Supporting Information (SI)

Contents

Experimental section

Iron(III) chloride hexahydrate (Sigma Aldrich, puriss., p.a., ACS reagent, 98.0% - 102%), hydrochloric acid (Merck, 0.1 M) and sodium hydroxide solution (Merck, 0.1 M) were used as received to prepare the following solutions: 0.05 M NaOH, 0.01 M HCl and 0.1 M $FeCl_3$ x 6 H_2O in 0,1 M HCl. All chemicals were diluted with water of MilliQ quality. All glassware was cleaned after each titration with MilliQ water and the diffusion tips of the titration setup were regularly cleaned in 0.1 M HCl to remove iron (oxyhydr)oxide residues.

Titration Assay. Iron(III) chloride hydrolysis was carried out using an advanced titration assay, consisting of a titrator (titrando 905, 2.905.0020) and two dosing units (dosino 800, 2.800.0010) that were controlled by the titration software tiamo 2.3 (all Metrohm, Herisau, Switzerland). The dosing units were equipped with anti-diffusion tips, enabling exact dosing down to 0.2 µL. The experiments were carried out in a thermostated glass cell (Metrohm, 6.1418.220), that was connected to a thermostat FP50-MA (Julabo, Seelbach, Germany). For the titration experiment, 30 mL of 0.01 M HCl were brought to the desired temperature and the pH value was adjusted to 2.5 by addition of 0.05 M NaOH. The iron(III) chloride solution was added to the hydrochloric acid with a constant rate of 0.01 mL/min, while the pH value was monitored and kept constant by the automated counter-titration of 0.05 M sodium hydroxide solution. For some experiments, the turbidity was measured during the titrations, utilizing an optical sensor (Metrohm, Spectrosense, 6.5501.110) equipped with a 610 nm laser. Turbidity measurements were carried out at a maximum of 60°C owing to the limited applicability of the optical sensor at elevated temperatures according to the manufacturer's specifications. The pH value was monitored with a pH electrode (Metrohm, EtOH-Trode, 6.0259.100). The pH electrode was calibrated regularly with standardized buffer solutions (Mettler-Toledo, Giessen, Germany) and the electrolyte, 3 M KCl (Merck), was refilled after each experiment.

Hydrothermal Synthesis. For hydrothermal synthesis of hematite nanoparticles, 3.24 g of iron(III) chloride hexahydrate was dissolved in 600 mL HCl that was preheated to 100 °C. The reaction solution was placed in an oven at 100 °C for 24 hours.

PXRD. To obtain enough precipitate for characterization, the samples were drawn at late stages of the titrations, for low temperatures after running them over night. The concentration of added iron(III) ions at the time of sampling was 6.1, 8.6, 3.4 and 3.8 mM for 25, 45, 78 and 95 °C, respectively. At 95 °C another sample was drawn at 0.9 mM to investigate the early precipitate. For the isolation of the precipitates, the reaction solution was centrifuged in a preparative ultracentrifuge (Beckman Coulter, Brea, USA) for 45 min at 30,000 rpm using thick-walled polyallomer tubes (13 x 51 mm, Beckman Coulter). The sediment was freeze-dried for one day. This was done to minimize drying effects that might affect the crystal structure of the samples. However, as the diffraction was carried out *ex situ*, a phase transition during sample preparation cannot be excluded categorically. PXRD patterns were measured with an AXS D8 Advance diffractometer with a Göbelmirror PGM from Bruker. Cu K_α radiation was used and the data was collected at a scanning rate of 0.86 2 theta/min. The diffraction patterns were background corrected to account for iron fluorescence.

