Supplementary Information for

Impurity-Bearing Ferrihydrite Nanoparticle Precipitation/Deposition on Quartz and Corundum

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Summary

Six pages including two figures, experimental details, and data analysis.

GISAXS Critical Angle

Our GISAXS measurements were conducted at water-substrate interfaces. Here, we have used Snell Equation (Eqn. (1)) to calculate the critical angle (α_1) for total external X-ray reflection.[1]

$$\alpha_1 = \mathrm{acos}\left(\frac{1-\delta_{substrate}}{1-\delta_{water}}\right)\left(\frac{180}{\pi}\right) \qquad (1)$$

Where, $\delta_{substrate}$ and δ_{water} represent the refraction indices of the substrates and water, respectively. With density values of 2.68, 3.97, and 1.00 g/cm^3 for SiO_2, Al_2O_3, and H_2O and an X-ray energy of 14 KeV, the indices of refraction (δ) for SiO_2, Al_2O_3, and H_2O were calculated to be 2.85×10^{-6}, 4.14×10^{-6}, and 1.18×10^{-6}, respectively.[1] Applying Eqn. (1), the critical angles for total external X-ray reflection at water-SiO_2 and water-Al_2O_3 interfaces were calculated to be 0.105° and 0.136°, respectively. Therefore, 0.10° was chosen as the incident angle for all sample measurements.

XPS Measurements

X-ray photoelectron spectroscopy (XPS) measurements were also conducted to determine the oxidation states of Mn in the precipitates formed from FeMn solution. To collect enough precipitates, 500 mL FeMn solution (Table 1) was freshly prepared and let to sit for 1 hr. Then, the particles were collected using centrifugal filter unit, and were transferred to a gold wafer. After drying the sample in a desiccator overnight, the photo-electrons, produced via a monochromatic Al-k X-ray source (1486.6 eV) operated at 350 W, were collected on a Physical Electronics Model 5700 X-ray photoelectron spectroscopy (XPS) instrument. The analyzed area, collection solid cone and take off angle were set at 800 m, 5^o and 45^o, respectively. All spectra were acquired under vacuum condition (< 5×10^{-9} torr). Data processing was carried out using the Multipak™ software package. A Shirley background subtraction was applied. Unfortunately, the amounts of Mn in Mn-bearing ferrihydrite nanoparticles on substrates were lower than the detection limits of XPS measurements (Figure S2).

Mn^{2+} and Al^{3+} ion adsorption vs. $Mn(OH)_2$ and $Al(OH)_3$ precipitation on substrates

The zeta potential changes of the substrates in Mn and Al solutions could be caused by either Mn^{2+} and Al^{3+} ion adsorption or heterogeneous precipitation of $Mn(OH)_2$ and $Al(OH)_3$ on substrates. In our previous study, GISAXS control experiment with 0.5 mM $Al(NO_3)_3$ solution in contact with quartz under similar experimental condition (0.5 mM $Al(NO_3)_3$ and pH = 3.7 ± 0.1) was conducted. No GISAXS scattering curves were measured after background subtraction, indicating no $Al(OH)_3$ particle formation on quartz.[2] Accordingly, in this study, the formation of $Al(OH)_3$ particles on substrates was not expected as well. Meanwhile, at 25 °C, the solubility of $Al(OH)_3$ ($K_{sp} = 1.3 \times 10^{-33}$) is much lower than $Mn(OH)_2$ ($K_{sp} = 1.9 \times 10^{-13}$). Therefore, the solutions were slightly undersaturated with respect to $Al(OH)_3$ (saturation index = - 0.08) and highly undersaturated with respect to $Mn(OH)_2$ (saturation index = -10.8). That means, if the formation of $Al(OH)_3$ on substrates did not occur, the formation of $Mn(OH)_2$ on substrates should not be expected as well. Therefore, Mn^{2+} and Al^{3+} ion adsorption rather than heterogeneous precipitation of $Mn(OH)_2$ and $Al(OH)_3$ on substrates were likely to have occurred, which changed the zeta potential values of substrates.

