

Dear Editor, Dear Reviewer,

We appreciated the very detailed and constructive comments on different aspects of the study. We have addressed the suggestions given by the reviewer; in the following we report the point-to-point reply to the comments.

Best regards,
Alice Vho and co-authors

At the date of review, the database, which is used for the modelling and which is fundamental for the models, is currently under review for another journal and can hence not be accessed. This is somewhat problematic regarding the final publication of this manuscript, at which point the database should be accessible to readers (see comment below).

The manuscript underwent the last round of minor revisions and we are confident that it will be available soon. For the moment, the fractionation factors used for the calculations are also provided with the program (folder “WorkingDirectoy” of PTloop). This has been added in the section “Code availability”. The file DO18db2.0.3.dat contains the fractionation factors between quartz and any end-member used in the calculation.

10: For clarity, it should be added the Gibbs energy minimization is carried out for given whole-rock compositions.

The text has been modified accordingly (line 11).

15-20: The abstract would become clearer if a structure similar to the order/sections in the manuscript is adopted. For instance, the infiltration of an external fluid into mafic rocks is mentioned as point (1) in the abstract, but it is the last section in the results (3.3.4) and also near the end in the discussion. Better to first describe the simple case of dehydration only (“no interaction” case); it should also be mentioned that dehydration in the metasediments is also considered in the models. Second, the influx of MORB-derived fluid should be addressed; currently, MORB-derived fluids are not explicitly mentioned in the abstract, so this should be added as this process features prominently in the results and discussion. Finally, the influx of fluid derived from ultramafic rocks can be mentioned.

Abstract modified accordingly. The term “MORB” has been replaced by the term “metabasalt” when indicating the subducting mafic oceanic crust. Metabasalt_(h) refers to the hydrated MORB composition, while metabasalt_(a) to the altered mafic oceanic crust (lines 163 – 165).

82-90: Since sediment dehydration is also considered, this should be explicitly mentioned here. It is nicely described in the figure caption to Fig. 1 that the fluid produced in the “No Interaction” case is a mixture of MORB-derived and sediment-derived fluid.

Two sentences have been added to clarify this point (lines 95 – 99).

148: Reference to the database in Vho et al. (in review). As a reviewer of this manuscript for Solid Earth, I do not have access to this database and do not know the current status regarding publication of this database. This is somewhat problematic as the database is fundamental for the modelling performed in this manuscript. I am convinced that the authors are pursuing the publication of this accompanying manuscript as quickly and efficiently as possible, but I would like to see this the accompanying manuscript as accepted manuscript with doi number before the final version of this manuscript for Solid Earth goes online. The reason is that readers should be able to adequately follow and reconstruct all the information and proceedings of this article. This is difficult if the database is not accessible and may become problematic if the accompanying

manuscript is never published (I do not expect this to happen, but it seems a sensible approach notwithstanding the impeccable reputation of the present author team).

See above.

194: As these fractionation factors are explicitly mentioned, it would be useful to specify for which temperature the fractionation of 2 ‰ is representative of.

It has been specified that this values if for $T > 550$ °C (line 209).

203: white mica: The phase diagrams in Fig. 3 show “ph” (phengite), but in the text mostly “white mica” is used (but see line 212). Does “white mica” always stands for a potassic white mica? For consistency, only one term should be used throughout, and an explanation regarding the composition of the white mica would also be useful (e.g. the modelled composition might be a typical muscovite at lower grades but becomes more phengitic at higher temperatures and pressures).

The composition of the modelled white mica has been added in the text. According to the composition, the term phengite was used, with the exception of the abstract where the term “white mica” (line 21) refers to all variety of potassic white mica compositions.

212-224: There are a few minor issues in this section that should be addressed:

a) Modal phase changes are referred to partly in a neutral way (increase/reduction) but in other cases specific reactions are invoked (e.g. gln consumed in favour of jd+ank, lws breakdown producing grt). From a perspective of a metamorphic petrologist, one would be interested to see the full reaction equations. Two examples: If ankerite is produced, carbonate or CO₂ is required as reactant; which other phases are involved in the lawsonite breakdown reaction? However, in the context of this study, this detail may not be necessary, and it may be suffice to formulate in a way without referring to specific reactions.

This section was reformulated without referring to specific reactions since, as perceived also by the reviewer, this detail is not necessary.

b) Clinopyroxene composition: As the change from omphacite to jadeite is mentioned, please clarify at which compositional boundary (mol% jadeite component) the change in name is made. Or is it a pure end-member jadeite? The coexistence of jadeite and omphacite should also briefly be addressed as in natural rocks, one would presumably expect only one clinopyroxene with changes in the jadeite-component in omphacite.

