

Interactive comment on “Bromine speciation and partitioning in slab-derived fluids and melts: Implications for halogens recycling in subduction zones” by Marion Louvel et al.

Anonymous Referee #2

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This paper sets out to explore the partitioning of bromine (and therefore Chlorine by proxy) between silicate melts and aqueous fluids and to also determine the speciation of bromine within these fluids. This is an important area to investigate, as pointed out by the authors, to understand how subduction zones constrain the recycling of trace elements and metals, and to quantify the halogen fluxes to the atmosphere via volcanic degassing, which is vital for understanding climatic influences they may subsequently cause. Understanding the effects of halogens and other volatiles on these processes is vital. Therefore, this study should be published as it adds partitioning and speciation data to the literature; however, some minor concerns should be clarified.

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Firstly, the authors set about trying to attain Br partitioning between a fluid phase (water or NaBr solutions) and a haplogranite melt by performing diamond anvil cell experiments. I would like a little clarification on the following:

- 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?
- 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?
- 3) Please could you display the Br concentrations in both phases as well as the D values calculated?
- 4) Table 2- References such as Wohlers et al., 2012 are missing from the reference list
- 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?
- 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

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Al (lines 104-106). However, by calculating the overlap of Br using the Lb line one can accurately measure Br efficiently; this can be used to check your RBS data and to be consistent between all measurements.

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

8) 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?

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

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.

Unfortunately, I am not an expert in EXAF analyse and so cannot comment on the methodology employed here. However, whilst reading other papers such as Cochain et al 2015, they discuss the reference material that they employed in measuring Br speciation. 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.

Overall, I found that this paper is expanding our current knowledge of Br speciation by performing experiments between fluid and melt at higher pressures, and so should be published. If the above comments are addressed, I think that this will be a great addition to the literature in this area.

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