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# The chemical behaviour of halogens in silicate melts

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Although the halogens are minor constituents of magmatic and hydrothermal systems, they comprise important components of volcanic gases. On a molar basis, they are twice as effective as $H_2O$ at suppressing the liquidus temperatures of silicate melts [1]. The aim of this study is to understand the chemical behaviour of halogens in melts by experimentally determining their thermodynamic activities. We used halogen buffers Ag/AgCl, Ag/AgI and Ag/AgBr in which Ag (as oxide) is virtually insoluble in silicate melt under the conditions of the experiment. The buffer controls the fugacity of the halogen of interest. Experiments were performed at 5-20 Kbar and 1200-1500°C in a piston-cylinder apparatus. The effect of oxygen fugacity on Cl solubility was determined using Re-$ReO_2$ and C-$CO_2$ oxygen buffers.

Our experiments show (1) that chlorine solubility in haplobasalt at 15Kbar/1400°C can reach 5 wt%, even at $Cl_2$ fugacities as low as 0.0035 bar. 2) Cl concentration increases linearly with the square root of chlorine fugacity at fixed $f(O_2)$, obeying Henry's law up to ~3% Cl in the melt. Experiments with Icelandic basalt also showed a Henrian relationship with increasing $\sqrt{f}(Cl_2)$ but with lower Cl solubility at fixed Cl fugacity than the haplobasalt (Fig.1). (3) Cl solubility decreases with the fourth root of oxygen fugacity at fixed $\sqrt{f}(Cl_2)$. This implies that $Cl^-$ replaces $O^{2-}$ in the silicate framework as follows:

$$Cl_2^{(gas)}+[O^{2-}]^{(melt)} = 2[Cl^-]^{(melt)}+ \tfrac{1}{2}O_2^{(gas)}$$

For an Icelandic basalt with 9wt% FeO, the Cl content in wt% as a function of the different intensive variables can be expressed as:

$$log\mathrm{Cl}_{melt} = 0.984(64)-((930(70)P)/T)-0.25log(f(O_2))+0.5log(f(Cl_2))$$

From this relationship, we can show that basalts containing the typical concentration range of 0.05-0.5 wt% Cl should only begin to degas their chlorine significantly, as HCl, at pressures in the range 0-5MPa (Fig.2). We also find that Cl solubility at fixed oxygen and chlorine fugacity depends strongly on bulk composition. Cl behaviour is similar to that given by Webster [2] in that increasing CaO and MgO contents and decreasing $SiO_2$ concentration all lead to increasing Cl content.

[1] Filiberto, & Treiman., (2009). Geology, 263, 60–68.

[2] Webster J. D., et. al (2015) Am. Mineral. 100, 522–535.