

Polymorphic transformations of iron oxides: a thermodynamic view

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The system $\text{Fe}_2\text{O}_3\text{-H}_2\text{O}$ is represented by a variety of polymorphs: goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and maghemite ($\gamma\text{-Fe}_2\text{O}_3$), ferrihydrite ($\sim\text{Fe}(\text{OH})_3$), and many others. Our thermodynamic measurements show that the stable coarse-grained (bulk) phases in this system are only hematite and goethite (depending on water activity); the other minerals are metastable. Despite their metastability, all phases mentioned above are present in the environment not only as single phases but also as mixtures. Their persistence may not only be due to kinetic factors and small differences in Gibbs energy, but also to free energy variations with the particle size. If very fine particles are formed, the energy stored in their surfaces and interfaces becomes a significant contribution to the overall enthalpy and Gibbs free energy of the phase.

We have been measuring the surface thermodynamic properties of various iron oxide minerals. Surface enthalpy of different iron oxides varies from 0.34 J/m^2 to 1.2 J/m^2 . The enthalpies of water adsorption, crucial for the interpretation of the surface enthalpy measurements, have also been measured and will be presented. Our data suggest that a) the least stable phase (i.e., the phase with the highest enthalpy with respect to the stable assemblage) has the lowest surface enthalpy and that 2) the anhydrous phases (e.g., hematite) have higher surface enthalpies than the hydrated phases (e.g., goethite). The competition between surface energy and polymorphism in the Fe-O(H) system creates energy cross-overs, which will be discussed as a function of the particle size, hydration level of their surfaces, and temperature. These energy cross-overs explain the co-existence of several iron oxide phases and the complexity of their occurrence in the environment.