Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.30869

Thermodynamic model for aqueous species in the Na-Mg-K-Ca-Al-Si-Fe-C-O-H-Cl system for low-density hydrothermal fluids

FEDERICA SALOMONE AND DAVID DOLEJŠ
University of Freiburg

Thermodynamic properties of aqueous species are essential for the modeling and understanding of fluid-mineral equilibria occurring during magmatic devolatilization, metasomatic mass transfer, hydrothermal alteration and ore deposit formation. The thermodynamic properties of aqueous ions and neutral species have traditionally been described by the Helgeson-Kirkham-Flowers electrostatic model [1]. However, the electrostatic description of solute hydration suffers from several drawbacks: (i) the Born theory is not applicable to uncharged species; (ii) predictions of thermodynamic properties of aqueous species are increasingly inaccurate at low pressures and do not have correct physical limit; (iii) the electrostatic treatment is not extendable to higher accuracy and it does not explicitly account for volumetric effects of hydration. By contrast, classical thermodynamic descriptions of aqueous species starting from ideal gas state at 1 bar and linking volumetric properties of the solute to the solvent behavior [2] and to solute-solvent interaction via hydration or fluctuation solution approaches [3] offer much greater theoretical flexibility for accurately representing the solute thermodynamics over wide range of temperature and pressure conditions. This study aims at the development of a new thermodynamic dataset for aqueous species in the Na-Mg-K-Ca-Al-Si-Fe-C-O-H-Cl system, applicable to hydrothermal fluids from low to intermediate density. We adopt a low-parameter functional form that captures the principal contributions to the Gibbs energy of solute and is capable of robust extrapolation in the pressure-temperature space. The dominant contributions are as follows: intrinsic properties of solute in the ideal gas state (entropy, enthalpy, heat capacity), solute-solvent interactions accounted for by hardcore volume and volumetric compression in the hydration sphere. The thermodynamic parameters are calibrated for 42 aqueous species by fitting existing Gibbs energy data [4] in the range of 25-700 ^{o}C and 0.001-3.0 kbar. The new thermodynamic model improves modelling of aqueous speciation, fluid-mineral equilibria and reactive transport processes in shallow crustal magmatic and hydrothermal systems.

References:

[1] Shock E.L. et al. (1992) J. Chem. Soc. Faraday Trans. 88, 803-826.

[2] Plyasunov A.V. (2014) Fluid Phase Equil. 375, 11-17.

[3] Sedlbauer J. et al. (2000) Chem. Geol. 163, 43-63.

[4] Miron et al. (2017) Am. J. Sc. 317, 755-806.