Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supplementary Content

Sorption Selectivity of Birnessite Particle Edges: a d-PDF Analysis of Cd(II) and Pb(II) Sorption by δ-MnO_2 and Ferrihydrite

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1. High-energy X-ray Scattering and Differential Pair Distribution Function Analysis.

For high-energy X-ray scattering experiments, up to 20 mg of air-dried homogenized solids were tightly packed into 3 cm long capillary tubes with inside diameter of 0.3 mm and sealed with epoxy [1]. A mineral blank sample for each sorption series was also prepared as described above without the addition of Cd(II) or Pb(II). Several exposures lasting 0.5-5 s were taken and summed for each sample, for a total detection time of 5-10 min per sample. An empty capillary tube and a CeO_2 standard (NIST 647b) were measured to aid in background subtraction and X-ray calibration, respectively.

The total structure function, $S(Q)$, was extracted from the raw 1D plots of scattering intensity versus scattering angle with the program PDFgetX2 [2]. Following previous approaches [3-6], the chemical formulas of MnO_2 and $Fe(OH)_3$ with varying water contents were used to correct for Compton scattering in samples containing δ-MnO_2 and Fh, respectively. The chemical formula also included the mol fraction of sorbed metals based on wet chemical measurements. The PDF was obtained by direct Fourier transformation of $S(Q)$ with a Q_{max} value of 21 Å^{-1}. In a separate d-PDF study [7], we reported the results of a systematic analysis of the effects of varying i) the chemical formula used to correct for Compton scattering and ii) the Fourier-transform range on the PDF peak positions and relative intensities. This sensitivity analysis showed that the relative peak intensities and positions of the PDF are robust at R-values above 1.0 – 1.5 Å. All d-PDFs were R-averaged over normalization ripples with a moving average of over R-space of $\Delta R = 2\pi/\Delta Q = 0.3$ Å following similar procedures [8, 9].

2. Determination of PDF Instrumental Resolution of pair distribution functions.

The method used to synthesize Goe in our study yields primary crystallites larger than 90 Å in size [10]. Accordingly, the decay in the Goe PDF at R > 2.5 nm is considered due to instrumental resolution. Thus, to obtain the instrumental resolution parameter, Q_{damp}, which is used in the d-PDF calculations, we fit the decay of peak intensity with R in the Goe PDF using PDFgui [2]. In the fit of the Goe PDF, the starting structure was based on the model of Gualtieri and Venturelli, (1999)[11] and the scale factor, unit cell parameters (a, b, c), isotropic displacement parameters (U_{ISO}), and correlated atomic motion parameter (δ) were refined over the R-range 1-20 Å. A Q_{damp} value of approximately 0.054 was returned by the refinement, which is in good agreement with previous studies using a similar rapid acquisition beam line set-up and detector geometry [12, 13]. Consequently, Q_{damp} was set at 0.054 for all d-PDF calculations.

Table S1: Summary of structural parameters used in the d-PDF calculations

	Atomic Postions	$U_{Cd/Pb}$	$U_{Fe/Mn}$	U_{O1}	U_{O2}	Q_{broad}	δ	d_p (Å)
MnO_2	Lanson et al. [14]	-	a	a	a	-	0.07^b	40^b
Fh	Michel et al. [15]	-	0.0032^c	0.014^c	-	0.34^d	0.32^d	20^c
CdO_6	Weil [16]	0.0095^e	-	0.012^e	-	-	-	-
PbO_6	Kwon et al. [17] (MnO_2)	0.0133^f	-	0.02^f	-	-	-	-
PbO_3	Ye et al. [18] (Fh)	0.0133^f	-	0.02^f	-	-	-	-

The (-) symbol indicates parameters that were not included in the calculations. The Q_{damp} value obtained by the refinement of the Goe PDF was held constant at 0.055 for all calculations. Hydrogen atoms were not included in the d-PDF calculations.

a. Refinement of δ-MnO_2 PDF [6]. Anisotropic U values were used in the calculation: $U_{Mn11} = U_{Mn22} = 0.0012$, $U_{Mn33} = 0.0021$, $U_{O11} = U_{O22} = 0.0014$, $U_{O33} = 0.033$.

b. Refinement of δ-MnO_2 PDF [5].

c. Crystal structure of Fh [15].

d. Refinement of Fh PDF [4].

e. Crystal structure $Cd_3(SiO_3)_3$ [16].

f. Crystal structure of cerrusite [18].

