

Supplementary Materials for

**Vacancy infilling during the crystallization of Fe-deficient hematite:
An in situ synchrotron X-ray diffraction study of non-classical crystal growth**

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Figures. S1 to S4

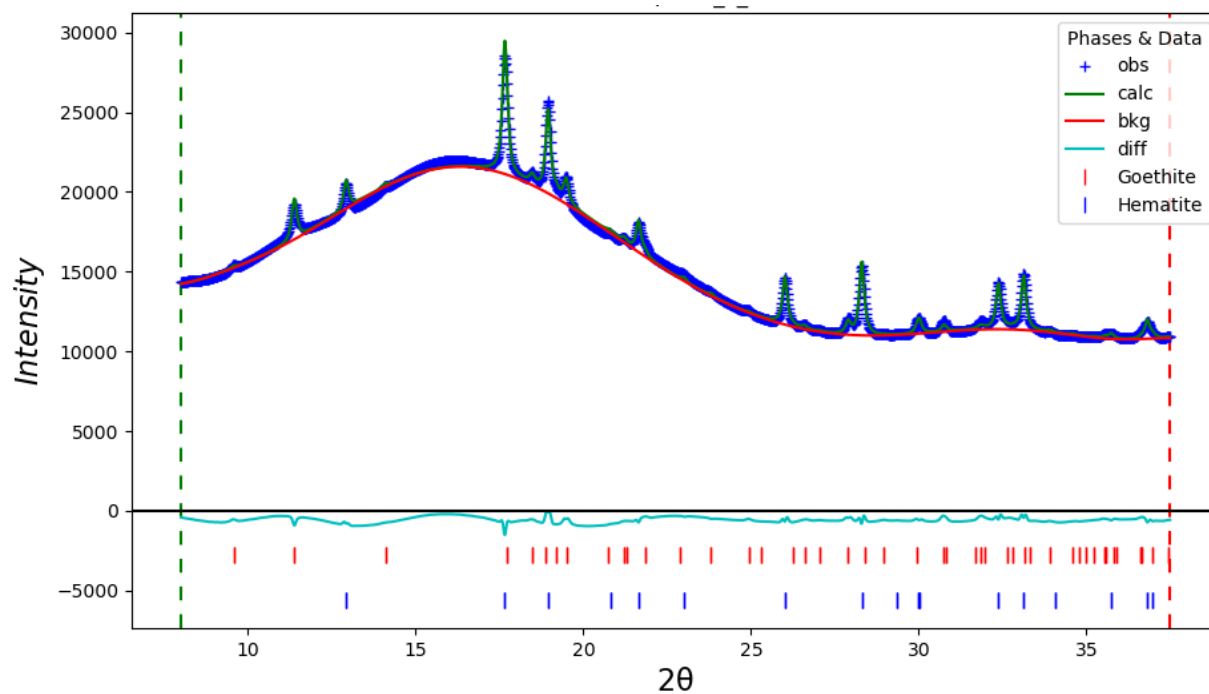


Figure S1. Rietveld structure refinement using synchrotron powder XRD data of the reaction products after heating ferrihydrite at 90 °C for 90 min, with an initial pH of 11. The products are a mixture of 71 wt% hematite and 29 wt% goethite. The Fe occupancy in hematite (space group $R\bar{3}c$) refined to 0.84. Goodness of fit: $\chi^2 = 0.9786$, $R_{wp} = 0.0079$.

