The effect of halogens (F, Cl) on the near-liquidus crystallinity of a hydrous trachyte melt

YVES FEISEL1,*†, JONATHAN M. CASTRO1, CHRISTOPH HELO1, AND DONALD B. DINGWELL2,3

1Institute of Geosciences, Johannes Gutenberg-Universität Mainz, 55128 Mainz, Germany
2Department für Geo- und Umweltwissenschaften, Ludwig-Maximilians-Universität München, 80333 München, Germany
3Gutenberg Research College, Johannes Gutenberg-Universität Mainz, 55128 Mainz, Germany

ABSTRACT

The effect of F and Cl on the liquidus temperature of a hydrous (~3.5–4 wt% H2O) trachytic melt (~66 wt% SiO2) at 925 to 990 °C and at 100 MPa has been experimentally investigated. We employed a novel disequilibrium approach involving diffusion couple experiments with the two-diffusion couple end-members differing solely in halogen concentrations. A shift of the liquidus temperature by ~50 °C was observed between a halogen-poor and halogen-enriched melt. Each experiment spanned the entire range of F and Cl concentrations between the two end-member compositions. We determined the halogen concentrations at the transition from crystal-bearing to crystal-free melt. These concentrations correspond to the liquidus halogen concentrations of the melt at each experimental temperature. We demonstrate that there is a limiting halogen concentration (~0.19–0.52 wt% F; ~0.07–0.24 wt% Cl), below which the melt crystallizes spherulitic clinopyroxene during heating to the run temperature. At high temperatures, upon diffusion of F and Cl into the halogen-poor melt, those crystals dissolve, leaving behind a dissolution front parallel to the diffusion interface. We propose that the dissolution is a consequence of F and Cl complexing with some of the main cationic components of clinopyroxene (Mg, Fe, Ca), thereby destabilizing this phase. Thus, the experimental dissolution of clinopyroxene is a manifestation of a liquidus depression caused by increased halogen content. Our results show that the liquidus shifts at a rate of ~1575(379) K/mol% of F and Cl in the melt, which is a minimum estimate, assuming both halogens equally drive dissolution. This liquidus depression is valid for a range of halogen concentrations (~0.06–0.87 wt% F; ~0.06–0.36 wt% Cl) and the experimental temperatures. Our findings illustrate that the degassing of halogens during or prior to an eruption can enhance crystallization in the melt and therefore influence magma physical properties that may ultimately affect eruption style.

Keywords: Halogens, liquidus depression, phase equilibria, diffusion couple, crystal dissolution; Halogens in Planetary Systems

INTRODUCTION

Volatile species (H2O, CO2, F, Cl, S, etc.) are important constituents of natural silicate melts and play a crucial role in determining melt properties (e.g., viscosity, density) and a magma’s phase assemblage (e.g., crystallinity, bubble content). Hence they can ultimately control the style of volcanic eruptions (e.g., Gonnermann and Manga 2007). Despite their typically moderate concentrations in magmas, compared to other major volatiles such as H2O or CO2, F and Cl may reach abundances of hundreds of parts per million up to few wt% and, thus may exert significant effects on their own (e.g., Aiuppa et al. 2009; Dolejš and Zajacz 2018). For example, F has long been known to decrease melt viscosity in silica-rich melts in a manner qualitatively similar to that of H2O (Dingwell et al. 1985; Dingwell and Hess 1998; Zimova and Webb 2007; Giordano et al. 2008). By contrast, although the details of the effect of Cl on melt viscosity vary, it has been shown that Cl cannot decrease viscosity with the same efficiency as F and that the effect on viscosity depends on the melt composition (Hirayama and Camp 1969; Dingwell and Hess 1998; Zimova and Webb 2006; Webb et al. 2014). The solubility of Cl in silicate melts has been demonstrated to be roughly an order of magnitude higher in basaltic melts than in rhyolitic compositions and increases with the availability of Mg, Ca, Na, Fe, K, Al, and F in the melt, while decreasing with the concentration of network-forming Si (Carroll and Webster 1994; Signorelli and Carroll 2002; Webster and De Vivo 2002; Chevychelov et al. 2008; Webster et al. 2015; 2018; Thomas and Wood 2021). These findings are consistent with spectroscopy-based investigations, which indicate a preferred complexing of Cl with Ca, Mg, and Fe (Zimova and Webb 2006; Evans et al. 2008; Webb et al. 2014; Bell and Webster 2015). F solubility has also been demonstrated to correlate with the concentration of Ca and Mg where they assume the role of network-modifiers and with increasing peralkalinity [molar (Na+K+Ca)/(Al] > 1; e.g., Koster van Groos and Wyllie 1968; Foley et al. 1986a, 1986b; Mysen et al. 2004; Brey et al. 2009]. Additionally, F dissolution in silicate melts increases in peraluminous melts with excess network-modifying Al in fourfold coordination (Webster et al. 2018 and references therein). F has been shown to replace bridging O atoms (Schaller et al. 1992; Dolejš and Zajacz 2018) and...