Supporting Information for

Environmentally Abundant Anions Influence the Nucleation, Growth, Ostwald Ripening, and Aggregation of Hydrous Fe(III) Oxides

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Summary

Fourteen pages, including 5 Figures.

1 Experimental Operation and Data Analysis Details

2 Cleaning procedure for the quartz single crystals. To remove organic contaminants, the quartz pieces were sonicated in acetone for 10 minutes, and then soaked for 1 h in a highly 3 concentrated sulfuric acid solution mixed with a commercial oxidizing agent, Nochromix. 4 5 Finally, they were rinsed with ultrapure water (resistivity > 18.2 M Ω -cm) and stored in micro-6 filtered distilled water. 7 **Solution preparation:** All solutions (Table 1) were prepared with reagent grade $Fe(NO_3)_3$. 8 9H₂O, NaNO₃, NaCl, and Na₂SO₄, and ultrapure water. Right before SAXS/GISAXS, DLS, or 9 pH measurements, ultrapure water was added to the weighed salt (0.0452 g NaNO₃, 0.0292 g 10 NaCl, or 0.0243 g Na₂SO₄) to make a final solution volume of 45 ml, and we shook the solution 11 to mix it. Then, ultrapure water was added to 0.0202 g Fe(NO₃)₃•9H₂O to get a final solution volume of 50 ml, which we also quickly shook to mix. Finally, 5 ml of this 10^{-3} M Fe(NO₃)₃ 12 13 solution was added into the 45 ml salt solution, and the solution was shaken. So, the final solution contained 10^{-4} M Fe(NO₃)₃ and had an ionic strength of 10 mM. Because hydrous Fe(III) 14 oxide precipitation started when the 10⁻³ M Fe(NO₃)₃ solution was prepared, timing started from 15 16 this moment, and only 3 min elapsed before the first GISAXS image was taken.

Preparing quartz powder in different acidic salt solutions. Quartz was ground to powder
with a mortar and pestle, allowed to settle in each salt solution (NaNO₃, NaCl, or Na₂SO₄, all

with an ionic strength of 10 mM and pH around 3.7 ± 0.2 , adjusted with HNO₃) for 10 min. Then, the upper region of the solution, which contained only small suspended quartz powder particles, was injected into a zeta cell for zeta potential measurements.

22 **Preparing precipitates for HRXRD**. To accumulate more precipitates for mineral phase identification, 500 ml of each of the solutions in Table 1 was prepared, and after 2 h, the 23 24 solutions were centrifuged at 5000 rpm with Millipore Amicon ultra-15 centrifugal filter units. 25 The precipitates that accumulated on the filters were collected on glass slides and dried in a desiccator for 2 h. Then, these precipitates were collected in Kapton[®] capillary tubes, stored at 26 room conditions, and sent to ANL. Within 7 days, synchrotron-based high resolution X-ray 27 28 diffraction (HRXRD) analysis, which requires only a small sample volume, was performed at 29 sector 11-BM of APS in ANL. Both fast scan (3 min/sample) and slow scan (1 hr/sample) were 30 performed. No difference was observed, indicating no X-ray induced artifact.

Invariant calculations. In the definition of invariant Q, the integration region over q is infinite; however, during our SAXS/GISAXS measurements, only a certain q range could be measured. In both nitrate and chloride systems, the Lorentz-corrected GISAXS intensities (Figure 3A1 and 3A2) at both bounds of the measured q range are close to zero, indicating that the integration over the measured q range represents the total volume of the particles that precipitated on the quartz surfaces. For particles formed in these solutions, extrapolations were 37 conducted in the Lorentz-corrected intensity plots, as indicated by the dashed lines in Figures
38 3B1 and 3B2, to get the total particle volume. The big particles formed in the presence of sulfate
39 were out of the measurement range of GISAXS/SAXS; thus, we could not calculate the
40 invariants.

The evolutions of the GISAXS invariants calculated between triplicate runs were very consistent, as indicated by the small error bars in Figure 4A. The evolutions of the SAXS invariants fluctuated within the range indicated by the box in Figure 4A. Several reasons could have caused the large fluctuation of the SAXS invariants: The particles in these solutions were larger than those formed on quartz surfaces, and fewer particles in these solutions were hit by Xray than those on quartz surfaces. Also, the particles can move around in solutions.