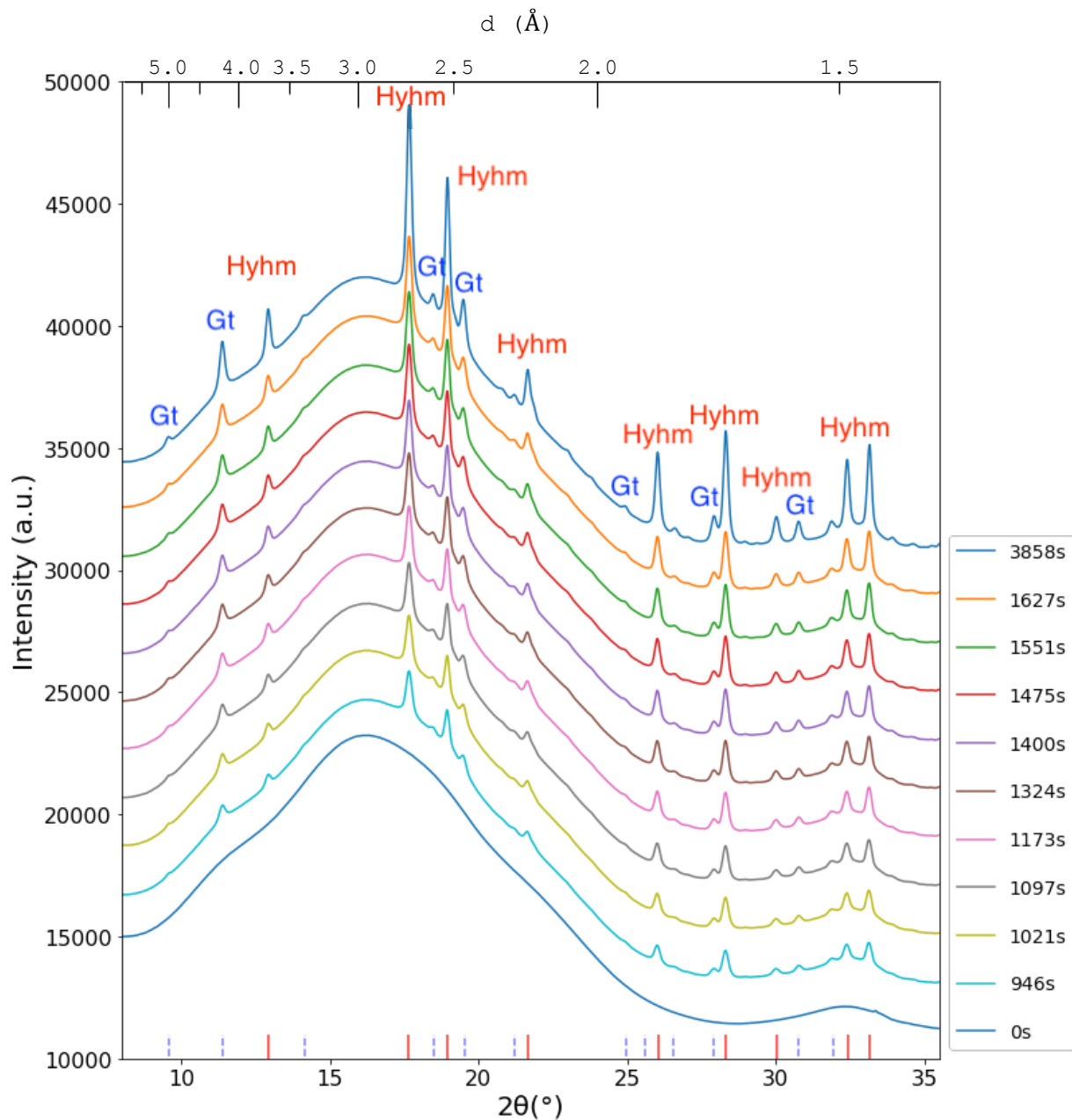


Figure S2. A 2D waterfall of stacked TRXRD patterns that were collected at 90 °C pH 11, showing the transformation of ferrihydrite (0 s) to hydrohematite (hyhm) and goethite (Gt) with time. Each pattern was refined for Rietveld structure analysis in our present study. Full peak positions of hydrohematite and goethite are marked with red solid guide line and blue dashed line in the bottom of the graph.

