# A time-resolved synchrotron X-ray diffraction study of the transformation from ferrihydrite to goethite and hematite

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The structural mechanisms of the transformation from two-line ferrihydrite to goethite (α-FeOOH) and hematite (α-$Fe_2O_3$) were investigated using 2-day batch experiments and *in situ* X-ray diffraction over temperatures of 70°C to 170°C and pH from 2 to 11. Our Rietveld analyses of both batch and time-resolved synchrotron X-ray diffraction (TR-XRD) data indicated that temperature and pH are two significant factors that control the transformation pathway and the relative concentrations of the final products. As expected based on the thermodynamic stability of hematite, higher temperatures favored the formation of hematite, particularly between pH 3 and 5. Within three hours, our TR-XRD data revealed that ferrihydrite transformed to goethite and hematite simultaneously at pH 6 and 7, whereas ferrihydrite transformed directly to hematite at pH 5 when solutions were heated at 130°C. Thus, our results did not support the conventional assumption that goethite forms as an intermediate transitional phase before hematite formation [1, 2].

More surprisingly, at pH 8, ferrihydrite transformed first to goethite and "hydrohematite", a hydrous and highly iron-defective iron oxyhydroxide, and the hydrohematite subsequently evolved into stoichiometric hematite. Our results are apparently inconsistent with the long-term results presented in Cornell and Schwertmann (2003), who analyzed the transformation of ferrihydrite in batch experiments from 0 to 30°C over 12 years [3]. We hope that a continuation of these TR-XRD experiments will provide constraints for the formation of hydrohematite with respect to solution pH and temperature.

[1]Vu *et al.* (2008) *MinMag*, **72**, 217-220. [2]Schwertmann *et al.* (2004). *Clay Minerals*, **39**, 433-438. [3] Cornell & Schwertmann (2003). The Iron Oxides, Wiley.