

Answer to Referee 2:

First of all, we would like to thank Referee 2 for the relevant comments and for acknowledging the importance of the present study. The referee raised several questions about the partitioning experiments, to which we answer as follows:

Comment 1: The results outlined in table 2 show that some silicates have been extracted from the silicate melt and dissolved into aqueous fluid, varying from 0.7% to 11.1% in H₂O and 12.8% in the NaBr solution. This change in the composition may greatly influence the solubility and therefore partitioning of Br. As stated in this paper, Br complexation with alkalis is an efficient transfer mechanism, therefore, with up to 12.8% silicate components going into the fluid, including Na₂O and K₂O may drastically change the partitioning coefficients attained in this study. Can any limitations on this effect be noted in this study?

Answer:

We did not observe Br-Na complexation until more than 50-60 wt% Si and Na were dissolved in the aqueous fluid (Table 3, Fig. 6), so we do not expect any complexation with alkalis to have occurred in the fluid in the partitioning experiments.

Further explanations for the scattered D_{Br} values and the lack of pressure-density-composition trends are given in the answer to Referee 1 and have been added to the revised manuscript (**Lines 316-342**).

Comment 2: In Table 2, point 5, it is stated that solubility of silicate components into the aqueous fluid is calculated from albite solubility data of Anderson and Burnham (1983) – how reliable is this? How similar in compositions are yours from theirs?

Answer:

The ideal way to estimate the high *P-T* fluid composition requires knowledge of partition coefficients for Si, Na, K and Al between granitic fluids and melts. Those data are currently lacking and Anderson and Burnham's solubility data (as well as Wohlers et al., 2010) are the closest composition we found to describe the exchange between the haplogranite melt and the aqueous fluid.

In general, our system involving peralkaline haplogranite glass is expected to contain more alkalis than the albite-H₂O system. Yet, as mentioned above, the amount of dissolved Si and Na in the high *P-T* aqueous fluid remains low enough to prevent Br-Na complexation. Thus, the uncertainties in our fluid composition calculations are not expected to significantly affect Br partitioning behaviour.

Comment 3: Please could you display the Br concentrations in both phases as well as the *D* values calculated?

Answer:

Bromine concentrations were not directly determined in this study because the D_{Br} values were directly calculated from the fluorescence signal after correction for the density and effective transmission of each phase. Accurate back calculations of the bromine concentrations from the partition coefficients require estimations of the volume of melt and fluid in the high *P-T* chamber, which are difficult to estimate since 1) the volume of hydrous melt is different from that of glass initially loaded in the cell and 2) the 2D visual observation do not enable to take into account changes in the thickness of the Re gasket with increasing *P-T*.

Nevertheless, to better address the referee's comment, we recalculate Br concentrations in the high *P-T* fluids and melts from the partition coefficients, assuming that the fluid:melt volumetric ratio was similar to the initial fluid:glass ratio. We consequently provide in the text (**Lines 339-341**) the range of concentrations of Br in the melts at the investigated *P-T* condition and report Br concentrations in the coexisting fluid and melt in Run1 on Figure 2. However, as those numbers are only indicative and have an unknown uncertainty, we prefer not to report them in Table 2. It should be stressed that these uncertainties are almost cancelled in equation (1) and *D* values are calculated with better accuracy (errors <10%).

Comment 4: Table 2- References such as Wohlers et al., 2012 are missing from the reference list.

Answer:

The missing reference was added to the reference list.

Comment 5: Partitioning was determined via the intensities of Br in the fluid and the melt (equation 1), with Figure 2 showing Br K α intensity maps which are utilised to calculate Br concentrations. In this figure, the Au displays that its intensity is similar, if not greater than that of Br rich phases this could be a function of the gating used during analysis, as Br K α is 11.9, and Au L β is 11.5 which might explain its relative intensity on par with the measured Br. This begs the question: what gating size was utilised in this analysis, and did it have any effect on the overall Br concentrations recorded?

Answer:

It should be noted that Br fluorescence spectra were always collected far away from the Au chip, so that no Au signal was detected in the spectra. The Au L β was only observed in the spectra when analysis were taken $\sim 5 \mu\text{m}$ away from the Au chip (horizontal beam size $8 \mu\text{m}$) thus demonstrating the excellent beam shape and resolution, as well as the lack of secondary excitation that could compromise the quantitative analysis. **A sentence addressing this issue has been added to the revised manuscript (Lines 224-229).**

Comment 6: Br concentration was determined in the starting composition mixtures by various techniques. Noting the limitations of measuring Br via EPMA due to the overlap with Al (lines 104-106). However, by calculating the overlap of Br using the L β line one can accurately measure Br efficiently; this can be used to check your RBS data and to be consistent between all measurements

Answer:

We thank the reviewer for this comment and will consider this option in future work.

Comment 7: Partitioning of Br is not measured in the same composition as those studied for speciation, making any comparison challenging.

Answer:

As Referee 1, Referee 2 argued that comparing the partitioning and speciation data may be challenging due to the different glass/melt compositions investigated in the two different set of experiments. **This comment has been addressed in the Answers to Referee 1 and a note has been added in Lines 479-482** to clarify this point and emphasize the similarities between the haplogranite and NS2 systems.

Comments 8 and 9: Once plotted all D values, versus P or T, shows little relationship and a lot of dispersion. Which makes it difficult in understanding how the partitioning of Br may vary along a subduction zone. Also, plotting D values in a density plot against P and T show no clear trends. Can this be discussed?

Can further discussion go towards how your results depict a change in Br partitioning with subduction?

Answer:

Explanations for the lack of P-density-composition relationship have been provided to referee 1. In the present manuscript, the fluid-melt partition coefficients are only used to discuss the capacity of fluids and melts to incorporate Br (and Cl, by extension) and carry it inside and outside the subducting slab. Our conclusion is that both fluid and melt can be efficient media to mobilize Br and transfer it to the mantle wedge. We now further underline this point by reporting an average D_{Br} value in the

abstract (**Lines 20-21**). We also point to the fact that a previous study by Bureau et al. (2010) also did not display any obvious P dependency at $P > 0.2$ GPa (**Lines 327-329**).

Comment 10: Figure 3 – the label at the bottom of the graph is not correct – this shows that Br preferentially is partitioned into the fluid. Br should have partitioned into both phases, but preferentially into the fluid.

Answer:

The point has been taken and the misleading labels were changed to ‘*Br partitions preferentially into the fluid/melt*’.

Comment 11: Were any standards measured at the synchrotron under the conditions tested, or are all the results based on those referenced in the paper such as Ferlat et al 2002 etc? If so a plot or a discussion of how good the fit to each speciation might be useful.

Answer:

A NaBr powder was analysed as the structural standard. This sample however yielded a noisy spectrum, probably due to some issues with the preparation of the pellet. Thus, we used the 3 wt% NaBr solutions (room conditions) and added the extra fit for the Ferlat et al. 2002, to ensure that our fitting procedure also enabled us to reproduce previous EXAFS analyses.

Additional comments:

- The title has been updated to specify the nature of fluids (ie., aqueous) and melts (ie., silicate).
- Supplementary materials have been incorporated into the main manuscript text to better provide the reader with as many details as possible and to better address the reviewers’ concerns (**Lines 103-108; 115-118; 121-130**).
- A set of dashed lines was added to Figure 5 to underline the shift of EXAFS oscillations with change in composition. The caption of the figure was changed accordingly.