SAXS measurements. For SAXS analysis, a solution prepared in the same way as for hydrothermal synthesis was investigated. SAXS experiments were performed at the ESRF beamline ID02 (Grenoble, France) at an X-ray energy of 12.46 keV which corresponds to a wavelength of $\lambda = 0.995$ Å. Samples were measured in a quartz capillary that was kept at a temperature of 60°C with sample-detector distances of 1.5 m and 5 m to cover the scattering vector q range from 0.05 to 5 nm^{-1} (q is the scattering vector, $q=(4\pi/\lambda)\sin(\theta)$, 2θ is the scattering angle). A syringe was used to transport small amounts of the sample solution into a flow-through cell with an embedded quartz capillary. The capillary exhibits a wall thickness of ~ 10 µm, and an internal diameter of 1.6 mm. The scattering patterns were obtained with a short exposure time (from 0.1 s to 30 s). The SAXS patterns were normalized to an absolute scale and azimuthally averaged to obtain the intensity profiles, and the solvent background was subtracted. For SAXS experiments on solution samples measured in a capillary with a very thin wall, water and solvent are also measured in the same capillary with the same instrument configuration. The final scattering intensity of the sample is[1]

$$I(q) = \frac{\frac{I(q)_s}{t_s T_s} - \frac{I(q)_b}{t_b T_b}}{\left(\frac{I_w}{t_w T_w} - \frac{I_{EC}}{t_{EC} T_{EC}}\right)_{1nm^{-1} \leq Q \leq 4nm^{-1}}} * 0.0164$$

Where $I(q)_s$, $I(q)_b$, $I(q)_w$, and $I(q)_{EC}$ are the measured intensity of sample, solution background, water and empty capillary, respectively. The bottom term in the high q range is a flat scattering (q independent), whereas T is the transmission and t the irradiation time.

The approach used to evaluate the SAXS data applies a set of general laws (Porod’s law, Guinier analysis, Kratky analysis) that yield results right after data reduction. Then the scattering curves were fitted with models that yield accuracy parameters for data analysis.

Cryo-TEM. Samples were drawn directly from the reaction solution and spread on lacey carbon filmed copper TEM-grids by blotting with a filter paper. The thin film resulting from this preparation was vitrified with liquid ethane near its freezing point by quickly plunging the specimen into it. The examination was carried out with a Zeiss / LEO EM922 Omega TEM at temperatures around 90 K. The images were processed by using a background-subtraction routine and, if appropriate, a smoothing filter for noise reduction was used (Butterworth filter).

Determination of thermodynamic parameters. The equilibrium constant K was determined for the first stage of the hydrolysis reaction during which the base consumption shows a linear behavior. K was calculated according to the law of mass action:

$$K = \frac{[(FeOH)^{2+}]}{[Fe^{3+}][OH^{-}]}$$

where $[(FeOH)^{2+}]$ can be obtained from the amount of reacted NaOH. $[Fe^{3+}]$ is given by the base consumption subtracted from the corresponding concentration of added iron(III) ions. The hydroxide concentration results from the measured pH value and the autodissociation of water at the respective temperature. ΔG was calculated using the Van't Hoff equation:

$$\Delta G = -RT \ln{(K)}$$

with the gas constant R and the temperature T. The calculations were carried out for three titrations at the same temperature and the average and standard deviations were determined. Plotting ΔG versus T gives the reaction enthalpy ΔH as the intercept and the entropy ΔS from the resulting slope obtained by linear regression according to:

$$\Delta G = \Delta H - T\Delta S$$

As mentioned in the article, at temperatures above 45°C, a systematic error in the pH measurements makes these calculations impossible. At higher temperatures, the detected amount of reacted NaOH exceeds that of added iron ions. This is most likely due to a systematic error in the pH measurement at these temperatures. If the detected pH value is lower than the actual pH present in the solution, the amount of NaOH that is dosed for keeping the pH constant is larger than the amount actually needed. As the calculation of hydroxide ions reacting with iron ions is based on the measured pH value, it will result in a too high value. Even though the calibration of the pH electrode was conducted at higher temperatures as well, a systematic error is likely to occur as pH measurements at higher temperatures are difficult to conduct. Other effects that have not been evaluated but most likely play additional roles are the changed acidities of the different compounds at higher temperatures. Calculation of the thermodynamic parameters is possible at temperatures ≤ 45°C.

