Internally consistent thermodynamic data for aqueous species in the Na-K-Al-Si-O-H-Cl system

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The quality of geochemical calculations relies on the robustness of thermodynamic models and on the accuracy and internal consistency of the thermodynamic dataset. The available aqueous thermodynamic datasets were obtained from sequential evaluation of mineral solubilities, with the values from an earlier step subsequently fixed. Erroneous or inaccurate data from the earlier step may result in error accumulation during the process; uncertainties and correlations of the adjusted parameters are difficult to obtain.

In the current study, we explore and develop strategies for generating an internally consistent thermodynamic dataset for hydrothermal fluid-rock equilibria. The following tasks were performed: 1. Results of mineral solubility experiments were collected and critically evaluated (quartz, corundum, gibbsite, alumosilicates, feldspars, micas). Experimental datasets were assessed for the quality of data. 2. The GEMSFITS [1] fitting tool was developed for regressing consistent thermodynamic parameters against various types of experimental data. 3. Results from new high-precision conductance experiments on electrolyte association were used to derive more reliable and accurate equilibrium constants for weak complexation. 4. Conductance and potentiometric data on the association constants of several complexes were collected to constrain the properties of such complexes when they are insensitive to the solubility data. 5. A computational method was developed that allows to freely optimise the properties of some aqueous species while constraining others trough reactions using the data from speciation equilibria.

Application of our consistency strategies and tools in the Na-K-Al-Si-O-H-Cl system results in equal distribution of errors over the pressure, temperature and compositional space; yields confidence intervals for the optimized parameters; and permits straightforward repetition of fitting procedures when the new or improved experimental data become available.

[1] Miron *et al*. (2015) *Appl. Geochem*. **55**, 28-45.