Details on the pyroxene composition have been added in the text (lines 218 – 237). For consistency, also the composition of the garnet has been reported. A note about the interpretation of the coexistence of two pyroxenes has been added (lines 241 – 242) in line to what was already written for amphiboles.

The authors point out that the co-existence of two amphiboles is of little relevance for the oxygen isotope modelling – is this similar for the pyroxenes? This should be clarified.

Yes, it is similar for the pyroxenes and this point has been added in the text (lines 241 – 242).

227: Initial water-saturated conditions: Please explain and justify the choice of water-saturated conditions, in particular for the fresh MORB. If one assumes that fresh MORB is initially composed of nominally anhydrous minerals only, where does the water come from? In the discussion later, the water released from the slab is dominated by the MORB-derived fluid, and presumably this is due to amounts of water stored under water-saturated conditions initially. Hence, does this initial assumption affect (at least some) of the model calculations, and how large is the effect? I appreciate that not all possible scenarios can be addressed in a single manuscript, but a brief justification of the choices made would be useful.

In this case the main difference is that the amount of released fluid due to breakdown of hydrous phases would be smaller. This point has been added (lines 255-256).

234: Glaucophanite and actinolite and the intermediate fluid pulse: It seems in the figure that the growth of talc takes up the water released by consumption of actinolite and glaucophanite, as the modal proportion of talc increases from 580 to 600°C, whereas the amount of water appears to increase at >600 °C when the modal proportions of talc and then lawsonite decrease. Please check carefully and modify the text accordingly.

Talc takes only part (ca. 50%) of the water released by amphibole breakdown, because of the small abundance of talc (ca. 14 wt% in the metabasalt_(h), ca. 6 wt% in the metabasalt_(a), incorporating ca. 4 wt% of H₂O) with respect to the consumed amphiboles (ca. 50 wt% in the fresh MORB and ca. 40 wt% in the altered MORB, water content of 2.0 – 2.2 wt%). This results in a peak of fluid release at 600 °C as can be observed also in figure 5. This point has been specified in the text (line 254).

236: The liberation of water from the carbonate sediment is specified, but release of CO₂ is not mentioned. Does any release of CO₂ occur? Carbonate phases appear to remain stable, but the aspect should still be briefly explained for clarity.

This is an important point and we acknowledge both the reviewers for the comments. The main reasons why we did not to include CO₂ in the calculation are the following. (1) The amount of CO₂ involved in this model is limited. The maximum CO₂ content in the altered MORB-derived fluid is ca. 10 mol% at 700 °C and 2.6 GPa, and it is lower (2 – 7 mol%) at the conditions of the major fluid pulses. In the carbonate sediment the CO₂ content is > 7 mol% at T > 560 °C and P > 2.18 GPa, where a negligible amount of fluid (i.e. << 0.01 vol%) is released. (2) The oxygen isotope fractionation between CO₂ and H₂O is still poorly constrained and presents limitations (see below); therefore it was not included in the internally consistent database version used for this study. Published experimental calibrations involving CO₂ are limited (e.g., Böttcher, 1994 for norsetite-CO₂; O'Neil and Adami, 1969 for H₂O-CO₂) and were performed at T < 100 °C, making the validity of the available fractionation factors at high temperature questionable. Zheng (1994) provides fractionation data for calcite-CO₂, quartz-CO₂ and H₂O-CO₂; however, incremental calculations have strong limitations and must be used with caution (e.g., Chacko et al., 2001). For the H₂O-CO₂ pair, the available calibrations (Friedman and O'Neil, 1977; O'Neil and Adami, 1969; Zheng, 1994) are in strong disagreement and predict fractionations of 1.50 ‰, -1.87 ‰ and -4.41 ‰ at 700 °C and of -8.85 ‰, -11.45 ‰ and -10.99 ‰ at 350°C respectively. Overall, the H₂O-CO₂ fractionation is large (-5 – -12 ‰) at T < 440 °C, where CO₂ is absent or present in negligible amount in the fluid phase in our model; it decreases to -2 – -6 ‰ at T = 550 °C, where the amount of CO₂ present in the fluid phase in our model is minor (ca. 3 mol% in the fluid released by the MORB, ca. 6 mol% in the fluid released by the sediment); it is moderate (ca. -5 ‰) to absent (depending on the chosen calibration) at T ≥ 600 °C, where the amount of CO₂ in the fluid increases. The consideration of the CO₂ component would produce a negligible to minor shift on the fluid δ¹⁸O at the condition of significant release (0.1 – 0.2 ‰ at 520 °C and 0.0 – 0.6 ‰ at 620 °C for the MORB-derived fluid and 0.1 – 0.3 ‰ at 480 °C and 0.2 – 1.1 ‰ at 620 °C for the sediment-derived fluid, depending on the calibration).

