3.6.25

Iron(III) hydrolysis in hydrothermal solutions

A. STEFANSSON

Sience Institute, University of Iceland, Dunhaga 3, 107 Reykjavík, Iceland (as@hi.is)

A knowledge of the stability and stoichiometry of aquoeus iron complexes in hydrothermal solutions is essential for quantitative interpretation of the geochemistry of iron in natural hydrothermal fluids. The equilibrium constants among iron species are also necessary for understanding the geochemical behaviour of many metals which occur in trace quantities in natural waters and which display geochemical characteristics comparable to those of iron. The hydrolysis constants of iron(III) in hydrothermal solutions as a function of pH and ionic strength are beeing experimentally determined. In acidic solutions the experiments were carried out using static and flow-though potentiometric titrations where free concentration of both H^+ and Fe^{3+} were measured by glass electrode and a Pt-electrode, respectively. In neutral and alkaline solutions the hydrolysis constants were determined from solubility measurements of freshly precipitated iron hydroxide. A non-linear least squares treatment of the data demonstrate that Fe^{3+} hydrolysis to form $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$ in acidic solutions at $m_{Fe(III),total} < 0.01$, $Fe(OH)^{2+}$ and $Fe(OH)_3^0$ at neutral pH and $Fe(OH)_4^-$ in alkaline solutions. The cumulative and stepwise formation constants for the respective species have been calculated as well as their thermodynamic properties.

3.6.31

The activity of water in albite melt

R.A. LANGE

Dept. of Geological Sciences,, University of Michigan, Ann Arbor, MI 48109-1063 (becky@umich.edu)

The activity-composition relation for the H_2O component dissolved in $NaAlSi_3O_8$ (Ab) liquid is determined from an analysis of the water-saturated fusion curve of albite, which shows how variable amounts of dissolved water lower the melting temperature of albite by different amounts. Delta T (ΔT) is the difference between the melting temperature of albite under anhydrous conditions and in the presence of water. Values of ΔT vary as a function of X_{H2O}, and thus X_{Ab}, across the $NaAlSi_3O_8$-H_2O binary. This information is combined with the Gibbs-Helmholtz equation to determine how the activity of the $NaAlSi_3O_8$ liquid component varies with different values of ΔT. Thus, the a-X relation for the $NaAlSi_3O_8$ (Ab) liquid component is obtained along the $NaAlSi_3O_8$-H_2O binary. Data on the water-saturated fusion curve allow the activity coefficient (γ_{Ab}) and its natural log, $\ln\gamma_{Ab}$, to be obtained across 80 % of the binary. The functional form of $\ln\gamma_{Ab}$ vs. X_{H2O} is used to extrapolate $\ln\gamma_{Ab}$ to $X_{H2O} = 1$. Next, the Gibbs-Duhem equation is used to obtain $\ln\gamma_{H2O}$ across the binary, which gives the a-X relation for the dissolved H_2O component in $NaAlSi_3O_8$ liquid. A test of the validity of this a-X relation is to use it to model measured H_2O solubility in $NaAlSi_3O_8$ liquid between 50-800 MPa and 825-1300°C [1]. The measured volumetric properties of dissolved H_2O in $NaAlSi_3O_8$ liquid [2] are input and not fitted. Thus, only two parameters are fitted from the solubility data: the enthalpy and entropy of solution of the H_2O component at one bar. The results give ΔH – 14.47 kJ/mol and ΔS=-79.7 Jmol-K, with an average residual of ± 0.18 wt % H_2O. All but one (of 34) residuals are within ± 0.50 wt % H_2O. These results can be further used to calculate crystal-melt-fluid equilibria across the Ab-H_2O binary at various pressures and temperatures.

References
[1] Behrens et al. (2001) *Chem. Geol.* **174,** 275-289.
[2] Ochs & Lange (1997) *CMP* **129,** 155-165.