American Mineralogist, Volume 90, pages 1852–1860, 2005

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

SAMUEL SHAW,* SARAH E. PEPPER,† NICHOLAS D. BRYAN, AND FRANCIS R. LIVENS

Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, Manchester, M13 9PL, U.K.

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 ferrihydrite 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.