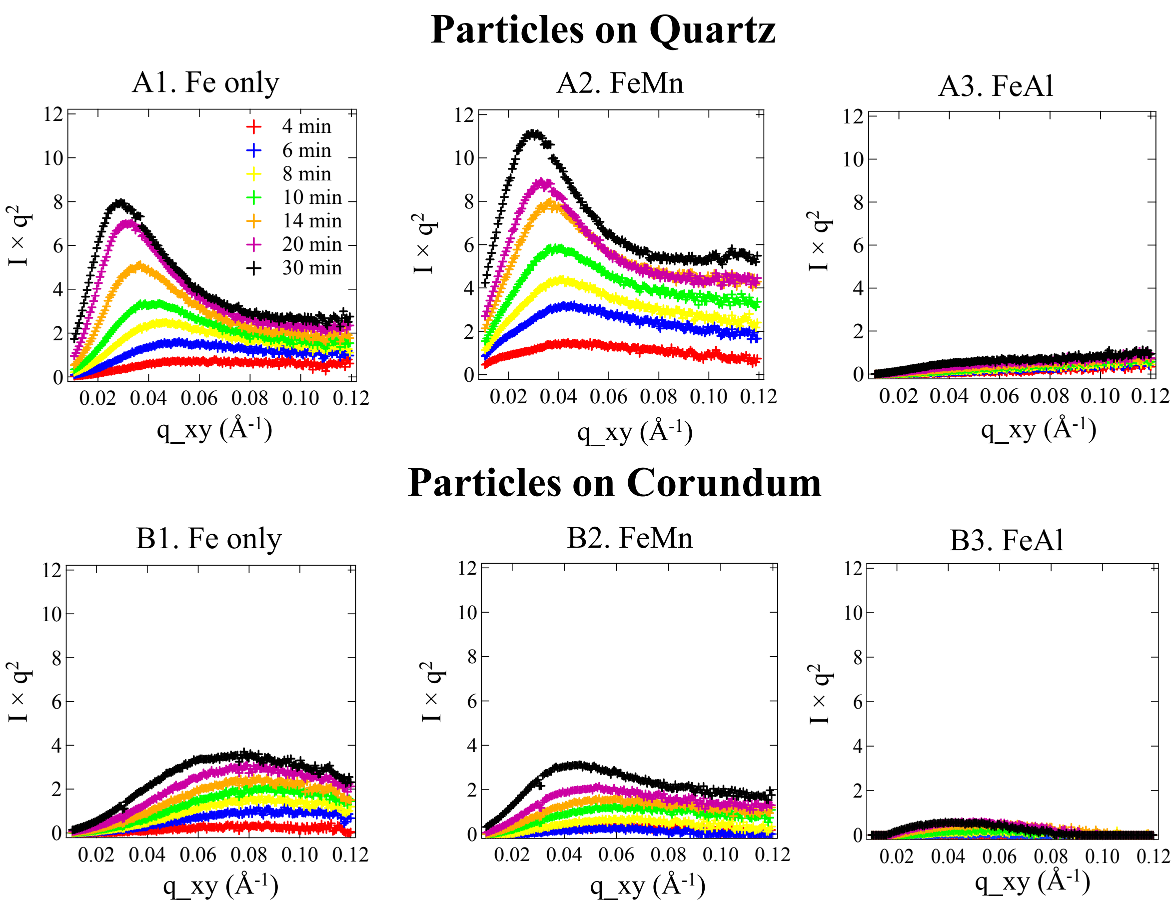

Figure S1. Lorentz-corrected intensity curves of GISAXS scattering caused by ferrihydrite nanoparticles precipitated/deposited on quartz (Figures A1-A3) and corundum (Figures B1-B3)

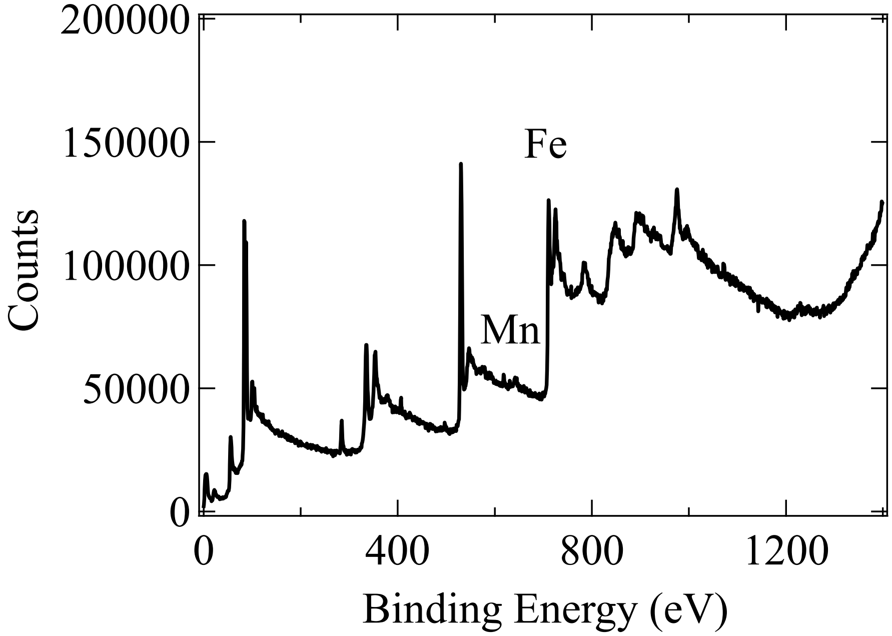

Figure S2. XPS measurements of ferrihydrite particles formed in FeMn solution

References

1. B. L. Henke, E. M. Gullikson and J. C. Davis, *Atomic data and nuclear data tables*, 1993, **54**, 181-342.