in the last two rows assume different ocean depths (1 km in g and h and 5 km in i and j). Values of other parameters are the same as those in the standard simulation (e.g., Fig. 1). See the caption of Fig. 1 for the explanation of gray zones in a, c, e, g and i.

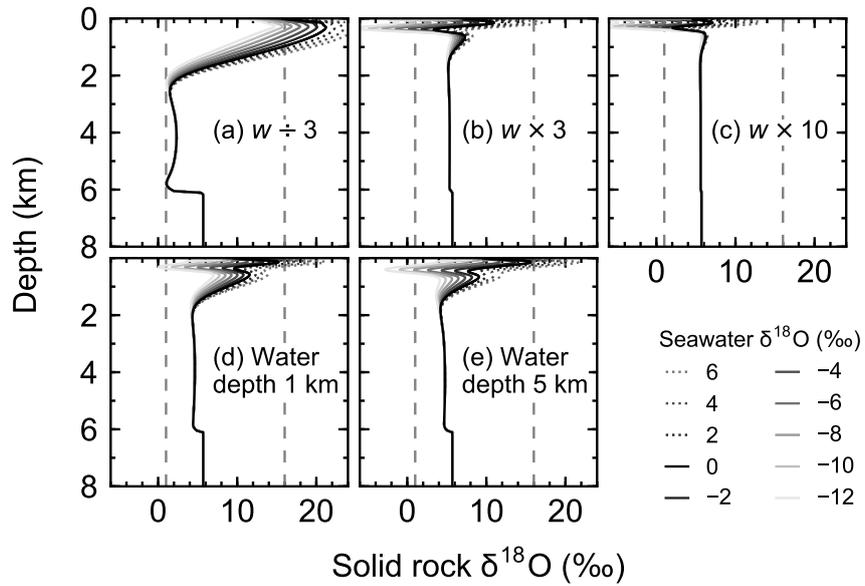


Figure 8. Solid rock $\delta^{18}\text{O}$ as function of depth at 30 km from the ridge axis ~~with 0, -2~~ at seawater $\delta^{18}\text{O}$ values of 6, 4, ..., -12 ‰ of seawater $\delta^{18}\text{O}$ from simulations with different spreading rates and ocean depths. Dashed lines denote 1 and 16 ‰, between which observed $\delta^{18}\text{O}$ of ophiolites and/or oceanic crust ranges (Gregory and Taylor, 1981; Barrett and Friedrichsen, 1982; Cocker et al., 1982; Elthon et al., 1984; Alt et al., 1986, 1995; Agrinier et al., 1988; Schiffman and Smith, 1988; Vibetti et al., 1989; Lécuyer and Fourcade, 1991; Stakes, 1991; Bickle and Teagle, 1992; Holmden and Muehlenbachs, 1993; Muehlenbachs et al., 2003; Alt and Bach, 2006; Furnes et al., 2007; Gao et al., 2012). Standard parameter values are assumed except for the parameterization denoted at each panel.

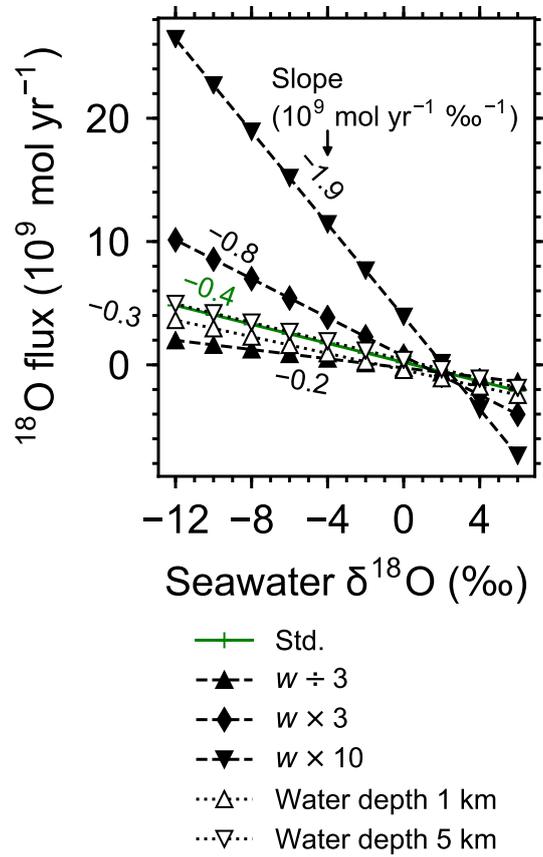


Figure 9. Net ^{18}O flux to the ocean from hydrothermal systems as function of seawater $\delta^{18}\text{O}$ from simulations with different spreading rates and ocean depths. See the legend for the types of symbol and line for individual simulations. Slope values are denoted near the lines.