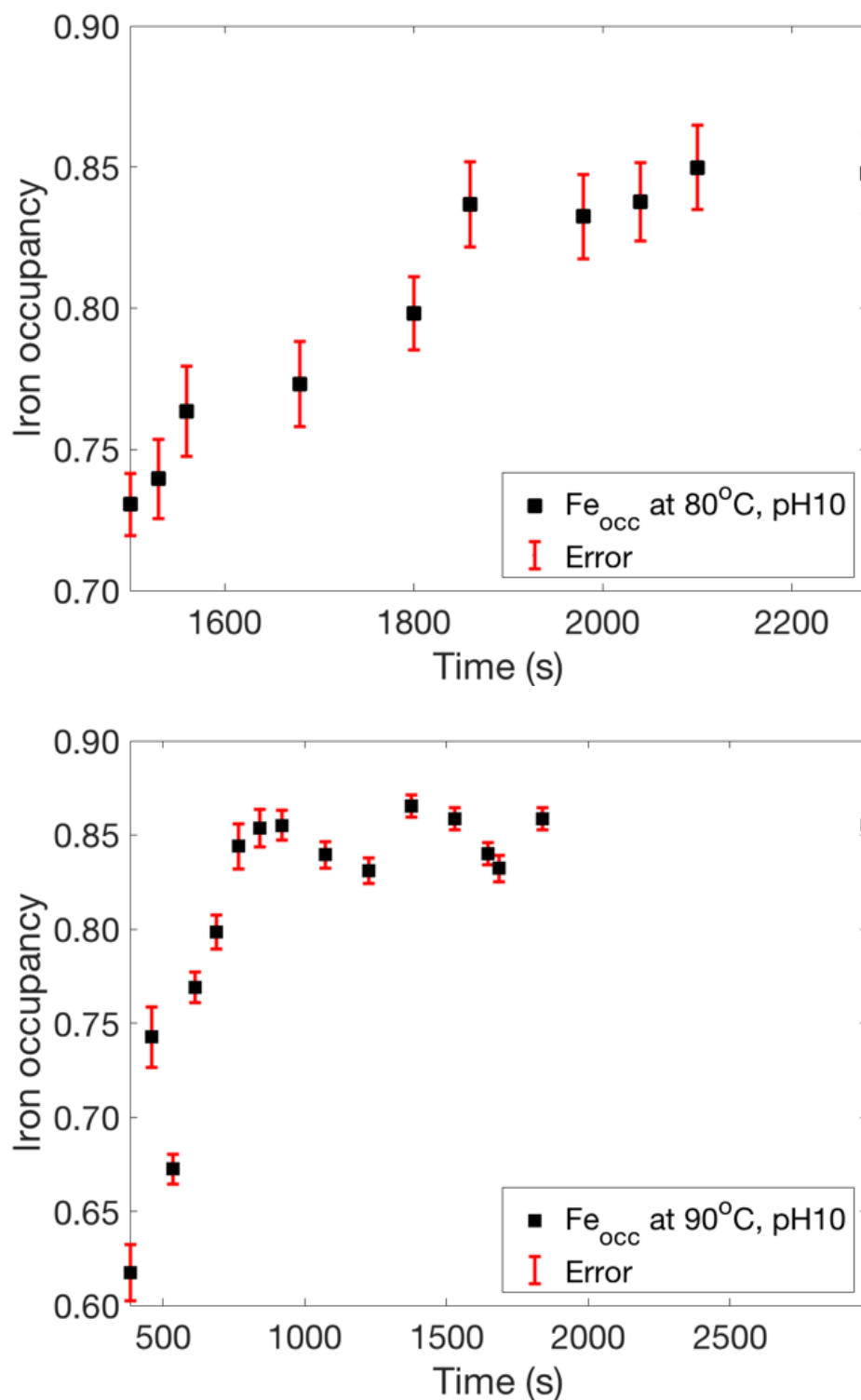


Figure S3. Refined Fe occupancy as a function of time at 80 (Left) and 90 °C (Right), pH 10.

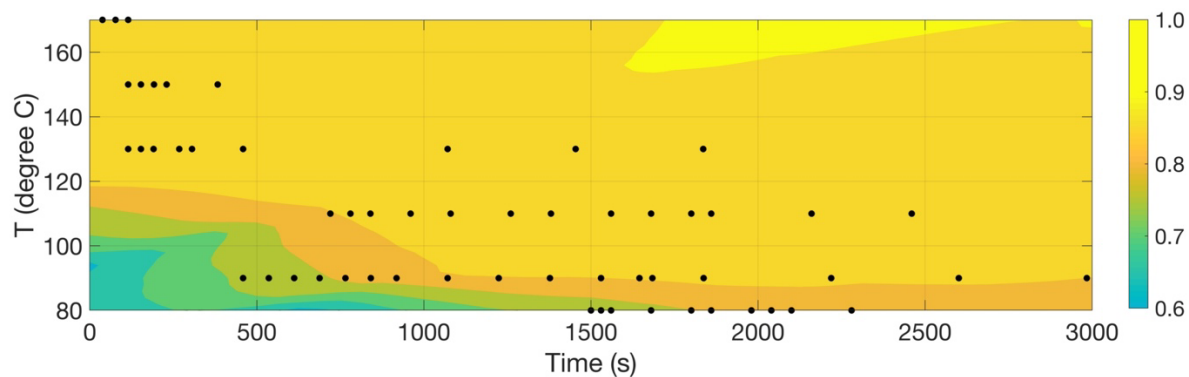


Figure S4. The dependence of Fe occupancy on transformation time and temperature (80-170 °C) as revealed by the projected surface of Figure 4. Our refined Fe occupancy using TRXRD data at pH 10 are indicated by black dots.