Epitaxial overgrowth of goethite on hematite synthesized in phosphate media: A scanning force and transmission electron microscopy study

VIDAL BARRÓN,1 NATIVIDAD GÁLVEZ,1 MICHAEL F. HOCHELLA JR.,2 AND JOSÉ TORRENT1

1Departamento de Ciencias y Recursos Agrícolas y Forestales, Universidad de Córdoba, Apdo. 3048, 14080 Córdoba, Spain
2Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

ABSTRACT

We used X-ray diffraction (XRD), scanning force microscopy (SFM), transmission electron microscopy (TEM), and color to investigate the effect of phosphate on the crystallization rate, nature, and morphology of iron oxides prepared from ferrihydrite in the laboratory. Synthesis was performed at two temperatures (323 and 373 K) and two pH values (9 and 12) from ferric nitrate, for P/Fe atomic ratios ranging from 0 to 2.5%. The presence of phosphate retarded crystallization, tended to favor hematite over goethite, and markedly influenced the morphology of the goethite crystals formed at high pH. Application of SFM in the deflection mode was useful to investigate the morphology of the small goethite crystals, with careful attention paid to operating conditions; in particular, sharp silicon probes were found to produce fewer artifacts than coarser silicon nitride ones. At low P/Fe ratios (<0.2%), the goethite crystals were thin, elongated, multidomain laths; at high P/Fe ratios (>1.5%), star-shaped, twinned crystals were produced. All the theoretical shapes, derived from the assumption that star-shaped crystals result from the epitaxial growth of goethite on a hematite core, were observed by SFM and TEM. The presence of such hematite nuclei was supported by XRD, selected-area electron diffraction, color, and preferential dissolution of the samples in HCl, because it is known that hematite dissolves faster than goethite in acid. With increasing P/Fe ratio, the arms of the star-shaped crystals became shorter. This was likely due to the higher density of P-adsorbing pairs of singly coordinated OH groups on terminal {021} faces relative to prismatic {110} arm faces.

INTRODUCTION

The laboratory synthesis of various iron oxides (a term used here to indicate iron oxides, hydroxides, and oxyhydroxides) has provided a better understanding of the origin and behavior of these oxides in natural environments, as well as the basis of their industrial applications (e.g., Schwertmann and Taylor 1989; Schwertmann and Cornell 1991; and references therein). Synthesis variables that have been explored include, among others, temperature, pressure, starting materials, formation additives, and pH. They modify the crystallochemical nature of the ferric (hydr)oxide grown and affect properties such as adsorption behavior, aggregation, and color.

Regarding formation additives, iron oxides have been synthesized in the presence of trace to minor amounts of Al and Si, transition metals (Ti, Mn, Co, Cu, and Zn), organic acids (citric, tartaric, oxalic, and lactic), and phosphate (a review of synthesis additives is given in Cornell et al. 1989, or more recently in Cornell and Schwertmann 1996). The present study concerns phosphate because of its importance in soil fertility, and its association with and presumed inhibitory effects at relatively low solution concentrations on the formation of hematite and goethite. Occasionally, fertilizer phosphate can be a major cause of freshwater eutrophication. Therefore, it is important to investigate the fate of excess phosphate in soil, particularly the amount that can be adsorbed onto or occluded within iron oxides during their nucleation and growth, and how it can influence the crystallization of such oxides.

Several studies have described the influence of phosphate on the formation of ferric and ferrous iron oxides (Barton 1990; Schwertmann 1969; Reeves and Mann 1991; Kandori et al. 1992; Morales et al. 1992; Matijevic 1993; Sugimoto et al. 1993; Ocaña et al. 1995). These papers, except Kandori et al. (1992), deal with the mechanism of formation of ellipsoidal hematite particles from ferric salt solutions in the presence of small amounts of phosphate. Nevertheless, no mention has ever been made of morphology modification of goethite in the presence of phosphate. Morphology, however, plays a key role in controlling the surface area per unit mass of the oxide, as well as the crystal faces (and their specific reactivity) that dominate that surface area. Furthermore, the iron oxide-phosphate system has never been studied with scanning force microscopy (SFM). Scanning probe microscopy (SPM; this includes both scanning tunneling microscopy and SFM) should be apt for this type of study. SPM can image details on surfaces down to the sub-nanometer range, and it can also be used to measure