

Hydrothermal Formation of Hydrated Ferric Oxides: An *in situ* Synchrotron Study

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Introduction

Hydrous ferric oxides (HFO) such as ferrihydrite ($\text{Fe}_4(\text{O},\text{OH},\text{H}_2\text{O})_{12}$) and goethite (FeOOH) are abundant in near earth surface environments. Ultra fine particles of HFO's occur both suspended in groundwater and as coatings on mineral grains. Their high specific area and reactive surfaces mean that they exert a very important control over the mobility of trace contaminants (metals, anions and organics) in the natural environment. The sorption properties of these phases changes with crystallinity, solution pH and ionic strength. Therefore a detailed understanding of the crystallisation mechanisms and kinetics of HFO phases is required to fully understand their effects on trace element migration. Despite a large body of work (Jambor and Dutrizac, 1998) the transformation from poorly ordered ferrihydrite to crystalline HFO phases (e.g. goethite) is not fully understood. This study has investigated, using synchrotron based *in situ* hydrothermal Energy Dispersive Powder Diffraction (EDPD), the transformation of 2-line ferrihydrite to goethite and/or hematite. The main aims being to investigate the influence of temperature, pH, aluminium content and phosphate content on the kinetics, phase stability and reaction mechanisms in this system.

Method

The *in situ* hydrothermal synthesis experiments for this work were carried out using the on-line EDPD facilities on station 16.4 at the SRS, Daresbury Laboratory. The hydrothermal synthesis equipment consists of a modified Anton Parr bomb with a section of the wall milled down to allow sufficient X-ray transmission through the cell (Evans et al. 1994, Shaw et al. 2000). The bomb was heated externally and the contents were continually stirred to ensure the amount of solid material in the beam remained constant throughout the experiments. Diffraction patterns of the cell contents were collected using 3 solid-state energy dispersive

detectors, each placed at a slightly different angle of 2θ in order to collect a wide range of d-spacings (1–10Å).

The starting materials for these reactions consisted of freshly precipitated 2-line ferrihydrite (not dried) mixed with either 1 M or 0.1 M KOH giving an initial pH of either ~13.7 or ~10.9 respectively. Experiments were performed at temperatures varying from 60 to 140°C. For the experiments at the higher pH the composition of the initial ferrihydrite was varied from 0–15 mole% aluminium and from 0–0.3 mole% phosphate replacing iron. The contents of the hydrothermal bomb was analysed as the ferrihydrite recrystallised with diffraction patterns taken every 1 or 2 minutes to allow the complete reaction to be followed from poorly ordered starting material to crystalline end product.

Results

All the reactions were complete within 500 minutes (Figure 1). At high pH (~13.7) conditions the 2-line ferrihydrite transforms to goethite exclusively at all temperatures possibly via a dissolution and re-precipitation mechanism (Schwertmann and Murad, 1983). Addition of aluminium produced a mixture of goethite and hematite with the hematite/goethite ratio increasing with increasing aluminium content and temperature. The crystallisation rates of the aluminium containing reactions were slower than those in the pure iron system. Addition of phosphate did not affect the phase stability as goethite was the only end product to form at all temperatures, although the crystallisation rates were reduced compared to similar experiments in the pure iron system. At lower pH (~10.9) hematite was the dominant end product forming via an internal dehydration/recrystallisation mechanism (Schwertmann and Murad, 1983). The crystallisation rates at this pH were slower than those for reactions at the higher pH, at the same temperature. Data reduction is currently in progress to fully quantify the crystallisation kinetics of these reactions.

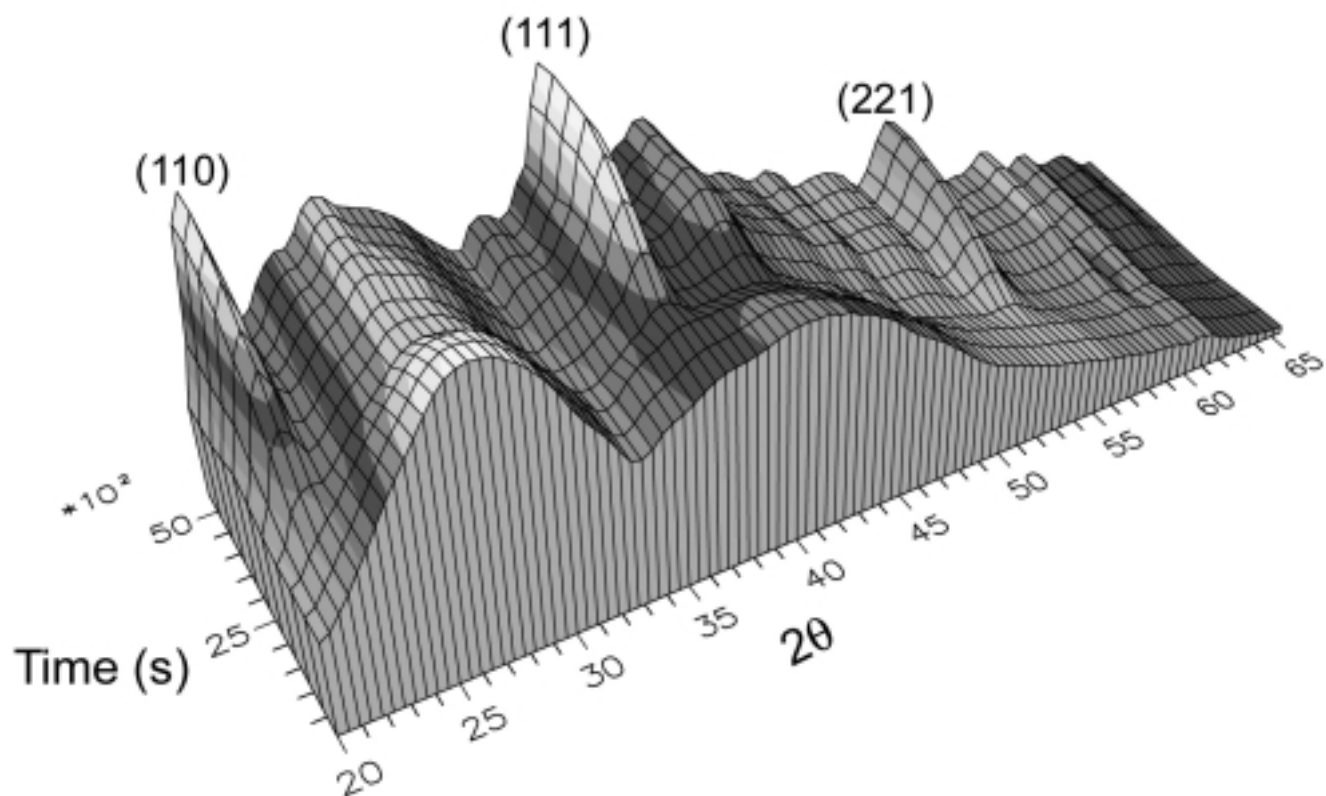


Figure 1: Time-resolved EDPD pattern showing the formation of goethite from 2-line ferrihydrite at 120°C and pH 13.7. The original energy scale has been converted to a 2θ scale calculated assuming a Cu $K\alpha$ wavelength.

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