Diffusion of F and Cl in dry rhyodacitic melt

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ABSTRACT

Chemical diffusion of F and Cl has been experimentally determined in a rhyodacitic melt obtained from remelting a sample of Hekla pumice (Iceland). Diffusion couple experiments were conducted in a vertical tube furnace over a temperature range of 750–950 °C and in air for durations of 1 to 35 days. Concentration profiles of F and Cl were obtained for the quenched samples using an electron microprobe.

Fluorine and chlorine exhibit Arrhenian behavior over the range of temperature investigated here. The pre-exponential factors of F and Cl are \( D_0(F) = 4.3 \times 10^{-4} \) and \( D_0(Cl) = 1.6 \times 10^{-4} \) m²/s. Fluorine diffusion coefficients vary in the order of \( 1 \times 10^{-13} \) to \( 1 \times 10^{-11} \) m²/s, whereas Cl diffusivity is up to two orders of magnitude slower. The activation energies for F and Cl diffusivities are equal within error at 223 ± 31 and 229 ± 52 kJ/mol, respectively.

The difference in diffusivity between F and Cl is particularly pronounced in the melt of our study, compared to results obtained for other magmatic melt compositions. This means that the potential for diffusive fractionation exists and may occur especially under conditions of magma ascent and bubble growth, as this would favor partitioning of the relatively fast-diffusing halogens into growing bubbles, due to H₂O exsolution. A dependence of diffusivity on atomic radius observed here is enhanced over that observed in more basic, less viscous melts, indicating that diffusive fractionation is more likely to be pronounced in more silicic, more viscous systems. A proper parameterization and modeling of diffusive fractionation of halogens in actively degassing volcanic systems thus holds the potential of serving as a tool for quantifying the processes responsible for volcanic unrest.

Keywords: Halogens (F, Cl), diffusion, silicate melt, diffusion couple, experimental volcanology

INTRODUCTION

Volatile species are an important constituent of melts and play a significant role in igneous processes. The chemical composition of the volatile phase crucial for the style of volcanic eruptions depends on parameters such as solubility, partitioning, and diffusion of the different species, which in turn are controlled by compositional parameters (e.g., initial volatile content, magma composition) and ambient conditions (e.g., pressure, temperature). While the dominant components of volcanic volatiles are water (H₂O), carbon dioxide (CO₂), and sulfur species, halogens (F, Cl, Br, I) can be highly concentrated in silicic melts (e.g., tin and topaz rhyolite, Carroll and Webster 1994; Webster and Duffield 1994) and are a significant component of volcanic gases (Symonds et al. 1994; Aiuppa et al. 2009; Webster et al. 2018) venting from active silicic volcanic centers. Halogens affect magma viscosity and diffusivities (e.g., Dingwell et al. 1985; Dingwell and Hess 1998; Baasner et al. 2013) as well as phase equilibria (Manning 1981) and directly influence the stability of hydrous minerals and halogen-bearing phases in igneous rocks (e.g., micas, fluorite, topaz; Webster et al. 2018). Schipper et al. (2017) showed that the degassing of F and Cl into isolated pores of slowly cooling magma could cause silica redistribution and the formation of vapor-phase cristobalite.

Halogen degassing is also essential for the formation of ore deposits in active volcanic systems and can have a major impact on Earth’s climate and environment including potential destruction of ozone in the stratosphere (Aiuppa et al. 2001, 2009; Bobrowski et al. 2003, 2007; von Glasow et al. 2009; Boichu et al. 2011; Surl et al. 2015; Roberts 2018). The escape of F and Cl from ascending magma has been argued to occur at relatively shallow depths (Spilliaert et al. 2006). Thus, their study in volcanic gas emissions can help identify and characterize pre- or syn-eruptive volcanic degassing and might augment volcano monitoring.

The potential for widely varying diffusivities between the halogens may mean that diffusive fractionation between the halogens may provide further insights into the timing of magma ascent and volatile exsolution (Alletti et al. 2007). Halogens are also increasingly routinely measured in volcanic plumes.

Despite investigations to date, our knowledge of halogen solubility and diffusivity in silicate melts is far from complete. Rhyolitic volcanoes are commonly known to be the most explosive and hazardous and typically comprise melts with the highest F concentrations (e.g., Aiuppa et al. 2009). Yet, halogen diffusivity data are scant for such systems. Instead, most studies describing volatile behavior in silicate melts have concentrated on H₂O, CO₂, and S. Previous studies on F and Cl diffusion are available for simplified model systems such as albite, jadeite, or Na-aluminosilicate (Dingwell and Scarfe 1984; Dingwell and Scarfe 1985, only for