Supplementary Figures

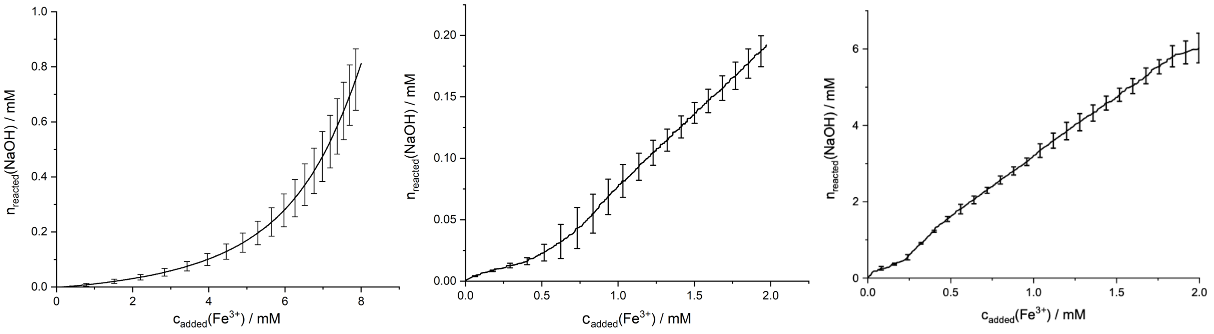

Figure S1 | Titration curves with error bars (+/- 1-σ-standard deviation, N=3) for; left, 25°C; middle, 78°C; right, 95°C. A curve for 50°C is not shown with error bars here, as a corresponding long-term titration was only carried out once at this temperature. The reproducibility for the pre-nucleation parts of the curves is very good at all temperatures. The larger post-nucleation error bars are due to the fact that nucleation is a stochastic event, and curves for individual measurements bend upwards at somewhat different points that are inherently difficult to reproduce.

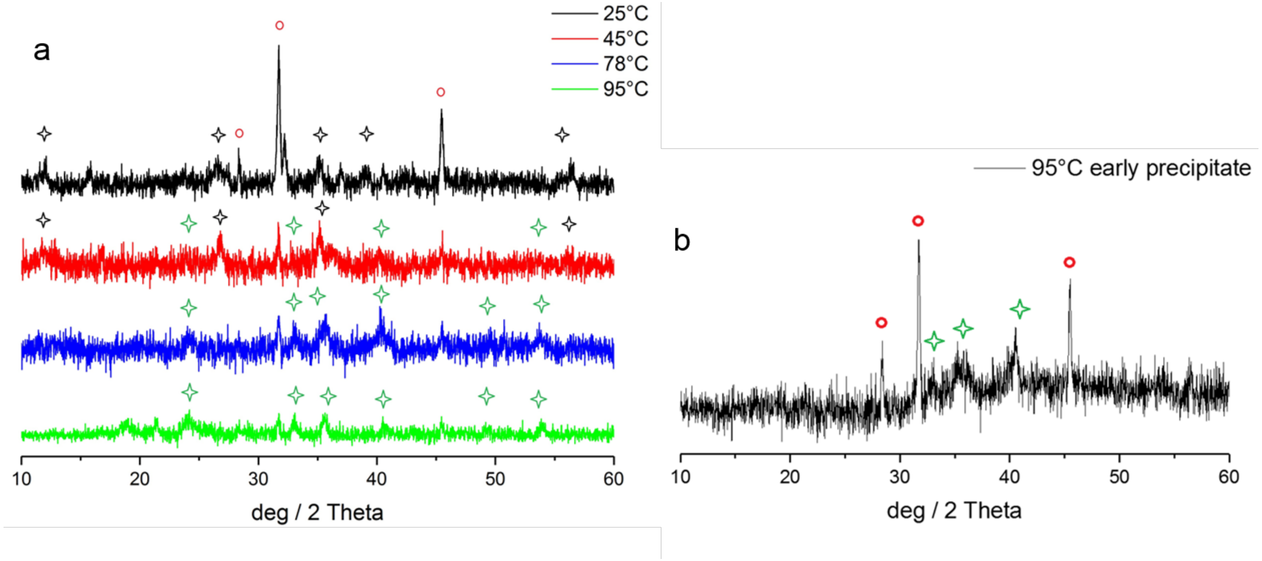

Figure S2 | a) PXRD diffraction pattern of the precipitates obtained from titrations at different temperatures as indicated (samples were drawn at 6.1, 8.6, 3.4 and 3.8 mM added iron(III) concentrations for 25, 45, 78 and 95°C respectively). b) Diffraction pattern of the early precipitate at 95°C (sample drawn at 0.9 mM added iron(III) concentration). Reflections due to akaganéite and hematite are labeled with black and green diamonds, respectively. Red circles in the diffraction pattern of the sample at 25°C label reflections due to NaCl.

