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Solubility and speciation of lithium chloride in water vapor at 400–600 °C: Implications for lithium transport in volcanic and subduction environments

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Lithium and chlorine are highly fluid-mobile elements widely used to trace fluid sources in subduction zones and magmatic–hydrothermal systems. Their mobility is generally attributed to high solubility in aqueous fluids; however, solubility and speciation change fundamentally across the liquid–vapor transition of water. In low-density water vapor, reduced dielectric properties and molecular clustering limit ionic solvation and favor neutral gas species, potentially modifying Li and Cl transport in upper crustal environments.

We present new experimental data on LiCl solubility in water vapor at 400–600 °C and 25–300 bar, spanning conditions typical of <5 km depth in magmatic–hydrothermal systems. Experiments were conducted using a high-temperature U-tube reactor enabling precise equilibrium determinations. Measured LiCl solubilities range from 1.2×10^{-7} to 1.6×10^{-3} mole fraction, corresponding to partial pressures of 10^{-6} to 10^{-1} bar. Solubility increases systematically with both temperature and pressure. At pressures above 150 bar, Cl/Li ratios approach unity, indicating stoichiometric dissolution. At lower pressures, excess Cl and acidic condensates indicate non-stoichiometric behavior and LiCl hydrolysis and HCl in the vapor phase.

The data are interpreted using a Gibbs free energy hydration model describing the reaction: $LiCl(s) + nH_2O(g) = LiCl\cdot(H_2O)_n(g)$. Non-linear regression of equilibrium constants identifies discrete hydrated gaseous species with n = 0, 4, 6, 8, and 10 as dominant contributors to total solubility. Hydration increases strongly with water fugacity. Derived thermodynamic parameters indicate increasing enthalpy and strongly decreasing entropy with hydration number, reflecting stabilization by water clustering.

These results demonstrate that lithium transport in vapor-dominated volcanic systems occurs primarily as neutral hydrated LiCl gas complexes rather than as free ions. Pressure-dependent hydration and hydrolysis reactions exert strong control on Li mobility, fractionation from Cl, and potential Li deposition during vapor ascent and decompression. The new thermodynamic dataset provides a quantitative framework for modeling Li behavior in volcanic gases, fumaroles, and shallow subduction-related hydrothermal systems.