The Influence of Silicate Species on the Morphology of Goethite (α-FeOOH) Grown from Ferrihydrite ($5Fe_2O_3{\cdot}9H_2O$)

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In the presence of 9.6 mol% silicate species, goethite (α-FeOOH) grows from ferrihydrite ($5Fe_2O_3{\cdot}9H_2O$) at pH 12.5 as a mixture of pseudohexagonal plates and bipyramids, whereas in the absence of silicate species, acicular crystals of goethite are formed.

Goethite (α-FeOOH) is an important iron oxyhydroxide that finds industrial use as a pigment and as the precursor of maghemite (γ-Fe_2O_3) for magnetic tapes. Both applications require crystals with specific morphology and size. Goethite exists in two modifications, as twinned and acicular crystals.[1] Although goethite can be synthesized from ferric and ferrous sources by a variety of pathways, marked modifications of crystal habit are difficult to effect.

We are carrying out a systematic investigation of the mechanisms by which foreign ions influence the growth of goethite. We report here the effect of silicate species (henceforth refered to as Si) on the crystal habit of goethite grown from ferrihydrite ($5Fe_2O_3{\cdot}9H_2O$). The presence of Si induces goethite to grow as pseudohexagonal plates and as bipyramids; this appears to be the first observation of a new morphology of goethite.

Si-free goethite was synthesized by holding ferrihydrite at pH 12.5 and 70 °C for 50 h. Ferrihydrite was precipitated from 0.01 M $Fe(NO)_3{\cdot}9H_2O$ solution with 1.0 M KOH. Si doping was achieved by coprecipitating 0.1, 1.0, or 9.6 mol% Si with ferrihydrite. Si was added as H_4SiO_4 solution ($\leqslant$0.002 M) and was present as monomeric species.[2] The kinetics of the transformation were followed by determining the amount of unconverted ferrihydrite remaining at any time, by extraction with acid–ammonium oxalate solution.[3] Soluble Fe was measured by atomic absorption spectroscopy and soluble Si was determined photometrically using a molybdenum blue method.[4] At least 80% Si added initially was taken up by the ferrihydrite and subsequently released into solution as the ferrihydrite dissolved.

Si retarded the transformation of ferrihydrite into goethite. Complete transformation was achieved in 100 h with 0.1 mol% Si and in 12—13 months with 9.6 mol% Si. The resulting Si-goethite was examined using transmission electron microscopy, *X*-ray powder diffraction (x.r.d.), energy dispersive *X*-ray spectroscopy (e.d.x.s.), and classical chemical analysis.

At pH 12.5, acicular crystals of Si-free goethite with average lengths and widths of 450 nm and 40 nm respectively, formed. Most crystals had rounded ends, Figure 1(a). Similar crystals formed in the presence of 0.1 mol% Si. As the Si : Fe ratio was increased, the crystals became shorter and thicker. Those grown in the presence of 1.0 mol% Si were 300—500 nm in length and 100—140 nm in width. Such crystals also showed well-developed angular ends due to (021) or (111) and (121) faces, Figure 1(b). These faces are also well-developed in macroscopic goethite.[5]

With 9.6 mol% Si, the crystal morphology altered; a mixture of shortened acicular crystals (*ca.* 100—200 nm length), pseudohexagonal crystals (100—200 nm diameter), and bipyramids (500—1000 nm) resulted. X.r.d. indicated that all samples consisted of well-crystallized goethite.

The pseudohexagonal crystals that form in the presence of the highest levels of Si appear to be very short, thick acicular crystals in which development of the terminal faces has been strongly enhanced, Figure 1(c). These crystals formed mainly during the first 30—40% of the transformation. The bipyramids are bounded by (021) or (111) and (121) faces, Figure 1(d). These crystals can be regarded as acicular crystals in which the prism faces have been eliminated. A number of bipyramidal intergrowth twins were observed, Figure 1(d) (arrowed). Bipyramidal crystals formed mainly during the later stages of the transformation. E.d.x.s. indicated that Si was associated with this goethite. Si can adsorb on goethite[6] and can also replace *ca.* 0.2 mol% Fe in the goethite lattice.[7] Classical chemical analysis showed that more Si (*ca.* 1—2 mol%) had been taken up by the modified crystals of goethite (after complete conversion of ferrihydrite) than could be accommodated in the lattice. Presumably, this Si was adsorbed on the surface of the goethite.

Goethite forms from ferrihydrite by a dissolution–reprecipitation mechanism.[8] Interference by Si can occur at several different stages during the transformation. Adsorbed Si stabilizes ferrihydrite[9] and strongly retards its dissolution, whereas soluble Si hinders nucleation of goethite[7] leading to fewer, larger crystals. At pH $\geqslant$ 13.3 adsorption of Si on goethite is negligible. Goethite crystals grown at this pH in the

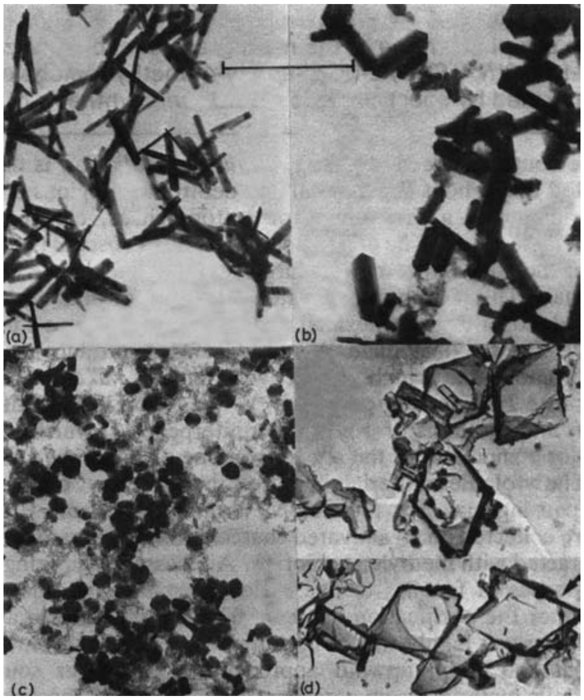

Figure 1. Electron micrographs of goethite prepared in (a) the absence of Si; (b) the presence of 1.0 mol% Si; (c) the presence of 9.6 mol% Si after 30—40% transformation of ferrihydrite; (d) the presence of 9.6 mol% Si after 95% transformation; bar = 1 μm. (d) shows replicas of goethite crystals: the amorphous background material in (b), (c), and (d) is unconverted ferrihydrite.

presence of 9.6 mol% Si retain the typical acicular shape despite very slow growth (months). At lower pH changes in crystal morphology can be attributed to adsorption of Si on specific planes of the growing crystal. The terminal faces have a high density of Fe atoms and hence sites for Si adsorption. Preferential adsorption of Si on these planes retards their growth and hence enhances their development. This effect becomes more pronounced as the concentration of Si in solution increases. Crystals with different habits develop at different stages during the transformation because the concentration of Si in solution increases as the reaction proceeds and ferrihydrite dissolves.

As modifications of goethite morphology appear to have been effected by adsorption of soluble Si on the growing crystal rather than on the Fe precursor, Si would be expected to influence the morphology of goethite grown from Fe^{II} systems as well as that grown from ferrihydrite. In this context, it is of interest that modified crystals of goethite grown from Fe^{II} in the presence of Si have been observed recently in living organisms.[10]

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