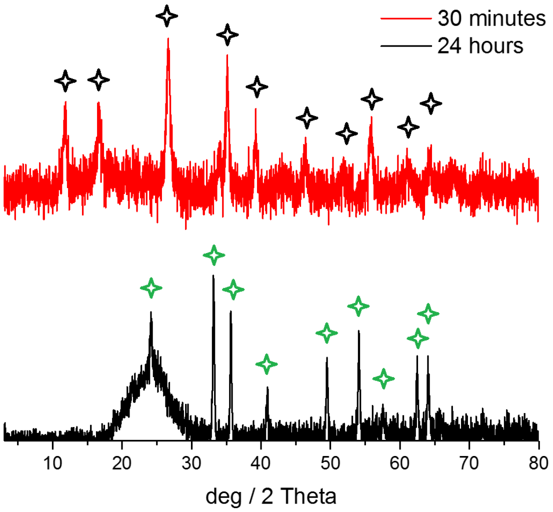

Figure S3 | XRD pattern of samples drawn from the hydrothermal method after 30 minutes and 24 hours. Hematite and akaganéite reflections are labeled with green and black diamonds, respectively.

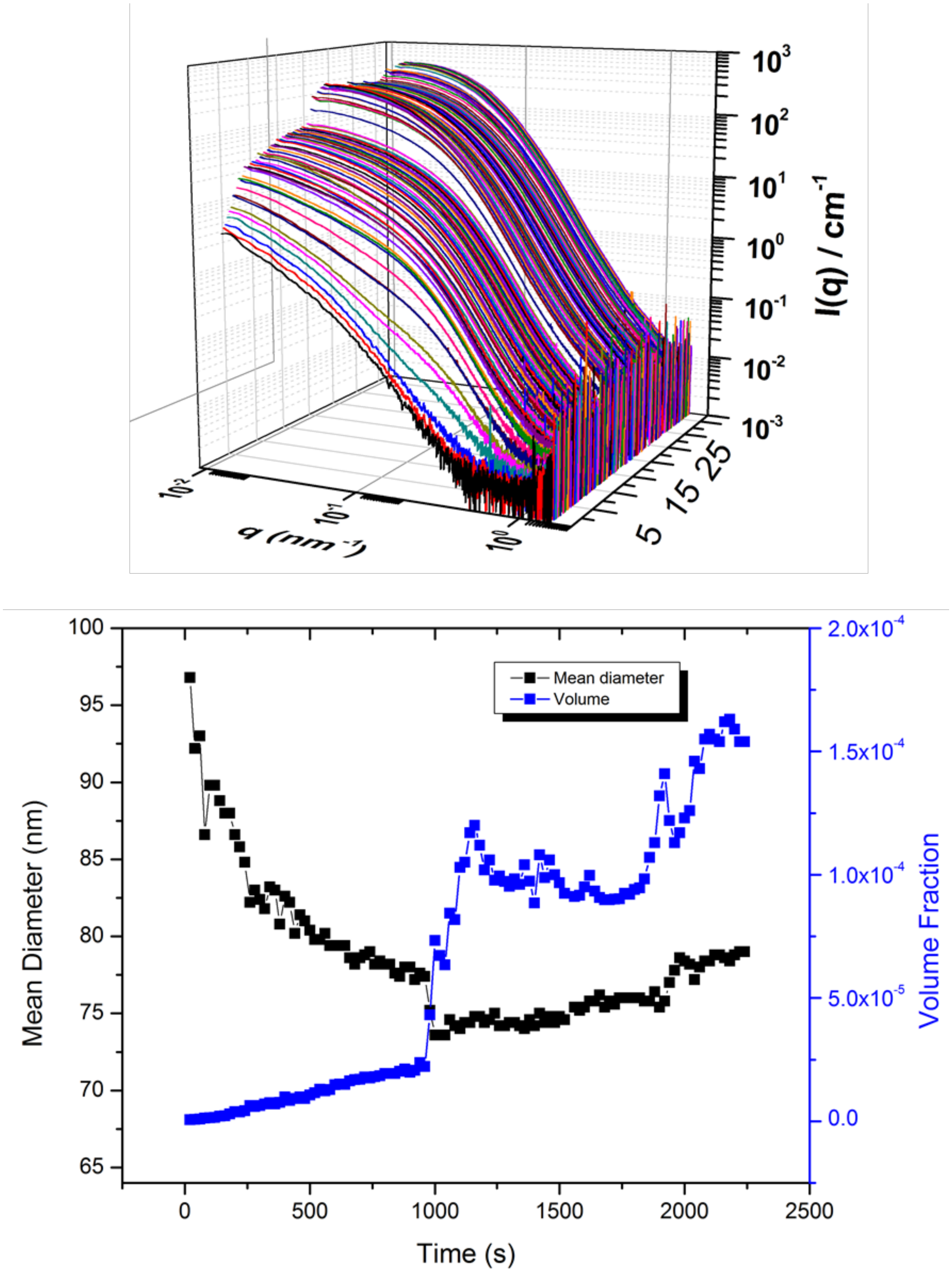

Figure S4. SAXS data of a 0.02 M iron(III) chloride solution in 0.002 M hydrochloric acid kept at 60°C **a)** 3D SAXS profiles plotted against the scattering vector q as a function of time. **b)** Mean size (diameter) and volume