


# Chlorine in silicate melts: controls on dissolution, bonding, evaporation, and brine exsolution


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Chlorine is an important constituent of volcanic systems and volcanic gases, stabilising in solution metal cations and playing a key role in ore-formation. We report experimentally-determined thermodynamic activities of chlorine in silicate melts, measured using an Ag-AgCl buffer that controls the chlorine fugacity. The major-element composition is not perturbed by the buffer because Ag is virtually insoluble in silicate melts at experimental conditions. 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 by using either Re-ReO<sub>2</sub> or C-CO<sub>2</sub> oxygen buffers, in addition to the Cl buffer. Our experiments show that 2Cl<sup>-</sup> replace O<sup>2-</sup> in the silicate framework, with the equilibrium constant of the dissolution reaction equating to the chloride capacity (C<sub>Cl</sub>, eq1):

 eq1.png

 chap2figure2\_Cl\_vs\_sqrtfcl2\_FORPRESENTATION.jpg

Equation [1] was used to parameterise Cl content as a function of pressure, temperature, the fugacities of Cl<sub>2</sub> and O<sub>2</sub>. Further experiments were then performed on 40 major element compositions ranging from rhyolite to basalt. We found that Cl content increases with temperature and decreases with pressure while Ca, Fe, K and Si are the most important compositional controls on chloride solubility, and <4.3 % H<sub>2</sub>O has negligible effect. Association of dissolved Cl with 2<sup>+</sup> cations was confirmed by XAFS. Parametrisation of the Cl capacities of silicate melts results in the following equation:

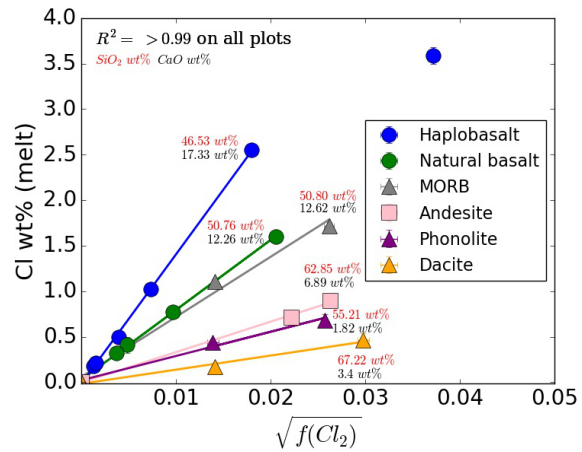
$$\log C_{Cl} = 1.601 + (4470X_{Ca} - 3430X_{Si} + 2592X_{Fe} - 4092X_K - 894P)/T \quad [2]$$

We find that Cl should degas late, and at shallow depths (0-5MPa) during magma ascent. Furthermore, basaltic, silica-poor melts exhibit higher Cl solubilities, and thus lower tendencies to degas HCl, than silica-rich melts which are poorer in Ca and Fe.

Finally, experiments were conducted at NaCl saturation to investigate the activities of NaCl in brines released by natural melts. Combining our results with literature data we find:

$$\log(Cl) = \log(a_{NaCl}) + 0.06 - (2431X_{Ca} + 3430X_{Si} - 2592X_{Fe} + 3484X_{Na} + 4092X_K - 2417)/T \quad [3]$$

Where (Cl) is the Cl content of the melt in weight %, and a<sub>NaCl</sub> is the NaCl (liquid) activity. Our results show that basalt dissolves approximately 8 times as much Cl as rhyolite at a given NaCl activity and that 0.5% Cl in rhyolite corresponds approximately to NaCl saturation (a<sub>NaCl</sub> = 1) at 900°C.



$$C_{Cl} = \frac{Cl \text{ (wt\%)}}{\sqrt{f(Cl_2)}} \times \sqrt[4]{f(O_2)} \quad [1]$$