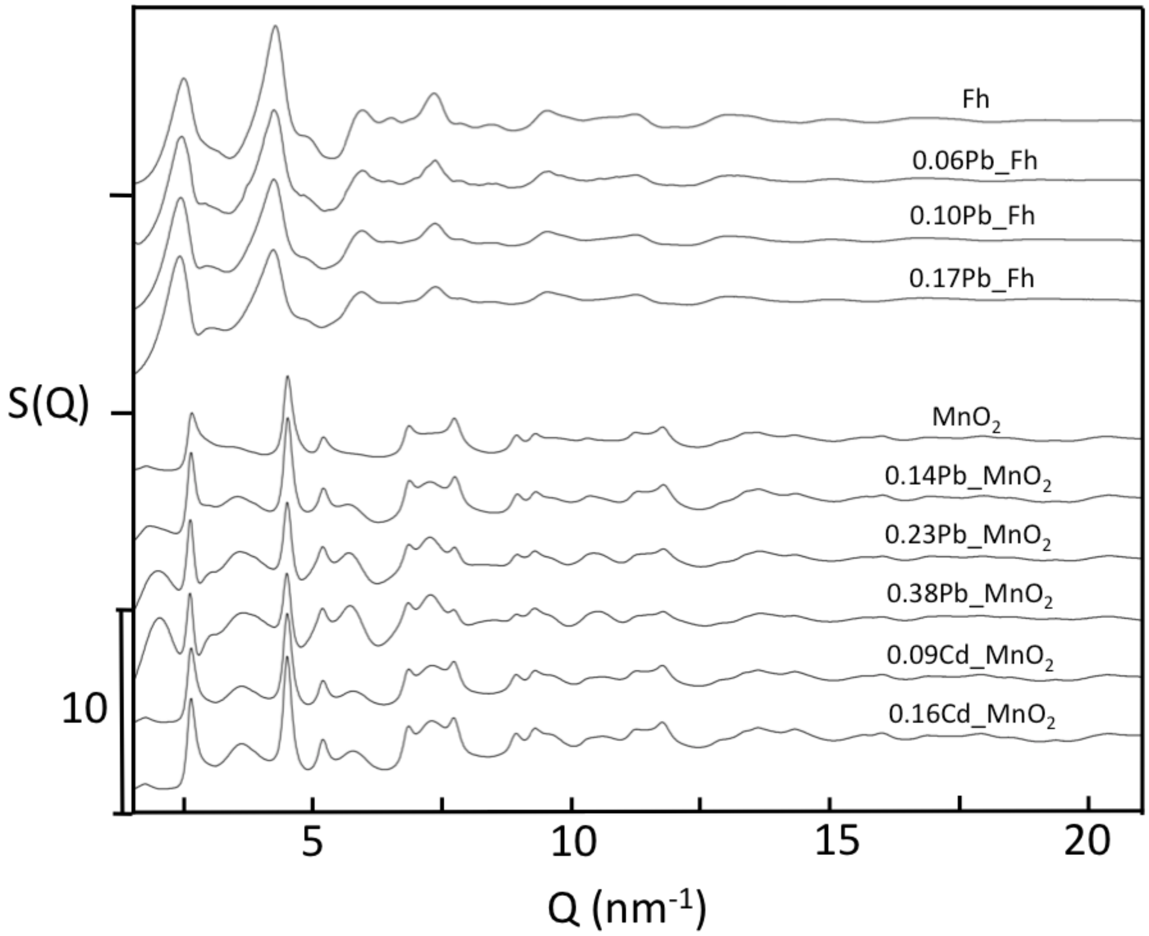

Figure S1: Total structure functions of mineral blanks and sorption samples. The appearance of broad humps in the scattering at 3 nm^{-1} may be due to changes in sheet stacking.