47 **Primary particle size, total volume, number and surface area calculations.** The evolutions 48 of the relative total volumes of particles detected by X-ray scattering were calculated using the 49 definition of invariant (Figure 4A). The 1D scattering curves were fit to eqn. (1), where $P(q, r, \sigma)$ 50 is the form factor, and $S(q, I_{0s}, d, R_h, v_f)$ is the structure factor.

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$$I(q) = I_0 P_0(q, r_0, \sigma_0) S(q, I_{0s}, d, R_h, v_f) + I_1 P_1(q, r_1, \sigma_1)$$
 (1)

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$$P(q, R, \sigma) = (\Delta \rho)^2 \int n(R, \sigma) V^2 \frac{9(\sin(qr) - qR\cos(qR))^2}{(qR)^6} dR$$
 (2)

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$$S(q, I_{0s}, d, R_h, v_f) = I_{0s}q^d + S(q, R_h, v_f)$$

55 (3)

S3

56	For the form factor $P(q, r, \sigma)$, a polydisperse sphere model with the Schultz distribution as a
57	size distribution function was used, as shown in eqn. (2). $n(R, \sigma)$ is the Schultz distribution
58	function used to represent the observed size polydispersity of the particles.(1) A spherical model
59	was used because when the size distribution is broad and no form factor oscillation is found in
60	the scattering curves, the shape of particles is hard to resolve unless they are highly anisotropic.
61	Thus, the shape of particles is approximated to a low-resolution, highly symmetric shape, such as
62	a sphere. $\Delta \rho$ is the electron density difference between the nanoparticles and solutions, and V is
63	the particle volume.
64	For the particles precipitated on the quartz surface in the presence of nitrate, an additional
65	peak was observed on the Lorentz-corrected GISAXS curves in the later stage (Figure 3A1),
66	indicating the presence of a bimodal particle size distribution. Thus, the 1D scattering curves
67	(Figure 2A1) were fit to a polydisperse sphere model with the bimodal Schultz distribution as the
68	size distribution function. P_0 and P_1 respectively denote the large particles formed from the early
69	stage and the small 1 nm particles formed in the later stage. For the particles precipitated on the
70	quartz surface in the presence of chloride, only one peak was observed on the Lorentz-corrected
71	GISAXS curves. Thus, I_1 was set as 0. The larger particles showed interparticle distance peaks
72	and a power law behavior in the low q range, which can be modeled by the structure factor,
73	$S(q, I_{0s}, d, R_h, v_f)$, as shown in eqn. (3). Here $S(q, R_h, v_f)$ represents the hard-sphere Percus-

Yevick model, with R_h and v_f being the hard-sphere interaction distance and the volume fraction, respectively. The detailed equations for this model are provided in the book written by Lindman and Alexandridis.⁽²⁾ The smaller particles are well dispersed, and therefore the structure factor function is not required for them.

The fitted values of r and σ after reaction for different times were used to calculate the 78 79 evolution of the average radii of gyration (R_{o}) of the primary particles, according to the Schultz distribution function (Figure 4B). For the particles precipitated on the quartz surface in the 80 81 presence of nitrate, two primary particle sizes and their relative total particle volumes were obtained after the fitting. Then, the total primary particle number and surface area were 82 calculated as the sum of the particles with the two different sizes. Using the spherical particle 83 84 assumption for the calculation of individual particle volumes, given the total particle volumes (Figure 4A) and the average primary particle sizes (Figure 4B), the total primary particle 85 86 numbers (Figure 4C) and surface areas (Figure 4D) were calculated. All data analysis was performed with the Igor Pro program (V. 6.22A, WaveMetrics, Inc., Oregon). 87

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Comparison of the volumes of homogeneously and heterogeneously precipitated particles.

In this study, throughout the 2 hr experiments, in nitrate system, for the heterogeneously and homogeneously precipitated nanoparticles detected by X-ray, the ratios of the total particle volumes were around 42.6 ± 16.5 . In our previous study conducted with the presence of nitrate, 92 the ratio of heterogeneously to homogeneously precipitated iron oxide nanoparticles detected by 93 X-ray after 1.1 hr reaction time was 192:1,(3) higher than the ratio (42.6:1) observed here. In the 94 previous study, (100) surface of quartz was used. Based on our preliminary test, the (100) surface 95 of quartz is more reactive than the (102) surface of quartz used in this study, which might have 96 caused the difference.

