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Superhot Hydrothermal Fluids: Solubility, Speciation, and Geochemical Implications

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Superhot hydrothermal fluids with temperatures above 374 °C and at low to moderate pressures of ~1–40 MPa commonly occur near magmatic intrusions and represent a frontier for geothermal energy and chemical engineering. At these conditions, water no longer behaves as a continuous hydrogen-bonded liquid but develops strong density heterogeneity, with high-density, liquid-like clusters coexisting alongside low-density, gas-like regions. This dramatically reduces its ability to dissolve solids and solvate ions, while neutral gaseous species become increasingly important. Despite their occurrence in volcanic, porphyry, hydrothermal vent, and terrestrial systems, the solubility of most minerals and the behavior of solutes in superhot hydrothermal fluids remain poorly constrained.

Mineral solubility in superhot water typically increases with pressure, reflecting the growth of molecular water clusters that enhance solvation of gaseous species. Classical thermodynamic models, including Gibbs energy–based like HKF formulations, assume water to behave as a continuous dielectric solvent, an assumption that breaks down under low-density and high-temperature conditions. Developing accurate models is further challenged by the lack of experimental data on solute behavior in superhot fluids.

We present experimental results using a newly developed U-tube reaction system and theoretical calculations employing density functional theory, and MP2 ab initio calculations to constrain the solubility and speciation of some rock-forming elements under superhot conditions. We emphasize the role of key ligands, chloride, sulfur, carbon, and water, in controlling metal complexation and mineral stability across density regimes. Based on these results, thermodynamically consistent equations are being developed and parameterized. Establishing such a database grounded in experimental measurements and theoretical calculations is essential for predictive modeling of element mobility in superhot fluids and for advancing both geothermal and volcanic science and high-temperature chemical engineering.