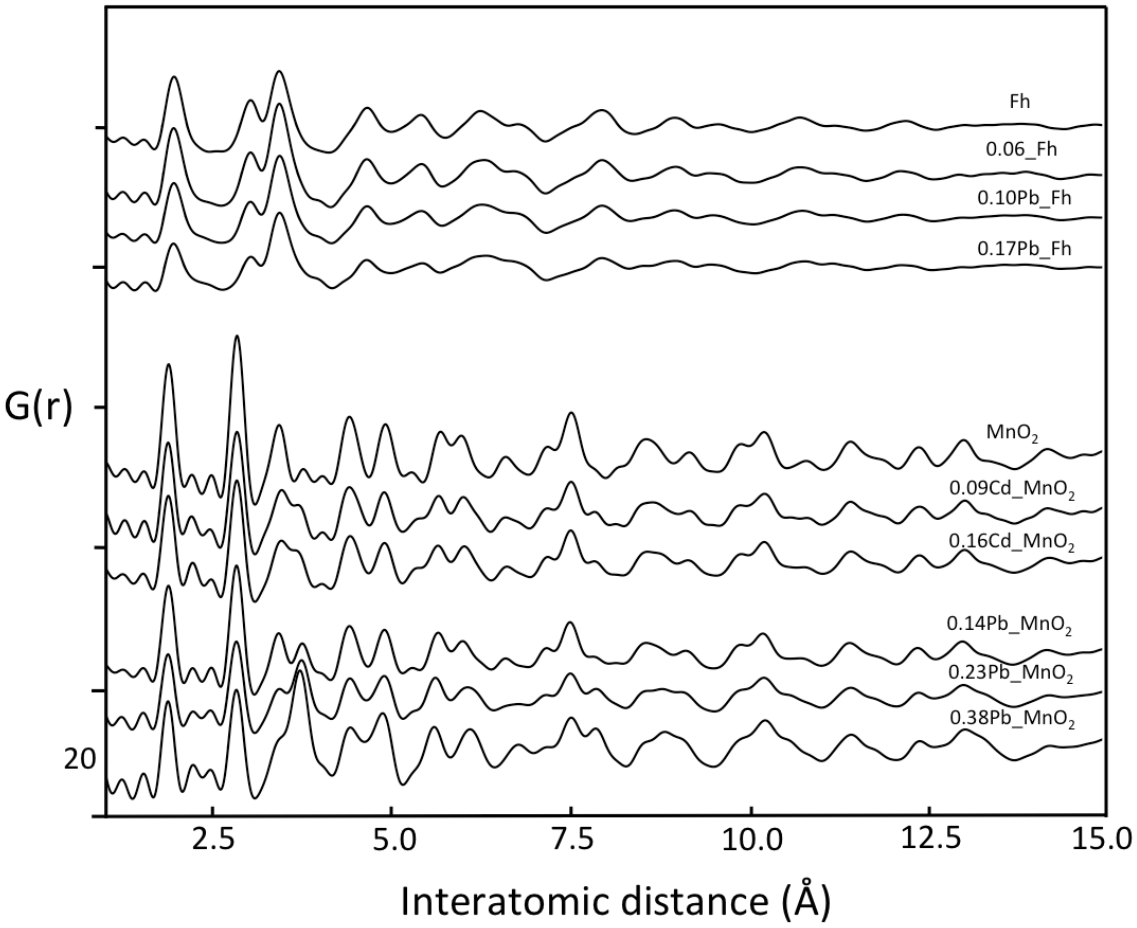

Figure S2: Pair distribution functions of all sorption samples and mineral blanks prior to d-PDF extraction.

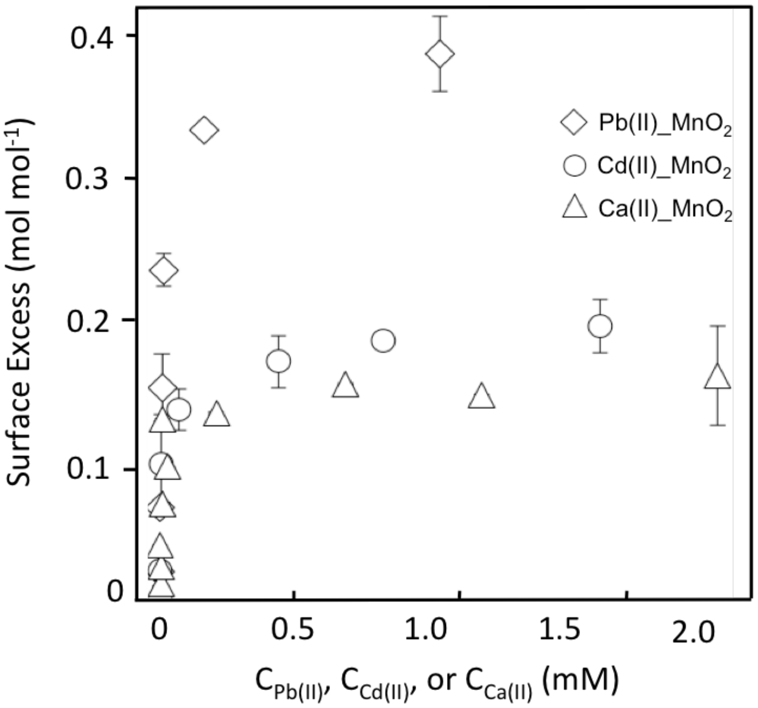

Figure S3: Comparison of Ca(II), Cd(II), and Pb(II) sorption isotherms for δ-MnO$_2$.

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