

Answer to Referee 1:

First of all, we would like to thank Referee 1 for appreciating the relevance of our *in-situ* study to further the current understanding of halogen deep cycle.

The referee's concerns are addressed as follows:

Comment 1: The results about partitioning are equivalent to those of a previous published study by another group (nothing new) and the discussion about one low pressure result (at 0.2 GPa) is not convincing (see specific comments below). The results about bromine speciation in high pressure fluids are new and they deserve to be published, unfortunately the partitioning of Br is not measured for the same chemical system (haplogranite, HPG) than its speciation ($\text{Na}_2\text{Si}_2\text{O}_5$, NS2), which makes any comparison difficult. Therefore I would recommend to delete the part about partitioning, or at least to provide convincing explanation (see specific comments), and to focus on the speciation results.

Answers:

- While the *in-situ* Br partitioning experiments are not the first of their kind, they provide a unique opportunity for cross-checking experimental reproducibility and thus, we believe they deserve to be included in the manuscript. References to previous work by Bureau can be found throughout the manuscript and the favourable comparison between their and our studies further supports the reliability of the *in-situ* measurements. It should be stressed that *in-situ* measurements as those reported here and in rare previous work are extremely challenging, but the only reliable way to assess element partitioning and speciation at extreme P-T conditions, and thus any new data would be a valuable contribution to the field. **Therefore, we prefer to keep the partitioning experiments as part of the current manuscript.**
- Partitioning experiments involved haplogranite melts (Si, Al, Na, K), while Br speciation in melts could only be determined for sodium disilicate ($\text{Na}_2\text{Si}_2\text{O}_5$) due to insufficient Br concentrations in the haplogranite melt (400-2000 ppm Br). Yet, both XANES and EXAFS analyses (Figures 4 and 5; Table 3) show that Br local environment is very similar in the haplogranite and NS2 glasses. Thus, it can be expected that Br incorporation mechanism in both melts is similar and controlled by the presence of alkalis, either Na or K, and that all peralkaline silicate melts will have affinity to incorporate high amounts of Br under high P-T conditions. A note has been added in **Lines 479-482** to clarify this point and emphasize the similarities between the haplogranite and NS2 systems.
- We believe that underlining the differences between our low $P D_{\text{Br}}$ (4.8 at 800 °C, 0.2 GPa) and those of Bureau et al. and Cadoux et al (17.5-20.2 at 900 °C, 0.2 GPa) is of relevance to this study to **highlight that significant amounts of Br (and Cl) may be retained in degassed lavas, as reported in natural context.** The discussion has been modified to highlight this point (**Lines 356-364**).

Comment 2: Br partition coefficients (D) are measured *in situ* for HPG system within the range 0.2 – 1.7 GPa and 592 – 840 °C: they are ranging from 4.1 to 15.3, they fall in the same range than those from Bureau et al., 2010, for similar conditions (0.66 – 1.7 GPa, 590-890°C, D from 2.18 to 9.2). However, if one plots all results in a diagram D versus pressure, data exhibits a lot of dispersion and no real relationship, as it should be expected (i.e. an increase of D with decompression due to degassing). This is not discussed at all.

Answer:

- Referee 1 was right to point out the dispersion of the data and the apparent lack of correlation with P. A similar lack of pressure dependency (as well as density, or composition) has previously been reported for vapour/brine partitioning of some metals (Cu, Au, Ag). It was suggested that large differences in the speciation of these elements in both phases could be

responsible for such a behaviour (Pokrovski et al., 2008). We thus suggest that the large differences in Br chemical and structural environment in between the coexisting fluid and melt phase could as well explain the scattered D_{Br} in our study and the apparent lack of simple trends with P, density or dissolved silicate content, since the physical-chemical controls of Br in the two phases are very different due to the different speciation. We would also like to point out that with a single exception at 0.2 GPa, all our data were recorded at $P > 0.5$ GPa, where the existing studies have also shown that D_{Br} values do not change significantly with pressure and exhibit a similar degree of scattering, between 1 and 10 (Bureau et al., 2010).

- We also note that additional discrepancies may arise from uncertainties on the estimation of the fluid composition, which will affect the calculated D_{Br} . We, for instance, recognize that the large D_{Br} value obtained at 1.7 GPa is clearly off the trend, probably due to the fact that the fluid composition was calculated using the albite solubility data of Wohlers et al. (2011) instead of Anderson and Burnham (1983), to take into account the higher P conditions in this experiment.
- We have added an additional discussion in the revised manuscript, both in the Results section (**Lines 316-342**) and in the Methods section, where we provide additional details about uncertainties on fluid and melt compositions and how they translate to the D_{Br} (**Lines 179-186 and 240-258**). We also agree with this referee that the discussion of the temperature effect in a single experimental run was of weak relevance in terms of partitioning behaviour, and hence we have removed it from the revised manuscript.
- The conclusions drawn from our partitioning experiments, however, remain unchanged: we confirm that although Br preferentially partitions into the aqueous fluid over silicate melt, high amounts of Br can yet be incorporated in hydrous granitic melts. To strengthen this argument, we added an estimation of Br concentration range in the high P-T melts of this study, calculated using the in-situ D_{Br} and initial phase proportions (**Lines 339-340**).

Comment 3: About the same value of D is obtained at 0.9, 0.8, 0.65, 0.2 GPa, respectively 4.4, 4.2, 4.1, and 4.8. High values of D are obtained at high investigated pressure (15 at 0.9 GPa and 9.7 at 1.7 GPa) where unity would be expected due to imminent total miscibility. Why? Such a discrepancy may be due to the pressure determination. The authors use the diffraction of gold and its equation of state. However, it is well known that gold diffraction is not a good tool to for low pressure determination, as an example see Heinz and Jeanloz, JAP, 1983, where the first measurements are performed at 4.42GPa. Furthermore, in a recent intercomparison of the use of EOS for pressure determination (including Au), Ye et al., JGR, 2017, it is conclude that at high temperature, accuracy cannot be better than 1 GPa, from 2.5 GPa up to 140. For that reason, the discussion from line 278 to 294 is not relevant and should be suppressed.

Answer:

- The choice of gold as the in-situ pressure calibrant was motivated by its chemical stability in high P-T fluids and melts. Although we agree that the absolute accuracy of this method may not be better than 1 GPa (Ye et al., 2017), the actual relative precision is much better and is likely to be within 10% of the P value, as reported in Louvel et al. (2014). Moreover, the unit cell volume of Au displayed systematic changes as a function of increasing P-T in the HDAC, thus demonstrating that Au is sensitive to relatively small pressure changes during the run, and special care was taken in the HDAC alignment/centering to preserve the sample-detector distance to ensure the reliability of the unit cell volume variations. Therefore, we are confident that the relative pressure variations during the run are captured by the Au pressure calibrant. To further support the appropriate pressure determination, we emphasize that the phase relations, including miscibility, in the haplogranite-H₂O system are within the P-T range reported for other alkali silicate systems (e.g. Paillat et al., 1992; Stalder et al., 2000).

- As mentioned above, additional discussion on the uncertainties of our calculations is now added both in the methods and result sections. Note that all fluid and melt properties (composition, density and effective transmission) were calculated assuming an uncertainty on pressure determination of 10% (**Lines 183-186 and 245-246**).

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 Ka 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 ~ 5 μ m away from the Au chip (horizontal beam size 8 μ 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.