Br diffusion in phonolitic melts: Comparison with fluorine and chlorine diffusion

HÉLÈNE BALCONÉ-BOISSARD1,*,†, DON R. BAKER2, BENOIT VILLEMANT3, JEAN CAUZID3, GEORGES BOUDON4, and E. DELOULE5

1ISTEP (UMR 7193)–Sorbonne Université, 4 pl. Jussieu, 75252 Paris, France
2Earth and Planetary Sciences, McGill University, 3450 rue University, Montréal, Quebec H3A 0E8, Canada
3G2R–UMR 7566, Université de Lorraine, BP 70239, 54506 Vandoeuvre-lès-Nancy, France
4Institut de Physique du Globe de Paris, Sorbonne Paris Cité, UMR 7154 CNRS, F-75005 Paris, France
5Centre de Recherches Pétrographiques et Géochimiques, UMR 7358, CNRS-Université de Lorraine, 54501 Vandoeuvre-lès-Nancy, Cedex, France

Abstract

Bromine diffusion was measured in two natural phonolitic melts: (1) a K,O-rich (~10 wt%) one synthesized from the white pumice phase of the 79 AD eruption of Vesuvius (Italy), and (2) a Na,O-rich (~10 wt%) one corresponding to the most differentiated melt of the 12 000 BC eruption of the Laacher See (Germany). Experiments were performed at 0.5 and 1.0 GPa, 1250 to 1450 °C, at anhydrous and hydrous (2.65 ± 0.35 wt% of dissolved water) conditions. Experiments conducted with the diffusion-couple technique in the piston cylinder were performed with only bromine diffusing and with the simultaneous diffusion of a halogen mixture (F, Cl, Br) to evaluate the interactions between the halogens during diffusion. The diffusion profiles of Br were measured by X-ray fluorescence using synchrotron radiation microprobe (SYXRF), ID18F, at the European Synchrotron Radiation Facility (ESRF, France). Bromine diffusion displays Arrhenian behavior under anhydrous conditions that is similar when it diffuses alone and when it diffuses with F and Cl. The Br diffusion coefficients range between 2 × 10⁻¹² m²/s at 1250 °C and 1.5 × 10⁻¹¹ m²/s at 1450 °C for the Na-rich melt and between 3 × 10⁻¹² m²/s at 1250 °C and 2.5 × 10⁻¹¹ m²/s at 1450 °C for the K-rich melt, at 1.0 GPa. Although Br mobility is independent of F and Cl in anhydrous phonolitic melts, its behavior may be dependent on the dominant alkali in the melt, as previously observed for Cl, but not F. For hydrous experiments, although the data are scattered, the Br diffusivity increases slightly with water and the Na/K ratio seems to influence Br diffusivity. Similarly to noble gases, halogen diffusivity at a given temperature in the phonolitic melts appears related to the ionic porosity of the silicate structure. Compared to basaltic melt, Br diffusivities are approximately one order of magnitude lower in the Na-phonolite melt, because of the difference of the pre-exponential factor. Br mobility appears to be decoupled from melt viscosity, considering the results here.

Keywords: Bromine, phonolite, diffusivity, ionic porosity, alkali; Halogens in Planetary Systems

Introduction

Volatile play a significant role in igneous processes; they not only affect magma properties (e.g., viscosity) and therefore transport in magmatic conduits, but also influence diffusion and bubble growth rates, possibly leading to dramatic explosive eruptions. Among the volatiles, halogens (F, Cl, Br, I) have received increasing attention in recent years, despite their low abundances on Earth (e.g., Auuppa et al. 2009). In addition, determination of halogen distributions and the geochemical processes controlling their mass transfer between solid and fluid reservoirs on Earth are relevant since they can be used to address many significant questions in various geoscience fields of research (Hanley and Koga 2018), such as the source and evolution of hydrothermal fluids, and the role they play in ore deposit formation, metamorphic processes, the reconstruction of marine sedimentary paleo-environments, and the tracking of mantle-to-crust mass transfer associated with subduction (Shinozohara et al. 1989; Carroll and Webster 1994; Auuppa et al. 2009; Baker and Balcone-Boissard 2009; Webster et al. 2009; Vigneresse 2009; Lecumberri-Sanchez and Bodnar 2018). Moreover, halogens exert a significant influence on the physico-chemical properties and the structure of silicate melts (Manning 1981; Mysen and Virgo 1985; Webster et al. 1989, 2018; Webster and Holloway 1990; Mysen et al. 2004; Dalou et al. 2015; Grousset et al. 2015).

Halogens are incompatible (lithophile) elements during mineral-melt partitioning and behave as volatile elements. With decreasing ionic size from I to F, halogen anions describe an increasing energy of formation for NaX (where X is a halogen) salts, increasing short-range order in glasses with modifier cations such as Na, K, and Ca (Luth 1988; Zeng and Stebbins 2000; Louvel et al. 2020), and increasing volatility and solubility. Halogen diffusivity in silicate melts is of particular interest because the differences between the diffusivity of water, halogens, and sulfur appear to be significant enough on the basis of the published data (Alletti et al. 2007; Balcone-Boissard et al. 2009; Feisel et al. 2019) that during melt inclusion entrapment (Baker 2008), or during rapid bubble or crystal growth, diffusive fractionation between water and the halogens, and between halogens and sulfur, are expected...