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 CO2–H2O contents to assess the effects of changing fluid composition (XH2O) 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 XH2O = H2O/(H2O +CO2)] of 0.55 to 1, with redox conditions around the Nickel-Nickel Oxygen buffer (fO2 ≈ 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: DCl/fluid/melt = 3.4 (±3.7 1 s.d.), DBr/fluid/melt = 1.7 (±1.7), and DFluorine/fluid/melt = 7.1 (±6.4) for the Kelud starting material (bulk basaltic andesite), and DCl/fluid/melt = 11.1 (±3.5), DBr/fluid/melt = 0.8 (±0.8), and DFluorine/fluid/melt = 31.3 (±20.9) for Quizapu starting material (bulk dacite). The large range in average partition coefficients is a product of changing XH2O ratios, and lower temperatures. Bromine shows similar behavior, though it seems to be more sensitive to temperature and less sensitive to Na content and XH2O. In contrast, F partitioning into the fluid increases as the melt silica content decreases (from 72 to 56 wt% SiO2), 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 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

Introduction

Halogen behavior in magmas impacts a range of crustal processes, including magma evolution, degassing and ore mineralization, by influencing the physical and chemical properties of melts, fluids, and minerals (Aiuppa et al. 2009; Pyle and Mather 2009; Bodnar et al. 2013; Harlov and Aranovich 2018; Webster et al. 2018). Although halogens may partition into crystals, gases, and brine phases, this study concentrates on partitioning of halogens between the melt and aqueous fluid phase. Much previous work has concentrated on Cl, due to its ease of measurement in glasses by electron microprobe; and substantial advances in our understanding of Cl behavior in melts can be attributed to J.D. Webster. Chlorine fluid/melt partitioning (DCl/fluid/melt) behavior has been quantified for a range of silicate melt compositions (Webster and Holloway 1990; Webster 1997; Webster et al. 2014), pressures (Alletti et al. 2009; Botcharnikov et al. 2015;