

## ***Interactive comment on “Tracing fluid transfers in subduction zones: an integrated thermodynamic and $\delta^{18}\text{O}$ fractionation modelling approach” by Alice Vho et al.***

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The manuscript by Vho et al presents a new phase equilibria- $\delta^{18}\text{O}$  model capable to predict  $\delta^{18}\text{O}$  variations in rocks and fluid, potentially at a very large scale, in subduction zones. There is no doubt that this work is timely and could have a significant impact on an international scientific audience. There is also no doubt that this work represents an important step forward towards understanding fluid-rock exchanges in subduction zones (and not only). Although, in my opinion, additional steps will be needed to improve this tool in the future, this early work certainly represents an excellent start. My sincere congratulations for the great work. Below I will list a series of issues that are

C1

not considered (or not clearly explained) in the text, and that may potentially impact the results and interpretations of the modeling (I think they really do impact the results). For the sake of clarity, I am not suggesting modifying the code or the presented models for this paper, but rather to clarify that these missing (?) issues are part of the assumptions of this early study. In my opinion, this would avoid unnecessary criticisms during this fundamental stage of development.

- Chemical system: carbon is not present in the list at line 164. It certainly exists in the models (carbonate present), but it is not clear if  $\text{CO}_2$  (as well as other species such as  $\text{CH}_4$  and  $\text{H}_2$ ) in the fluid was considered or forced not to form. It is clear, however, that  $\text{CO}_2$  and other species (if any) were not considered in the  $\delta^{18}\text{O}$  budgets (line 118). Same for S. A sentence should be added. - The text should clarify if  $\text{CO}_2$  was considered as a negligible parameter in this model (non just not considered). To be honest, I do not see how percolation of potentially high fluid fluxes through the carbonate layer should not mobilize (not just equilibrate) a large portion of the bulk carbonate O. Take the example of Ague and Nicolescu (2013 Nat Geo): an almost complete carbonate devolatilization along a fluid channel. Or the reverse carbonation (Piccoli et al 2016; Scambelluri et al 2016). Can O-bearing fluid species other than  $\text{H}_2\text{O}$  modify the model assumptions? If yes (e.g. Baumgartner and Rumble), something should be said. If not, why? The sentence at line 118 is not enough in my opinion and a more detailed presentation of the related biases should be provided. - There is no mention to the potential effect of evolving redox (e.g. when  $\text{H}_2\text{O} + \text{CH}_4$  go to  $\text{CO}_2 + \text{H}_2$ ) on the  $\text{H}_2\text{O}$   $\delta^{18}\text{O}$ . Of course, the cap delta between  $\text{H}_2\text{O}$  and minerals would not change, but the relative signatures would. This should be at least mentioned and/or justified. This is relevant because, for example, in the terrigenous layer, a fluid in equilibrium with graphite (not considered in the model) may be strongly enriched in one or the other C-bearing species relative to  $\text{H}_2\text{O}$ . - Still on line 118: although the choice of considering molecular fluid species only does not fully reflect the technical means we have today (e.g. DEW model), I agree that this is probably the right choice for this early contribution. However, especially because this study centers on fluid-rock interactions

C2

and metasomatism, the effect of omitting ionic species and their effect of potentially large mineralogical/mass changes has to be introduced. The manuscript cites a series of natural examples of strong fluid-mediated O resets. These rocks are in most cases associated with dramatic major element variations that cannot be explained without species more complex than molecular H<sub>2</sub>O. The possibility that these species have a negligible effect on the  $\delta^{18}\text{O}$  of the system has to be demonstrated. For example, the  $\delta^{18}\text{O}$  cap delta between HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>O at room T is about 40‰. At higher T it should be lower, but maybe still significant if present in large amounts. At least for the carbonate layer, species like HCO<sub>3</sub><sup>-</sup> may be important at the considered conditions (see Facq et al 2014 GCA). Here again I suggest providing more details on these assumptions and potential biases. See also the potential effect of pH on stable isotope variations (Ohmoto 1972). - F/R ratios. The only values of F/R ratios that I could find in the text (apologies if I am wrong) appear very low to me, especially in the case of channelized fluid flow. As time is present in the proposed model, it could help having some idea on how the proposed fluid/rock ratios translate into time-integrated fluid fluxes. The proposed values should at least in part correspond to the time-integrated fluid fluxes estimated in pervasive vs. channelized fluid systems in crustal settings (see review by Ague 2014 for example). F/R ratios alone do not provide insights on the hydrology of the systems and are sometimes meaningless (Baumgartner and Ferry 1991). I understand that many times this choice is imposed by the numerical code itself, but here you have the means to do this conversion at least once in the text, for reference. This could be also introduced at line 52.

Line 19: bulk  $\delta^{18}\text{O}$  value: in the source? Line 85: and also on the fluid speciation... that is not considered here but that can strongly modify the  $\delta^{18}\text{O}$  evolution of the fluid/rock system. For example, at 500 °C, the Cc-H<sub>2</sub>O and CC-CO<sub>2</sub> cap delta for O differ by about 6‰. Line 110: "excluding" is misleading in my opinion. You mean removing from the reactive bulk, right? 161: can you clarify the meaning of natural profiles? Line 181-182: do the chosen values take into account processes like decarbonation? 193: this sounds like a model-driven assumption. Could you clarify? 323:  $\delta^{18}\text{O}$  of the

C3

water: this is still a model assumption. I would say fluid instead. 344: increase in bulk  $\delta^{18}\text{O}$ : increase in the reactive bulk  $\delta^{18}\text{O}$ ? 345: reactive bulk  $\delta^{18}\text{O}$ ? 361-366: Here is where I miss the effect of decarbonation/dissolution and species other than H<sub>2</sub>O in the model. I suggest adding a sentence to recall the assumptions. 492: Airaghi et al: I suggest adding a couple more reference on this topic.

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C4