



Quartz solubility in low-density aqueous fluids: evaluation and development of thermodynamic models

Federica Salomone and David Dolejš

Institute for Earth and Environmental Sciences, University of Freiburg, Germany (federica.salomone@minpet.uni-freiburg.de)

Solubility of quartz in aqueous fluids over a wide range of temperatures and pressures is crucial for our understanding of water–rock interaction. Experimental data cover a temperature range of 20 to 1130 °C and pressures from 1 to 20 kbar, and this dataset provides a useful basis for critical comparison and development of thermodynamic models for mineral solubility and aqueous solutes. Thermodynamic models for quartz solubility in pure water (1982-2021) are based on one of the following approaches: (1) successive hydration of solute, (2) correlation with solvent density, (3) virial equation of state for solute-solvent mixtures, or (4) Helgeson-Kirkham-Flowers (HKF) electrostatic equation of state. Predictions from these models generally converge at hydrothermal and supercritical temperatures in the fluid density range of 0.6-1.0 g cm⁻³. At high temperatures and fluid densities, the models based on successive hydration or virial expansion lose their physical meaning; the electrostatic approaches tend to overestimate the quartz solubility, although the large number of parameters in the HKF equation of state offers remarkably large calibration flexibility. At low pressures and low fluid densities, the individual approaches diverge: the density and virial models correctly approach the limiting case of ideal gas, but the virial equations of state tend to predict consistently higher solubilities. In this study we develop a more physically rigorous density-based model for quartz and test its performance in low-pressure aqueous fluids. Thermodynamic properties of aqueous solute are formulated as a function of hydration number that is typically variable at very low pressures (< 400 bar). At partial hydration, the thermodynamic properties of species are mainly controlled by enthalpy of stepwise hydration reactions and long-range solute-solvent interactions are minimal. At complete inner-sphere hydration the thermodynamic properties of aqueous species become a combined contribution of unhydrated species properties, mechanical interaction in the hydration sphere and standard-state conversion terms. When complete hydration of a species is achieved, Gibbs energy of species becomes linear with log water density at constant temperature, thus mimicking the linear log K – log density relationship for the mineral solubility equilibrium.