fraction plots (obtained by a Monte Carlo simulation on the SAXS profiles) [2] as a function of reaction time. The sudden change at ca. 1000 s is likely due to the drying of the solution in the capillary.

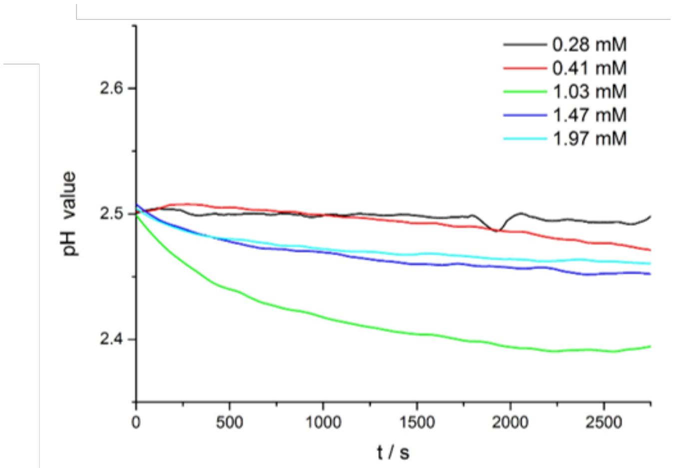

Figure S5 | Development of the pH value of the reaction solution of a titration experiment, where the addition of iron(III) solution and automatic titration with NaOH was stopped at different concentrations of added iron(III) ions as indicated (78 °C).

