The effect of composition on chlorine solubility and behavior in silicate melts

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ABSTRACT

We have performed experiments at 1.5 GPa and 1400 °C on 25 different bulk compositions to determine the effects of major element compositions on the Cl contents of silicate melts at known fugacities of Cl₂ and O₂. The experimental method involved mixing a “sliding” Cl buffer, a mixture of AgCl, AgI, and Ag with the silicate bulk composition and performing the experiment in a graphite capsule together with a source of CO₂ (AgCO₃). The graphite capsules were sealed inside welded Pt tubes to maintain a CO₂-CO atmosphere with oxygen fugacity fixed at the C-CO-CO₂ (CCO) buffer.

During the experiment, the Cl buffer segregates leaving a Cl-bearing melt, which quenches to a glass. We used the results to define chloride capacity CCl for each melt at the pressure and temperature of the experiment:

\[ C_{Cl} = \frac{\text{Cl (wt\%)} \times \sqrt{f(O_2)}}{\sqrt{f(\text{Cl}_2)}} \]

Chloride capacity was found to correlate positively with optical basicity and NBO/T and negatively with ionic porosity and the Larsen index. We combined our new data with the results of Thomas and Wood (2021) to derive an equation describing the composition, pressure and temperature dependence of the chloride capacity:

\[ \log C_{Cl} = 1.601 + \left( \frac{4470X_{Ca} - 3430X_{Si} + 2592X_{Fe} - 4092X_K - 894}{T} \right) \]

In this equation, X_{Ca}, X_{Si}, and so on refer to the oxide mole fractions on a single-cation basis, P is in GPa and T in K. The equation reproduces 58 data points with an r² of 0.96 and a standard error of 0.089. The addition of literature data on hydrous experiments indicates that the effects of <4.3 wt% H₂O are small enough to be ignored. We also performed experiments aimed at determining the conditions of NaCl saturation in melts. When combined with literature data we obtained:

\[ \log(Cl^-) = \log(a_{NaCl}) + 0.06 - \left( \frac{2431X_{Ca} + 3430X_{Si} - 2592X_{Fe} + 3484X_{Na} + 4092X_K - 2417}{T} \right) \]

where (Cl⁻) is the Cl content of the melt in wt% \( a_{NaCl} \) is the activity of NaCl (liquid) and the other symbols are the same as before. The results indicate that basalt dissolves ~8 times more Cl than rhyolite at a given NaCl activity i.e., Cl is ~8 times more soluble in basalt than in rhyolite.

Keywords: Basalt, rhyolite, Cl solubility in melts, compositional effects on Cl solubility, Cl degassing, chloride capacity, NaCl saturation in melts; Experimental Halogens in Honor of Jim Webster

INTRODUCTION

The volatile components whose behavior is best understood in silicate melts are H₂O and CO₂ (Symonds et al. 1994; De Vivo et al. 2005). In the case of H₂O, the reasons are its high abundance, the major effects it has on viscosity, the melting and crystallization temperatures of melts, and its importance in hydrothermal ore deposition associated with igneous activity. CO₂ came to be studied experimentally in the 1970s initially because of the observation that carbonatites were magmas with origins in the mantle. More recently concerns about volcano-genic CO₂ as a greenhouse gas have facilitated the establishment of a good database to describe CO₂ solubility in a wide range of melts over a wide range of physical conditions (Brooker et al. 2001; Stanley et al. 2011), allowing for the development of robust models, such as VolatileCalc (Newman and Lowenstern 2002) and MagmaSat (Ghiorso and Gualda 2015).

A third group of elements that are geologically and environmentally important and whose behavior in melts requires further elucidation is chlorine. Chlorine, the second most abundant of the halogens (after F) in both the primitive and depleted mantle, and in the bulk continental crust (Pyle and Mather 2009), is an important ligand in hydrothermal processes and plays a major role in transporting economically important metals such as Au and Cu in solution (Blundy et al. 2015). The