

Experimental determination of quartz solubility in H₂O–CaCl₂ solutions at 600–900 °C and 0.6–1.4 GPa

ADAM R. MAKHLUF¹, ROBERT C. NEWTON¹, AND CRAIG E. MANNING^{1,*†}

¹Department of Earth, Planetary and Space Sciences, University of California Los Angeles, Los Angeles, California 90095-1567, U.S.A.

ABSTRACT

Fluid-mediated calcium metasomatism is often associated with strong silica mobility and the presence of chlorides in solution. To help quantify mass transfer at lower crustal and upper mantle conditions, we measured quartz solubility in H₂O–CaCl₂ solutions at 0.6–1.4 GPa, 600–900 °C, and salt concentrations to 50 mol%. Solubility was determined by weight loss of single-crystals using hydrothermal piston-cylinder methods. All experiments were conducted at salinity lower than salt saturation. Quartz solubility declines exponentially with added CaCl₂ at all conditions investigated, with no evidence for complexing between silica and Ca. The decline in solubility is similar to that in H₂O–CO₂ but substantially greater than that in H₂O–NaCl at the same pressure and temperature. At each temperature, quartz solubility at low salinity ($X_{\text{CaCl}_2} < 0.1$) depends strongly on pressure, whereas at higher X_{CaCl_2} it is nearly pressure independent. This behavior is consistent with a transition from an aqueous solvent to a molten salt near $X_{\text{CaCl}_2} \sim 0.1$. The solubility data were used to develop a thermodynamic model of H₂O–CaCl₂ fluids. Assuming ideal molten-salt behavior and utilizing previous models for polymerization of hydrous silica, we derived values for the activity of H₂O ($a_{\text{H}_2\text{O}}$), and for the CaCl₂ dissociation factor (α), which may vary from 0 (fully associated) to 2 (fully dissociated). The model accurately reproduces our data along with those of previous work and implies that, at conditions of this study, CaCl₂ is largely associated (< 0.2) at H₂O density < 0.85 g/cm³. Dissociation rises isothermally with increasing density, reaching ~ 1.4 at 600 °C, 1.4 GPa. The variation in silica molality with $a_{\text{H}_2\text{O}}$ in H₂O–CaCl₂ is nearly identical to that in H₂O–CO₂ solutions at 800 °C and 1.0 GPa, consistent with the absence of Ca–silicate complexing. The results suggest that the ionization state of the salt solution is an important determinant of $a_{\text{H}_2\text{O}}$, and that H₂O–CaCl₂ fluids exhibit nearly ideal molecular mixing over a wider range of conditions than implied by previous modeling. The new data help interpret natural examples of large-scale Ca-metasomatism in a wide range of lower crustal and upper mantle settings.

Keywords: Metasomatism, quartz, silica, experimental, brines, fluids, halogens, solubility; Experimental Halogens in Honor of James Webster