

## Experimentally derived F, Cl, and Br fluid/melt partitioning of intermediate to silicic melts in shallow magmatic systems

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### ABSTRACT

The conditions under which halogens partition in favor of an exsolved fluid relative to the coexisting melt are key for understanding many magmatic processes, including volcanic degassing, evolution of crustal melt bodies, and ore formation. We report new F, Cl, and Br fluid/melt partition coefficients for intermediate to silicic melts, for which F and Br data are particularly lacking; and for varying CO<sub>2</sub>-H<sub>2</sub>O contents to assess the effects of changing fluid composition ( $X_{\text{H}_2\text{O}}$ ) on Br fluid/melt partitioning for the first time. The experiments were conducted at pressures 50–120 MPa, temperatures 800–1100 °C, and volatile compositions [molar  $X_{\text{H}_2\text{O}} = \text{H}_2\text{O}/(\text{H}_2\text{O} + \text{CO}_2)$ ] of 0.55 to 1, with redox conditions around the Nickel-Nickel Oxygen buffer ( $f_{\text{O}_2} \approx \text{NNO}$ ). Experiments were not doped with Cl, Br, or F and were conducted on natural crystal-bearing volcanic products at conditions close to their respective pre-eruptive state. The experiments therefore provide realistic constraints on halogen partitioning at naturally occurring, brine-undersaturated conditions. Measurements of Br, Cl, and F were made by Secondary Ion Mass Spectrometry (SIMS) on 13 experimental glass products spanning andesite to rhyolitic compositions, together with their natural starting materials from Kelud volcano, Indonesia, and Quizapu volcano, Chile. Fluid compositions were constrained by mass balance. Average bulk halogen fluid/melt partition coefficients and standard deviations are:  $D_{\text{Cl}}^{\text{fluid/melt}} = 3.4 (\pm 3.7 \text{ 1 s.d.})$ ,  $D_{\text{F}}^{\text{fluid/melt}} = 1.7 (\pm 1.7)$ , and  $D_{\text{Br}}^{\text{fluid/melt}} = 7.1 (\pm 6.4)$  for the Kelud starting material (bulk basaltic andesite), and  $D_{\text{Cl}}^{\text{fluid/melt}} = 11.1 (\pm 3.5)$ ,  $D_{\text{F}}^{\text{fluid/melt}} = 0.8 (\pm 0.8)$ , and  $D_{\text{Br}}^{\text{fluid/melt}} = 31.3 (\pm 20.9)$  for Quizapu starting material (bulk dacite). The large range in average partition coefficients is a product of changing  $X_{\text{H}_2\text{O}}$ , pressure and temperature. In agreement with studies on synthetic melts, our data show an exponential increase of halogen  $D^{\text{fluid/melt}}$  with increasing ionic radius, with partitioning behavior controlled by melt composition according to the nature of the complexes forming in the melt (e.g., SiF<sub>4</sub>, NaCl, KBr). The fundamental chemistry of the different halogens (differing ionic size and electronegativities) controls the way in which partitioning responds to changes in melt composition and other variables. Experimental results confirm that more Cl partitions into the fluid at higher bulk Cl contents, higher melt Na, higher fluid  $X_{\text{H}_2\text{O}}$  ratios, and lower temperatures. Bromine shows similar behavior, though it seems to be more sensitive to temperature and less sensitive to Na content and  $X_{\text{H}_2\text{O}}$ . In contrast, F partitioning into the fluid increases as the melt silica content decreases (from 72 to 56 wt% SiO<sub>2</sub>), which we attribute to the lower abundance of Si available to form F complexes in the melt. These new data provide more insights into the conditions and processes that control halogen degassing from magmas and may help to inform the collection and interpretation of melt inclusions and volcano gas data.

**Keywords:** Halogens, experiments, chlorine, fluorine, bromine, magma, volcanic gas; Experimental Halogens in Honor of Jim Webster