

Solubility of hematite and stability of Fe(III) chloride complexes at 200 to 300°C, SWVP

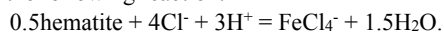
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New experiments using the AgCl solubility approach (Gammons et al., 1996, GCA 60, 4615-4630) show that FeCl_4^- is the dominant Fe(III) complex at 200-300°C, $\text{pH} < 2$, and $\Sigma\text{Cl} \geq 1.0$ m. At 200°C, Cl-ligand number decreases rapidly at $\Sigma\text{Cl} < 1.0$ m, inconsistent with a model that includes a full set of FeCl_n^{3-n} complexes ($n = 1$ to 4). We propose that the dominant complexes at 200°C are octahedrally-coordinated $\text{FeCl}_2(\text{H}_2\text{O})_4^+$ and tetrahedrally-coordinated FeCl_4^- , with the transition occurring at roughly 0.3 m ΣCl . At 250 and 300°C, only the tetrahedral FeCl_4^- complex was observed at $\Sigma\text{Cl} = 0.1$ to 3.0 m.

The solubility of hematite was measured under the same conditions by preparing a series of silica tubes with identical matrix chemistry and increasing concentration of $\text{FeCl}_3(\text{s})$. Hematite saturation was constrained by the tube with the lowest FeCl_3 concentration that precipitated hematite at high temperature. The solubility of hematite as FeCl_4^- is strongly temperature dependent, with preliminary equilibrium constants (\log_{10}) ranging from 4.7 at 200°C to 6.5 at 300°C for the following reaction:



Some experimental evidence suggests the presence of mixed hydroxy-chloride complexes $\text{FeCl}_n(\text{OH})_{(4-n)}^-$ at $\text{pH} > 2$, and such complexes could be important in nature. However, hematite solubility experiments at higher pH have been complicated by precipitation of ferric hydroxide on quench.

Our experiments show that acidic, hydrothermal brines are capable of dissolving hematite as Fe(III)-chloride complexes, with solubility increasing very quickly with an increase in temperature, increase in Cl^- concentration (power of 4), and decrease in pH (power of 3). Once formed, FeCl_4^- is an extremely effective oxidizing agent, capable of destabilizing any sulfide mineral and dissolving gold, copper, silver, platinum, and palladium as chloride complexes. In deep hydrothermal systems, FeCl_4^- is a more viable oxidant than dissolved O_2 gas, although its presence requires a source area with abundant hematite and a lack of reductants (organic carbon, sulfides). Dissolved ferric chloride could be an important and previously overlooked reactant in the formation of certain types of hydrothermal mineral deposits, including iron-oxide-copper-gold (IOCG), red-bed Cu-Co, and unconformity U ($\pm\text{Ni,Pt,Pd,Au}$) deposits.