Supplementary Information for

Optimizing a flow-through x-ray transmission cell for studies of temporal and spatial variations of ion distributions at mineral – water interfaces

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Time resolution estimation for exchange experiments.

The reflected signal is calculated by subtracting the background intensity from the total intensity within the signal window (Fig. S1c). The total number of photons counted in the signal window, I_{tot}, is expressed as

$$I_{tot} = \Phi t (R + \zeta B) \qquad \text{(S1)}$$

where Φ is the incident beam flux, t is the counting time, R, is the intrinsic reflectivity, and ζ is the size of the reflected beam relative to the intrinsic beam size. The value B is the scattering background intensity integrated over the solid angle corresponding to the ideally reflected beam cross section, and is estimated by interpolating the background intensity in the signal window using the measured intensity in the outside region of the signal window (i.e., shown as the hatched area in Fig. S1c). The reflected intensity, I, and its uncertainty, σ, are expressed as

$$\mathrm{I} = \Phi \mathrm{R} t = \mathrm{Itot} - \Phi t \zeta \mathrm{B} \qquad \text{(S2a)}$$

$$\sigma = [\sigma_{I_{tot}}^{2} + (\zeta \Phi t \sigma_{\mathrm{B}})^{2}]^{1/2} = = [\Phi t\ (\mathrm{R} + \zeta \mathrm{B}) + (\zeta \Phi t \sigma_{\mathrm{B}})^{2}]^{1/2} \qquad \text{(S2b)}$$

where σ_B is the estimation error of the background B. On the basis of eq. S2, the fractional uncertainty of the data, σ/I is expressed as

$$\sigma/\mathrm{I} = (1/\mathrm{R})\ [\ (\mathrm{R}+\zeta \mathrm{B})/(\Phi t) + (\zeta \sigma_{\mathrm{B}})^{2}\ ]^{1/2} \qquad \text{(S3).}$$

The time resolution, defined for a given significance of the measurement, $Z = |\Delta \mathrm{I}/\mathrm{I}|\ /\ (\sigma/\mathrm{I})$, can be estimated as

$$\delta \mathrm{t} = (\mathrm{R}+\zeta \mathrm{B})\ /\ \Phi[(\Delta \mathrm{I}/\mathrm{I})^{2}\ \mathrm{R}^{2}/\mathrm{Z}^{2} - (\zeta \sigma_{\mathrm{B}})^{2}] \qquad \text{(S4).}$$

In the most favorable case, the background intensities near the signal region are either constant or exhibit a linear gradient with position on the CCD. In this case, the value B is estimated by scaling the background intensity by the ratio of the background and signal windows. The value σ_B is derived from the counting statistics of the scattered intensity integrated in the background window area, *N* (normalized to the intrinsic beam size), as

$$\sigma_{\mathrm{B}} = [\mathrm{B}/(\Phi N t)]^{1/2} \qquad \text{(S5).}$$

Then, the σ/I and δt can be expressed as,

$$\sigma/\mathrm{I} = \frac{1}{\mathrm{R}\sqrt{\Phi t}} \sqrt{\mathrm{R} + \frac{N+\zeta}{N}\zeta \mathrm{B}} \qquad \text{(S6a) and}$$

$$\delta \mathrm{t} = \mathrm{Z}^{2}(\mathrm{R}+\frac{N+\zeta}{N}\zeta \mathrm{B}\ )\ /\ [\Phi(\Delta \mathrm{I}/\mathrm{I})^{2}\ \mathrm{R}^{2}] \qquad \text{(S6b),}$$

respectively.

