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The rate of ferrihydrite transformation to goethite via the Fe(II) pathway

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ABSTRACT

In this study, we quantified the rate of ferrihydrite conversion to goethite via the Fe(II) pathway using synchrotron radiation-based energy dispersive X-ray diffraction (ED-XRD). Ferrihydrite transformation experiments were conducted in oxygen-free solutions at neutral pH with synthetic 2-line ferrihydrite reacting with 100 mM Fe(II). The kinetics of goethite crystallization was measured in situ at temperatures ranging from 21 to 90 °C. The results showed that in the presence of ferrous iron, the transformation of poorly ordered ferrihydrite into crystalline goethite is rapid and highly dependent on temperature. The time-resolved peak area data fitted using a Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetic model yielded rate constants of 4.0×10^{-5}, 1.3×10^{-4}, 3.3×10^{-4}, 2.27×10^{-3}, and 3.14×10^{-3} 1/s at reaction temperatures of 21, 45, 60, 85, and 90 °C respectively. The activation energy for the transformation was determined to be 56 ± 4 kJ/mol. Comparison with the activation energy predicted for the phase conversion in the absence of ferrous iron indicates that Fe(II) acts as a catalyst that decreases the activation energy barrier by approximately 38 kJ/mol. The kinetic parameters derived from the experimental data suggest that goethite crystallization is controlled by a 1-D phase boundary growth mechanism with a constant nucleation rate occurring during the reaction.

Keywords: Crystal growth, goethite, geomicrobiology, ferrihydrite, kinetics, transformation