We added a paragraph in the section 3.2 describing the potential effect of the CO₂ component present in the fluid released by the altered MORB and the carbonate. The title of the section has been also changed from “Production of water” to “Production of aqueous fluid”. However, we did not introduce CO₂ in the computation for the reasons discussed above.

282: Mafic fluid (see also 288, 297, 300 and elsewhere): Using the terms mafic fluid and ultramafic fluid is not appropriate and should be avoided. The term “mafic” is derived from magnesium and ferrum (iron) rich, which is appropriate for rock compositions but not for the

fluids considered here. The same applies to “ultramafic fluids” (e.g. in lines 309, 311 and elsewhere), serpentinite-derived fluid should be used instead.

The term “mafic” has been replaced by “metabasalt-derived” and term “ultramafic” by “serpentinite-derived” when referring to fluids.

311: This statement is a bit vague. What exactly is the effect in the PI and NI cases on MORB? If the variations in the sedimentary rocks decrease to zero, does that mean there is no effect at all, or no change compared to the previous cases? Please formulate more precisely here.

The sentence has been rephrased and moved to the end of the section in order to make the point clearer.

331-337: The example of the granite appears to be out of place here, as granite has not been considered anywhere else in the manuscript. A dry basalt would be a more appropriate example, which can be linked to the scenarios considered much better. But the results presented show the limited effect on the O isotope variation anyway, so consider deleting this section altogether.

This example has been moved to the supplementary material S4.

363-364: This statement is important, and could be highlighted in abstract and/or conclusions.

The statement has been added in the abstract (line 17) and in the conclusions (lines 576 – 578).

387-393: This section would benefit from a few more details regarding the studies on oxygen isotope zoning in metamorphic minerals, and how the modelling results can be linked to these results (and possibly used to support interpretations or argue for alternative interpretations). Questions that are of interest to the reader include: What kind of zonation was observed in the minerals studied? With which of the modelled scenarios do these patterns coincide? Providing more details here and some specific examples would also be useful to emphasize the wider implications for studies based on natural samples.

Three examples of observed intragrain $\delta^{18}\text{O}$ variations in garnet from HP rocks have been reported (Martin et al., 2014; Rubatto and Angiboust, 2015; Vielzeuf et al., 2005b; lines 431 – 434).

403: Integrated Fluid/rock ratios: It is not entirely clear where the numbers come from as they have not been mentioned before. Please clarify.

The concept of integrated fluid/rock ratio has been now defined in the section 2.1 as “as the total mass of aqueous fluid that has passed through and interacted with the rock normalized to the mass of the rock”.

410: Serpentinite-derived fluid input into the sedimentary layer: Is this fluid in the models not a mixture of serpentinite-derived fluid and MORB-derived fluid since MORB also dehydrates? If so, clarify this point.

Yes, it is a mixture and the point has been clarified (lines 453 – 454).

413-415: Detection of serpentinite-derived fluids: It would be useful if the authors could refer to the (possible) detection of such fluids in real sediments to underline the relevance of their study.

Two natural examples have been reported (lines 457 – 462). Martin et al. (2014) describe a shift in $\delta^{18}\text{O}$ of -2.5 ‰ among different generations of HP garnet in a sample from the Corsica continental basement (garnet mantle $\delta^{18}\text{O} = 7.2 \pm 0.4$ ‰, garnet rim $\delta^{18}\text{O} = 4.7 \pm 0.5$ ‰). The authors associate this shift to an infiltration of serpentinite-derived fluids and, to a lesser extent, altered gabbro-derived fluid. Williams (2019) describe an extreme $\delta^{18}\text{O}$ shift of -15 ‰ between garnet core and rim in a metasediment from the Lago di Cignana Unit. Such an oxygen isotope composition variation has been related to a strongly channelized fluid influx originated from the dehydration of serpentinites.

416-418: Effects: The relatively “dry” system still starts with a water-saturated MORB; so the reader may wonder how things change if the system is really dry – would the oxygen isotopic effects even larger? (see also earlier comments).

The terms “wet” and “dry” have been removed for clarity: relatively water-rich and relatively water-poor systems are used instead. The main difference with considering undersaturated basalt as starting composition would be the release of less fluid (as has been specified at lines 155-256) and therefore less capacity to infiltrate upper lithologies and modify their $\delta^{18}\text{O}$ value.

419-437: This section seems rather unnecessary because it does not add much to the discussion on oxygen isotopes, the main statement emphasizing that the trends are similar to the ones shown earlier. The discussion on water release is fine but key points could be incorporated into the section “Model geometry” where some of the differences between the P-T paths are already highlighted.

We believe that this section is important to provide an overview of the possible variations associated to the use of different P-T paths for the model. It also serves the purpose to clarify the doubt on whether the chosen geotherm is representative for any natural system (see the comment on figure 2 below). Therefore, it has been kept in the text.

