Thermodynamics of Iron Oxide Nanoparticles

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Iron oxide nanoparticles are omnipresent in the environment, present in waters, soils, and rocks of variable origin (Cornell and Schwertmann 2003). They are characteristic by their very large surface area which enables them to control many geochemical reactions, although the abundance of these particles may not be very high. Until recently, the thermodynamic properties of many iron oxide minerals, either on the bulk or nanoscale, were not known well.

We have measured the thermodynamic properties of most iron oxide polymorphs (iron oxides *s.l.*, including iron oxides, oxyhydroxides, and hydroxides) by a combination of high-temperature oxide-melt, acid-solution, adiabatic, semi-adiabatic, and gas-adsorption calorimetry. The only two bulk phases that have a stability field in the system Fe_2O_3-H_2O are goethite (α-FeOOH) and hematite (α-Fe_2O_3); all other phases are metastable in bulk.

However, because the Gibbs free energies of the iron oxides phases are closely balanced, the relative stability may be significantly influenced by water activity, substitutions of other metals for Fe^{3+}, or by energy stored in surfaces. The latter variable has a significant impact upon the stability for nanoparticles. For example, we found that maghemite becomes stable with respect to hematite, if both phases attain particles size $<$16 nm and if the surfaces dry (Navrotsky et al. 2008). In hydrated environments, such as those commonly found on the surface of Earth, goethite is easily stabilized with respect to hematite by becoming nanocrystalline. An remarkable result of our study is that in nanoregime (particle sizes 2-4 nm), ferrihydrite may be in thermodynamic equilibrium with other iron oxides. This observations explains the ease with which ferrihydrite forms, and the tendency of ferrihydrite to convert to other iron oxide phases once it coarsens.

Cornell, R.M. and Schwertmann, U. (2003) *The Iron Oxides. Structure, Properties, Reactions, Occurrences and Uses*. Wiley-VCH.

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