97 During simultaneous homogeneous and heterogeneous precipitation, the ratio of the solution volume and the exposed surface area can affect the ratio of the total volumes of the 98 99 particles precipitated in solution and on the substrate surface. To calculate the total particle 100 volume formed in the entire solution volume and on the entire quartz surface, we considered the 101 geometry of the SAXS/GISAXS experimental setup and calculated the percentages of the 102 particles detected by X-ray during the experiments. The geometry of the quartz surface exposed 103 to solution was 1 cm \times 1 cm, and the geometry of the solution was 1 cm \times 1 cm \times 1 cm, resulting in a 1 cm² quartz surface exposed in 1 ml solution. The X-ray beam size was 100 μ m × 100 μ m; 104 105 thus, 1% (1cm \times 100 µm) of the entire surface of the quartz was hit by X-ray during GISAXS 106 measurement, and a 0.01% volume of solution (1cm \times 100 μ m \times 100 μ m) was hit by X-ray 107 during SAXS measurement. Normalizing the total volumes of the particles detected by X-ray 108 (Figure 4A) with their percentages to the total particles formed under the experimental 109 conditions, throughout the 2 hr experiments, the ratios of the total volumes of the heterogeneously precipitated particles on 1 cm² quartz surfaces over the homogeneously precipitated particles in 1 ml solutions were around 0.43 ± 0.16 and 0.06 ± 0.02 , in the presence of nitrate and chloride, respectively. In natural reservoirs, small quartz grains generate a much larger surface area exposed to solution than the single quartz crystal used in our experiments. With a higher ratio of exposed substrate surface area over the fluid volume, a higher ratio of the total volume of heterogeneously precipitated particles over homogeneously precipitated particles can be expected.

117 We also considered the deposition of the homogeneously precipitated particles on the quartz 118 surface. Once the particles formed in solution, it is possible that they could deposit on the quartz 119 surface by electrostatic forces. However, their contribution is insignificant compared to the total 120 particles observed on the quartz surface. Because if both deposition of homogeneously 121 precipitated particles and heterogeneous precipitation are dominant processes for particle 122 formation on the quartz surface, we should have observed abundant particles with two different 123 sizes on the quartz surface, owing to different sizes of particles from the two mechanisms. 124 However, based on AFM observations (Figure S5), only a few big particles (10-20 nm, indicated by the arrows in the AFM images) were observed on the quartz surfaces, while many small 125 126 particles were all over the quartz surfaces. The smaller particles were formed through 127 heterogeneous precipitation. The size of the bigger particles matched well with the sizes of the

128	hom	ogeneously precipitated particles in solution. They were thought to have formed in solution	
129	through homogeneous precipitation and later attached to the surface. As shown in the images, the		
130	contribution of the big homogeneously precipitated particles on the quartz surface is insignificant		
131	compared to those of the heterogeneously precipitated particles.		
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145 Figure S1. GISAXS/SAXS geometry. During the measurement, the scattered X-ray was 146 measured on the 2-D detector; meanwhile, a portion of the incident beam was transmitted 147 through the solution and hit the photodiode. Before analyzing any scattering data, we carefully 148 examined the photodiode values, and confirmed that no significant sample or beam movement 149 happened during the measurement. For GISAXS measurement, a small incident angle α_i (the 150 angle between the incident X-ray beam and the substrate surface) of 0.13° was chosen (98% 151 reflectivity at 12 keV).(4) With this incident angle, the X-ray beam probed only structures on the 152 substrate surface.

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157 **Figure S2.** Large aggregates on the quartz surface after reaction in 10^{-4} M Fe³⁺ solutions with

158 3.42 mM Na₂SO₄.



Figure S3. HRXRD patterns of the precipitates formed in solution. The XRD peaks of the particles formed in nitrate and chloride solutions match well with the reference of ferrihydrite, as indicated by the black dashed lines. In the sulfate system, the XRD peaks of the particles match well with the reference of schwertmannite, indicated by the blue dashed lines.





Figure S4. Variations of solution pH over time.

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173 Figure S5. AFM tapping mode observations of the quartz surfaces after reaction in nitrate (A)

174 and chloride (B) solutions for 2 h.