Modeling the transformation rate of ferrihydrite to goethite and hematite

Katsuhiro Tsukimura[1]; Masaya Suzuki[1]; Yohey Suzuki[1]; Takashi Murakami[2]

[1] AIST; [2] Deprt. of Earth Planet. Sci.., Univ. of Tokyo

Ferrihydrite ($5Fe_2O_3$ $9H_2O$) is a non-crystalline nano-size mineral, which is commonly observed in hot springs, mine drainage and soils. The mineral takes an environmentally important role because it adsorbs many kinds of toxic elements, such as Cu, As, U and Pu (Waychunas et al., 2002; Swedlund and Wester, 2001; Pierce and Moor, 1980; Logue et al., 2004; Novikov et al., 2006). The mineral, however, transforms to more stable crystalline phases, goethite and hematite in an aquatic solution (Fischer and Schwertmann, 1975). Thus, determining how long ferrihydrite persists in natural systems is important for estimating the behavior of toxic elements in the systems. Although transformation rates of ferrihydrite are measured experimentally (Schwertmann and Murad, 1983; Nagano et al., 1994; Shaw et al., 2005; Yee et al., 2006), we have to examine whether these results can be applied to a natural system. Even if the thermodynamic parameters, such as temperature and pH, are the same, the rate in a natural system can be different from the rate in a laboratory system. This is because the parameters other than thermodynamic parameters can affect the transformation rate. Thus, we need to develope the model to explain the transformation rate of ferrihydrite.

Schwertmann and Murad (1983) made a transformation experiment of ferrihydrite nano-particles at 297 K, and Shaw et al. (2005) and Yee et al. (2006) at high temperatures (333-410 K), and found that the amount of ferrihydrite decreases exponentially (Fig. 1). Yee et al. (2006) mentioned that the rate determining process is the dissolution of ferrihydrite. If it is true, the concentration of iron in a solution becomes close to the solubility of goethite or hematite, and we can approximate that the degree of unsaturation is constant. In such a case, the dissolution rate is proportional to the surface area of ferrihydrite because the dissolution rate of ferrihydrite is proportional to the surface area of ferrihydirite and the degree of unsaturation. If we assume that the size of ferrihydrite is uniform, the transformation rate becomes proportional to the amount of ferrihydrite. However, the dissolution of ferrihydrite cannot be the rate-determining process because the dissolution rate of ferrihydrite is about 100 times faster that the dissolution rate of hematite (Cornell et al., 1976). The results at high temperatures by Shaw et al. (2005) and Yee et al. (2006) are somewhat different from that by Schwertmann and Murad (1983). They observed that the ferrihydrite did not transform to goethite or hematite at first, and that the transformation started after some time elapsed, which they called induction time (Fig. 1b).

This paper describes the model to explain the transformation rate of ferrihydrite to goethite and hematite, which is based on three assumptions; (1) the crystals nucleate only on ferrihydrite, (2) the crystals stop growing at a certain size, and (3) the concentration of Fe in a solution is close to the solubility of ferrihydrite. On the basis of the assuptions, we have successfully explained the previous experimental results including the exponential decrease of ferrihydrite and the induction time. This model also shows that the size of a system, the concentration of ferrihydrite and minor elements in a solution, and the stirring of the solution can affect the transformation rate. This shows how we can apply the experimental data to natural systems.