

Dear Editor, Dear Reviewer,

We appreciated the constructive and helpful comments that shed light on important details that were missing in the previous version of the manuscript. We have addressed the suggestions given by the reviewer and the point-by-point response is reported in the following.

Best regards,
Alice Vho and co-authors

Chemical system: carbon is not present in the list at line 164.
It has been specified which lithologies contain carbon (line 177).

It is not clear if CO₂ (as well as other species such as CH₄ and H₂) in the fluid was considered or forced not to form. It is clear, however, that CO₂ and other species (if any) were not considered in the 18O budgets (line 118). Same for S. A sentence should be added.

We acknowledge the comments of both the reviewers about the importance of C since it is present both in the altered MORB and in the carbonate sediment. A sentence has been added at the end of the section 2.2 (line 118 in the original manuscript) that refers to the newly added discussion about the amount and possible effects of CO₂ in our model (section 3.2, see also the answer to the comments from reviewer 1). The implementation in the model of other species (i.e. CO₂ as well as CH₄, H₂) could be assessed, provided that (1) reliable constraints on the oxygen isotope fractionation between these species and water or minerals are determined and (2) their consistency with other available data is established. However, CH₄ and H₂ do not contain any oxygen, being less relevant for the model than CO₂. This point has been added in the section 4.6 “Model applications and future directions”.

S is not present in any of the considered bulk compositions and therefore no S species are involved in this model. Moreover, oxygen isotope fractionation between water and S-species is poorly constrained, especially at T > 350 °C, where no data are available.

The text should clarify if CO₂ 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 H₂O 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.

A discussion on the possible effects of CO₂ in our model have been added in section 3.2 (see above and answer to reviewer 1). The anticipation of future directions that might consider decarbonation/carbonation reaction, or more in general mineral dissolution, transfer and re-precipitation has been added in the section 4.6 “Model applications and future directions”.

There is no mention to the potential effect of evolving redox (e.g. when H₂O+CH₄ go to CO₂ + H₂) on the H₂O δ18O. Of course, the cap delta between H₂O 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 H₂O.

This effect of oxidation state on C, S and Cl stable isotope partitioning has been described (e.g., Chacko et al., 2001; Sharp, 2017). As explained by Sharp (2017), oxygen has one oxidation state and so it is not affected by the redox changes that occur in most of the other elements used for stable isotope studies. The heavy isotope of oxygen will be preferentially fractionated into short, strong chemical bonds (such as Si^{4+}) generally with a high oxidation state, however this is not always the case (for example, uraninite U^{4+}O_2 strongly incorporates ^{16}O relative to quartz), so that oxidation state alone does not always correlate with oxygen isotope enrichment. Therefore no evolving redox effect has been considered.

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 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 H₂O. 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 capdelta between HCO_3^- and H_2O 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_3^- 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.

Oxygen isotope partitioning between HCO_3^- and H_2O (as well as for other dissolved C-species) are poorly constrained and the data are obtained at low T (i.e. Halas and Wolacewicz, 1982, 25 – 45 °C; Usdowski and Hoefs, 1993, 19 – 25 °C). Therefore, any extrapolation to the temperature range relevant for this model and discussion on possible effects on the $\delta^{18}\text{O}$ partitioning among phases is disputable.

The study of Facq et al. (2014) points out the importance of HCO_3^- and CO_3^{2-} based on experiments on a very special system (a single aragonite crystal in water). They conclude that ion-pairing in deep crustal and mantle aqueous fluids may occur during the dissolution of carbonate minerals at high pressure, even if in natural system the complex interplay of pressure, temperature, and activity ratios imposed by the silicate and/or carbonate environment must be considered. Even if we would consider the presence of these C-species instead of CO_2 at high pressure, and we would assume to be able to extrapolate up to 700 °C the low T experimental data for oxygen isotope fractionation among them and H_2O (Usdowski and Hoefs, 1993), the fractionation between $\text{HCO}_3^- / \text{CO}_3^{2-}$ and H_2O is smaller than the one between CO_2 and H_2O , resulting in an even smaller effect than the one discussed for CO_2 in section 3.2. We acknowledge the importance of this study, but we believe that this is a very specific point still under investigation and there are too many uncertainties in the available data to consider it at this stage of the model. However, we mention the possibility of introducing additional C-species in future developments in the section 4.6 “Model applications and future directions”.