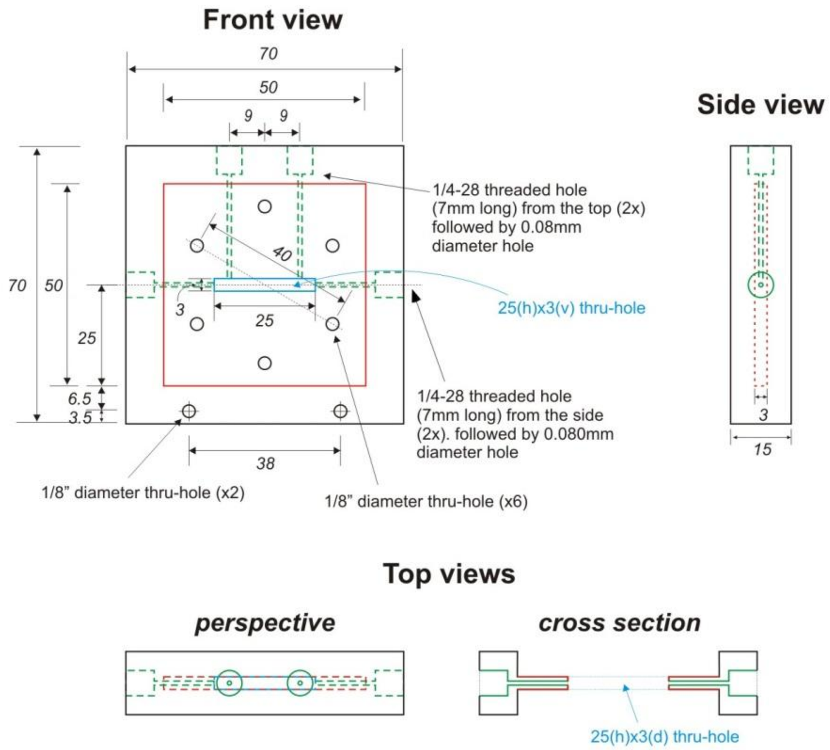

Figure S1. Machine drawing of the flow-through x-ray transmission cell. The length units are millimeters unless specified.

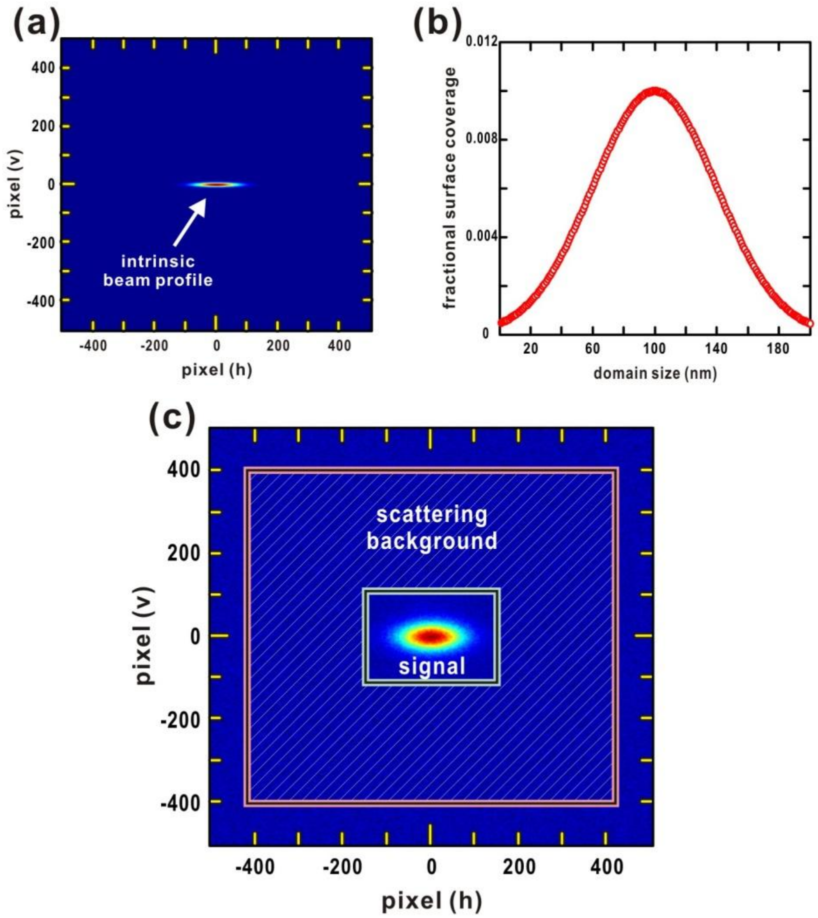

Figure S2. (a) Intrinsic x-ray beam profile simulated as a Gaussian function with vertical and horizontal rms widths of 100 μm and 1000 μm, respectively. The scattering plane is assumed to be transverse to the horizontal pixel position. (b) Fractional coverage of the surface domains on the simulated surface as a function of their size along the beam direction. (c) Image of a simulated x-ray reflection using the beam profile and the surface property shown in (a) and (b), respectively. The effect of a finite domain size shown in (b) leads to broadening of the reflected image in the vertical scattering plane. The calculations are based on a photon energy of E = 15 keV, $\Phi = 1\times10^{12}$ photons/sec, $R = 5\times10^{-7}$, $B = 1\times10^{-8}$, $\zeta = 4$, a CCD pixel size = 20 μm, the sample-to-detector distance = 1 m, and t = 1 sec. The signal box is shown in a green rectangle and the background area is shown as a hatched area.