450-468: Can the relevant equations that consider the subduction rate and the volumes of fluid released be shown here so that readers get a better understanding of the modelling approach?

A clarification about how the chosen subduction rate controls the amount of water infiltrating at a given point of the slab mantle interface has been added (lines 509 – 512). Given the column length of 1 m, a subduction rate of 1 cm/y implies that any fixed point (i.e. fixed P-T conditions) at the slab/mantle interface receives in 100 years the total amount of fluid that a single column can liberate at those conditions. Hence, in this example 4892.6 kg of water/100 years (i.e. the amount released by the considered column at the chosen conditions, as explained in the text) infiltrate the mantle wedge.

475: What exactly are “high” $\delta^{18}\text{O}$ arc lavas. Please provide some values or a range of values.

Values given in the cited studies have been reported (phenocrysts in lavas from Central Kamchatka: olivine $\delta^{18}\text{O} = 5.8 - 7.1 \text{ ‰}$ and clinopyroxenes $\delta^{18}\text{O} = 6.2 - 7.5 \text{ ‰}$, Dorendorf et al., 2000; New Guinea: silicate glass inclusions in olivine $\delta^{18}\text{O} = 8.8 - 12.2 \text{ ‰}$, clinopyroxenes in metasomatized lehrzomite $\delta^{18}\text{O} = 6.2 - 10.3 \text{ ‰}$, Eiler et al., 1998).

486: Another important statement relevant for the interpretation of natural samples, which may also be emphasized in the conclusions.

This statement has been added in the conclusions (lines 597 – 599).

515: Interesting aspect which may be of interest to studies on natural serpentinites. For instance, have such elevated O isotope signatures been observed in natural wedge serpentinites? Or can O isotopes be used to distinguish wedge from abyssal peridotites in the geological record? Briefly expanding on these aspects would widen the relevance of this study.

Theoretically, mantle wedge metasomatized/serpentinized rocks after interaction with slab-derived fluids are expected to increase the $\delta^{18}\text{O}$ with respect to the mantle signature of 5.5 ‰. It appears however impossible to use this point as main discriminant to distinguish sea-floor (or in general low-T) serpentinites from HP ones because the first type is highly variable in oxygen isotope composition (ranging between 1 and more than 10 ‰).

Figure 1: As in the text, please avoid the terms “mafic fluid” and “ultramafic fluid”. Add $\delta^{18}\text{O}$ to the numbers given in the figure. Clarify that 4.5 ‰ is a fluid value, not the value of the serpentinite. Give the sources for the $\delta^{18}\text{O}$ values used in the figure, or refer to the text. Figure and figure caption modified accordingly. To avoid confusion, only the $\delta^{18}\text{O}$ of the rocks (fluid sources) has been reported in the figure.

Figure 2: The meaning of the abbreviation D80 should be explained. Moreover, one may wonder whether an average geotherm is useful as it may not represent any real subduction zone. Typo in the figure “Syracuse”. Regarding the lines in this figure and in other figures, they are dashed rather than dotted and should be labelled accordingly.

The meaning of D80 has been explained as “the geotherm dominated by a steep T gradient at 80 km depth, which occurs at the transition from partial to full coupling”. The implications of the choice of a specific geotherm for the model, and the possible variations occurring when the P-T path is modified, are discussed in the section 4.4 “Effect of the subduction geotherm”.

The typo has been corrected and “dashed” has been used for the lines.

Figure 3: Mineral abbreviations should be explained. It would also help to indicate initial water contents in the figure or the caption.

Mineral abbreviation reference to Whitney and Evans (2010) has been added. Titanite field colour has been changed to be consistent with Fig. 4. The initial water content in vol% (< 1 vol% for the MORBs and the carbonate sediment, ca. 3 vol% for the terrigenous sediment) have been added in the caption together with a reference to Table 1 for details.

Figure 4: The line for titanite is almost invisible in a print out, a somewhat darker colour would improve visibility. For diagrams (g) and (h), I recommend presenting separate diagrams for the partial and high interaction cases because the distinction of the lines marked with stars is not very clear (the bulk trend could be copied into the respective other diagram for comparison). As above, lines are dashed (short bars) rather than dotted (points).

The colour of the line for titanite has been modified. The term “dashed” has been used for the lines. The figure has been split into two figures in order to make the diagrams (g) and (h) clearer. Figure 4 includes the diagrams (a), (b), (c), (d), (e) and (f) of the original figure, while figure 5 include 4 diagrams showing separately the partial interaction and the high interaction cases for both the sediments. In all the diagrams we plotted the no interaction case lines for comparison. Figure captions and references in the text have been modified accordingly.

Figure 6: Avoid terms “mafic” and “ultramafic” fluid.

Figure and figure caption modified.

Technical corrections:

All addressed.