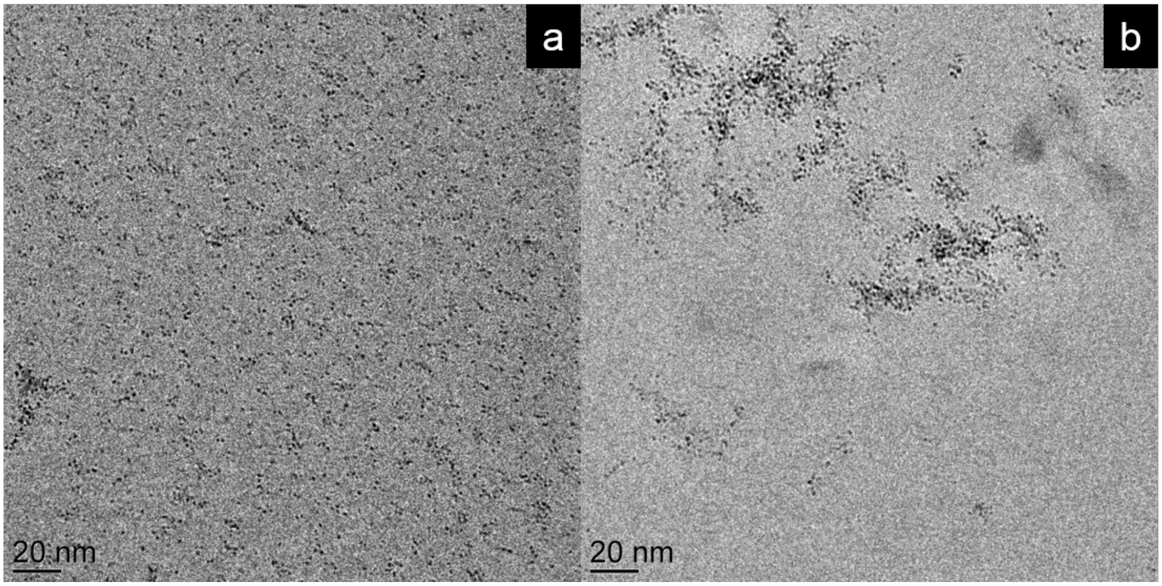

Figure S6 | cryo-TEM images of a sample prepared at room temperature. **a)** Pre-nucleation clusters in sample taken prior to nucleation. **b)** Aggregated particles formed from PNC precursors after nucleation.

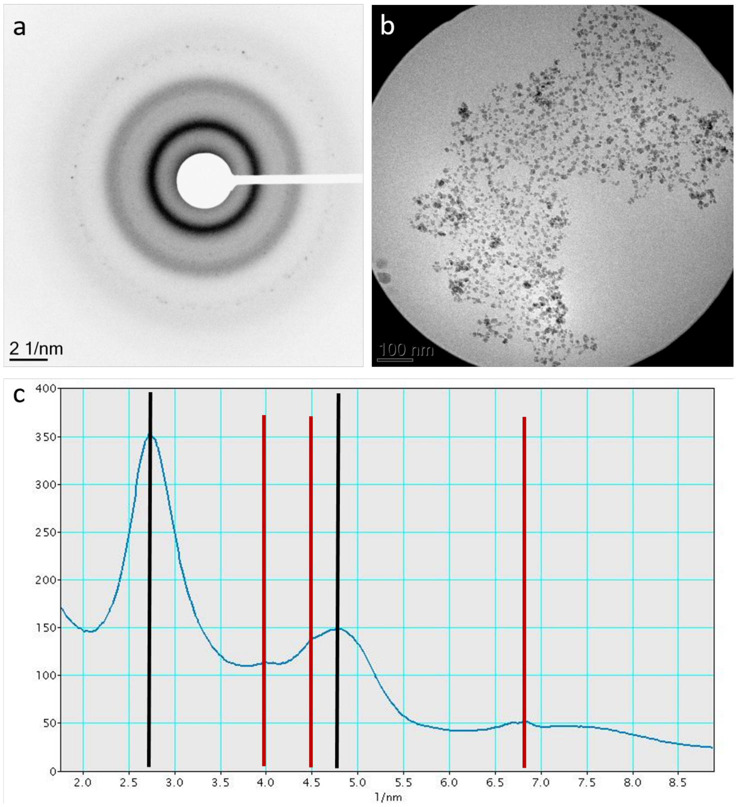

Figure S7. a) Negative of the ED pattern of the *cryo*-TEM image shown in **b)**. The sample was drawn from a titration at 95 °C after nucleation in the third regime, showing agglomerates of the primary species. **c)** cross section of the intensity of the ED pattern. The black vertical lines show reflexes of the water structure that derives from the film of ice in which the sample is embedded. The red vertical lines indicate the positions of reflections due to hematite.

References

[1] J. Scheck, B. Wu, M. Drechsler, R. Rosenberg, A. E. S. Van Driessche, T. M. Stawski, D. Gebauer, *J. Phys. Chem. Lett.* **2016**, *7*, 3123–3130.

[2] I. Bressler, B. R. Pauw, A. F. Thünemann, *J Appl Crystallogr* **2015**, *48*, 962–969.