See also the potential effect of pH on stable isotope variations (Ohmoto 1972).

Ohmoto (1972) described the effect of pH on S and C stable isotopes. The effect of pH state on C and S stable isotope partitioning has been described also in the more recent studies (Chacko et al., 2001; Sharp, 2017). No major pH effect on O stable isotope partitioning has been recognized with the exception of Fe(III)-oxides, for which large variations in experimental results at $T < 40$ °C might be attributed also – but not exclusively – to the difference in pH (Chacko et al., 2001).

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.

Values for integrated fluid/rock ratios (as defined in section 2.1, lines 88 – 89) in the sediments have been added in the results (section 3.3.1). In case of high interaction, the integrated F/R ratios are 0.75 kg/kg in the carbonate sediment (corresponding to 2.1 F/R volume ratio) and 0.35 kg/kg in the terrigenous sediment (corresponding to 0.98 F/R volume ratio). They drop to 1/2 in case of partial interaction. These values are consistent with the F/R ratios calculated by Konrad-Schmolke et al. (2011) of 0.15 – 0.3 for weakly deformed samples and 0.5 – 4 for mylonites in the Sesia Zone. Ague (2014) calculates fluid fluxes in the order of 1000 m³/m² (and up to 10⁴ – 10⁵ m³/m² in case of channelized fluid flow) for crustal column of 15 km. Our crust is 1 km thick and the fluid fluxes are 160 – 170 m³/m², therefore comparable in the order of magnitude with the one calculated by Ague (2014).

Line 19: bulk $\delta^{18}\text{O}$ value: in the source?

Yes. It has been specified (line 17).

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-H₂O and CC-CO₂ cap delta for O differ by about 6‰.

A discussion about the effect of a mixed H₂O-CO₂ fluid on the $\delta^{18}\text{O}$ has been added in the section 3.2 “Production of aqueous fluid” (see above).

Line 110: “excluding” is misleading in my opinion. You mean removing from the reactive bulk, right?

The term “removing” has been used instead of “excluding”.

161: can you clarify the meaning of natural profiles?

The sentence has been modified for clarity (line 173).

Line 181-182: do the chosen values take into account processes like decarbonation?

Those are the starting $\delta^{18}\text{O}$ values (25 – 35 ‰, retrieved from marine sediment measurements, where no decarbonation occurred). Possible decarbonation during subduction might decrease the starting $\delta^{18}\text{O}$ (i.e. because calcium carbonate has usually higher $\delta^{18}\text{O}$ than the bulk $\delta^{18}\text{O}$), and indeed the $\delta^{18}\text{O}$ of carbonate in HP metamorphic terrains could be lower. However, as already mentioned, decarbonation has not been considered at this stage of the investigation, but represents an important, although challenging, development as has been stated in the section 4.6.

193: this sounds like a model-driven assumption. Could you clarify?

The sentence has been modified (lines 206 – 208) to clarify that the choice of the serpentine $\delta^{18}\text{O}$ = 2.5 ‰ has been done in order to maximize the difference in $\delta^{18}\text{O}$ between the fluid-source and the fluid-sink lithologies, while using a feasible value for natural serpentinites. Any interaction with higher- $\delta^{18}\text{O}$ serpentinite-derived fluids will just reduce the effects described in this study.

323: $\delta^{18}\text{O}$ of the water: this is still a model assumption. I would say fluid instead.

The text has been modified accordingly (line 357).

344: increase in bulk $\delta^{18}\text{O}$: increase in the reactive bulk $\delta^{18}\text{O}$?

Yes, the text has been modified accordingly (line 373).

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345: reactive bulk $\delta^{18}O$?

Yes, the text has been modified accordingly (line 373).

361-366: Here is where I miss the effect of decarbonation/dissolution and species other than H_2O in the model. I suggest adding a sentence to recall the assumptions.

The assumption has been recalled (line 393).

492: Airaghi et al: I suggest adding a couple more references on this topic.

Few more references have been added (Cartwright and Barnicoat, 2003; Engi et al., 2018; Konrad-Schmolke et al., 2011; Rubatto and Angiboust, 2015) (line 549).