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Chlorine solubility and partitioning in hydrous silicate melts: high-pressure and high temperature insights from basalts to rhyolites

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We determined the solubility and behaviour of chlorine in hydrous silicate melts, ranging from MORB to high-silica rhyolite, at high pressures (0.5-1.5 GPa) and temperatures (1200-1300°C) using the chlorine fugacity control method of Thomas and Wood (2021). By systematically increasing the water content of the melt from 0 to 4 weight % while maintaining fixed chlorine and oxygen fugacities, we found that the addition of H_2O increased chlorine concentration under all conditions studied.

To develop a comprehensive equation for chlorine solubility, we combined our data for hydrous basalt, andesite, dacite and rhyolite (40 experiments) with 60 results from anhydrous compositions ([1],[2]). We define the chloride capacity (CCl) for each experiment as (eq. 1):

We fitted the results using stepwise linear regression, including terms for pressure, temperature, and composition. Non-significant terms ($\alpha = 0.05$) were excluded, resulting in the following fit equation, where P is pressure in GPa, and XSi and XCa are the mole fractions of SiO_2 and CaO, respectively (eq. 2):

The standard error of the fit is 0.083, with $R^2 = 0.963$. Surprisingly, the term in $HO_{0.5}$ was not significant, suggesting that water behaves as an ideal diluent for chlorine.

We applied our chloride capacity equation to calculate the activity of NaCl in hydrous melts of known chlorine content. This method combined chloride capacities with Na_2SiO_3 and SiO_2 activities derived from the Rhyolite-MELTS program. Additionally, we derived an expression for calculating HCl fugacity in a fluid in equilibrium with the experimental melts. We used these two expressions to calculate equilibrium partitioning of chlorine between NaCl and HCl in both our hydrous experiments and a range of literature experiments. Finally, we used these expressions to calculate fluid compositions in equilibrium with melt inclusions from various volcanic settings.

[1] Thomas, R. W., & Wood, B. J. (2021). The chemical behaviour of chlorine in silicate melts. *Geochimica et Cosmochimica Acta*, *294*, 28-42.

[2] W. Thomas, R., & J. Wood, B. (2023). The effect of composition on chlorine solubility and behavior in silicate melts. *American Mineralogist*, *108*(5), 814-825.

$$C_{Cl} = \frac{Cl\ (wt.\%)}{\sqrt{fCl_2}} \times \sqrt[4]{fO_2} \qquad (1)$$

$$logC_{Cl} = 1.492 + \frac{4331X_{Ca} - 3508X_{Si} + 2440X_{Fe} - 3921X_K - 741P}{T} \qquad (2)$$