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Special Issue: Exploring new frontiers in fluid processes in subduction zones

Authors: Alice Vho et al.

Title: Tracing fluid transfers in subduction zones: an integrated thermodynamic and  $\delta^{18}\text{O}$  fractionation modelling approach.

Review by Ralf Halama (Keele University), 8/10/19

### **General comments:**

This manuscript presents a new approach of combined thermodynamic and oxygen isotope fractionation modelling applied to fluid-rock interaction in subduction zones. It is an important step forward in using oxygen isotopes as a tool to track fluid-rock interaction because the oxygen isotope compositions of minerals and fluids can be predicted taking into account successive changes in pressure-temperature conditions. This approach can also be applied to other geological settings and the results of such modelling are relevant for interpreting oxygen isotope data of natural samples.

I have made several specific comments that should be useful to improve clarity and consistency in the text. One aspect that can be expanded upon, in my opinion, are the implications for interpreting oxygen isotope data of natural samples and providing links to observed oxygen isotope variations and the interpretations made thereupon.

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).

### **Specific comments:**

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

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.

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.

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).

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

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).

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 CO<sub>2</sub> 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.

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. 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.

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.

234: Glaucofane 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 glaucofane, 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.

236: The liberation of water from the carbonate sediment is specified, but release of CO<sub>2</sub> is not mentioned. Does any release of CO<sub>2</sub> occur? Carbonate phases appear to remain stable, but the aspect should still be briefly explained for clarity.

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.

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.

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.

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

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.

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

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.

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.

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).

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.

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?

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

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

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.

528-530: I have not checked or tested this version since I am not a user of Matlab.

Figures:

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 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.

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

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).

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

**Technical corrections:**

- 13: composed of
- 14: assemblages (plural, since mafic crust and sedimentary cover are considered)
- 28: reactions (plural)
- 45: An alternative approach follows what has been ...
- 48: Such an approach
- 52: fluid/rock ratios (plural)
- 56: in the last two
- 67: Delete "on average"; instead: "lithosphere is typically composed of a section of igneous oceanic crust ..." (adding igneous helps to clarify the sedimentary cover is considered separately).
- 78: Replace "is due to" with "was chosen to take into account" (to clarify that it was intentionally chosen).
- 79: unsatisfactory models (adjective)
- 83: migrates
- 87, 88: crust-derived (hyphen required because words cannot stand on their own)
- 101: P and T are already used in line 58, so the abbreviations should be explained there (that is, where they are first used in the text).
- 108: accounted for in the ...
- 143: Typo: "the its" – please correct
- 172: Replace "following" by "subsequent"
- 205-207: Sentence structure: For either composition, the volume of ... decreases from 480 °C and 1.90 GPa until complete ...
- 208: Replace "higher conditions" by "higher grades" or "higher P-T conditions"
- 229: 2.60 should probably be 2.06?
- 235: 2.03 should probably be 2.30?
- 253: Typo: starting
- 275, 276: Do these changes occur over the total temperature range modelled? Please specify.
- 282: decrease by
- 283: decrease by a maximum of
- 288: most of the fluid
- 318: decreases by
- 350: extent
- 393: measurements of oxygen isotopes
- 395, 396: Check citations Vielzeuf et al. (2005 or 2005a and 2005b).
- 426: what has been described
- 483: Replace extensive with pervasive.
- 503: "carbonaceous" instead of carbonatic
- 785, 787: "mixture" instead of "mixing"
- 826: all three