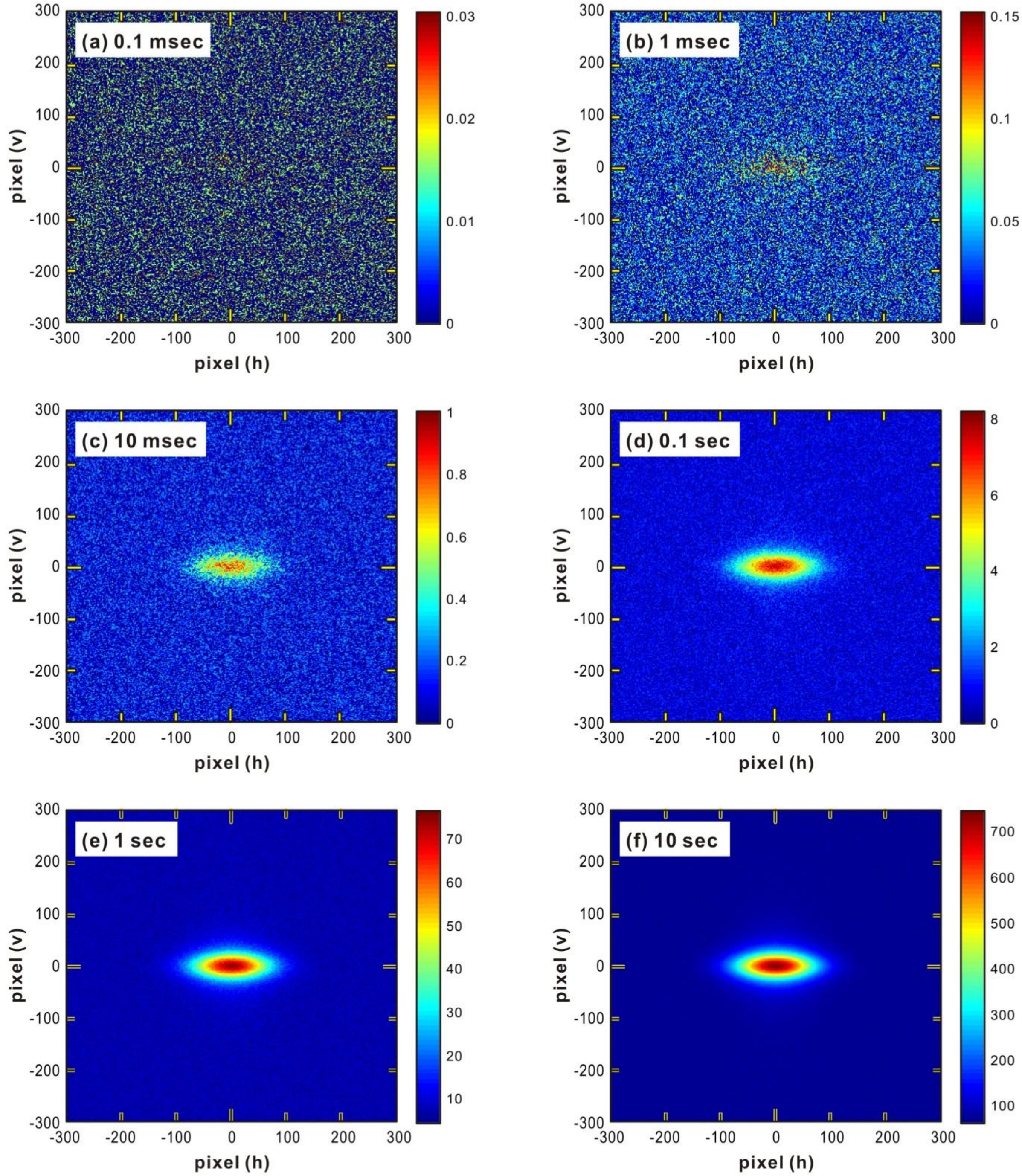

Figure S3. Simulated x-ray reflectivity images as a function of counting time. Refer to Figure S2 for the simulation parameters.