The kinetics and mechanisms of goethite and hematite crystallization under alkaline conditions, and in the presence of phosphate

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Abstract

The transformations of 2-line ferrihydrite to hematite (pH 10.7) or goethite (pH 13.7), and of phosphate-doped 2-line ferrihydrite to goethite (pH 13.7), were studied at 60–137 °C using synchrotron-based, in-situ energy dispersive powder diffraction (EDPD). The time-resolved data for the growth of the diffraction peaks were fitted with a pseudo first-order kinetic model. As shown in previous studies, the conditional rate constant of goethite formation increases with increasing pH and is significantly lower than that for hematite crystallization. The activation energies of nucleation for hematite (pH 10.7), pure goethite (pH 13.7), and phosphate-doped goethite (pH 13.7) are 24, 7, and 21 kJ/mol, respectively, whereas the activation energies of crystallization are 69, 39, and 26 kJ/mol. The crystallization of phosphate-doped ferrihydrite produced large rectangular goethite crystals with dense ferrihydrate cores on which the goethite grew epitaxially. The rate of goethite formation is greatly reduced in the presence of phosphate due to an increase in the entropic component of the free energy of activation. This increase in entropy arises from adsorption of phosphate on to the (210) crystal faces, with an associated increase in relative growth rate on the (101) faces.

INTRODUCTION

Ferric oxide and oxyhydroxide phases are ubiquitous in near-Earth-surface environments. Ultrafine particles (tens to hundreds of nanometers) of these phases occur suspended in aerobic natural waters (surface water and groundwater) and are major constituents of soils and sediments. The crystalline minerals goethite (α-FeOOH) and hematite (α-Fe₂O₃), and poorly ordered ferrihydrite, are among the most abundant Fe (oxyhydr)oxide minerals found in these environments. These phases are environmentally important because their abundance, high specific surface, and high sorption capacity exert important controls on the speciation and mobility of trace species (metals, anions, and organic molecules) in the natural environment (Cornell and Schwertmann 2003). The sorption properties of these phases change according to several factors, including crystallinity, structure, composition and solution composition (pH and ionic strength). Therefore, a detailed understanding of the mechanisms and kinetics of goethite (α-FeOOH) and hematite (α-Fe₂O₃) crystallization, and of the factors that change these processes, is required to understand fully how these phases affect trace element/component migration in the near-Earth-surface environment.

The transformation of poorly ordered ferrihydrite to goethite and/or hematite under aqueous and hydrothermal conditions has received considerable attention over the last few decades (Cornell and Schwertmann 2003 and references therein). Hematite formation is thought to occur via a solid-state transformation process involving internal recrystallization and dehydration of ferrihydrite (Fischer and Schwertmann 1975; Norlund-Christensen et al. 1980; Schwertmann and Murad 1983). Nucleation and very early stages of crystallization, before any crystalline hematite is detectable by X-ray diffraction (XRD), are associated with aggregation of ferrihydrite particles (Fischer and Schwertmann 1975) and an increase in the number of face-sharing octahedra in the ferrihydrite structure (Combes et al. 1990). The main crystallization stage is associated with dehydration of ferrihydrite and deprotonation of OH groups, the formation of oxy-linkages, and the redistribution of cation vacancies within the hematite lattice.

Two alternative mechanisms have been proposed for the transformation of ferrihydrite to goethite under aqueous conditions: first, a reconstructive dissolution/reprecipitation mechanism (Schwertmann and Murad 1983); and second, an oriented aggregation mechanism (Banfield et al. 2000). The dissolution/reprecipitation mechanism is consistent with the formation of goethite rather than hematite at both ends of the pH range where the solubility of Fe⁴⁺ is relatively high. The oriented aggregation mechanism has been demonstrated in biogenic ferrihydrite at ambient temperature and near-neutral pH (Banfield et al. 2000), but no evidence exists for the operation of this mechanism at higher temperatures or under alkaline conditions.

The growth of goethite in alkaline media is thought to involve dissolution of ferrihydrite to give a high concentration of [Fe(OH)₃]⁺ species in solution. These species are thought to be the most suitable basic unit for goethite crystal growth (Cornell et al. 1989; Schwertmann and Murad 1983) because only a single