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Supplementary Information to

Surface precipitation of Mn²⁺ on clay minerals

enhances Cd²⁺ sorption under anoxic conditions

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1. Characterization clay minerals



Figure S1: Powder X-ray diffractogram of the size-fractioned and Ca-saturated Syn-1 (a) and KGa-1b (b). All measured reflections correspond to the clay minerals KGa-1b and Syn-1, aside from the marked reflections of anatase (TiO₂) and boehmite (γ -AlOOH) impurities.

Element	Syn-1	Syn-1	KGa-1b	KGa-1b
(mg/kg)	treated	untreated	treated	untreated
Na	100	620	100	368
Mg	179.9	1080	<20	250
Al	173·10 ³	204·10 ³	194·10 ³	204·10 ³
Si	187·10 ³	233·10 ³	177·10 ³	206·10 ³
Р	100.6		298.9	
S	7.9		13.5	
Cl	25.5		5.6	
Са	9232	335	480	300
Ti	61.9	155	9473	10004
V	< 1.0		233.3	
Cr	5.8		90.3	
Mn	5.5		8.9	
Fe	255	875	1414	2460
Со	18.8		13.2	
Ni	5.4		10.3	17.87
Cu	< 0.5		18.1	25.24
Zn	7		9.9	
Zr	19.7		110.8	
Cd	< 0.3		< 0.3	
Ва	< 1.5		41.4	
Pb	1.8		25.4	32.5

Table S1: Elemental composition of size-fractioned and Ca-saturated (treated) Syn-1 and (treated) KGa-1b as measured by XRF and used in this study and of untreated Syn-1 and KGa-1b as published by the Source Clay Repository of the Clay Minerals Society.¹

2. Kinetic experiment for metal sorption



Figure S2: Sorption of Cd^{2+} (100 μ M) on Syn-1 (~1 g/L) at pH 8.6 as function of time.



Figure S3: Sorption of Cd^{2+} (50 μ M) and Mn^{2+} (50 μ M) on KGa-1b (~1 g/L) at pH 7 as function of time.

3. Modeling

It is known that clay minerals can be described by two types of sites, a permanent negatively charge site and a reactive surface hydroxyl groups located at edge surfaces. Both types of surface sites contribute to total cation binding. In this model we defined one type of permanently charged sites assigned to face surface areas and denoted as Ex^- and one type of pH-dependent charged sites assigned to edges surfaces areas and denoted as $\equiv SOH^{0.5-}$. The sorption on both face and edge surfaces were described with a 1-pK Three-Plane Model (TPM)² (see Figure S4).

Edge surface sites (≡SOH^{0.5-}) undergo protonation according to reaction (1):

$$\equiv SOH^{0.5-} + H^{\dagger} \rightleftharpoons \equiv SOH_2^{0.5+}$$
(1)

with the positive charge of H⁺ placed in the 0-plane. The edge sites were collectively represented by one type of surface site in accordance with successful models presented in the literature;³⁻⁵ this way the number of model parameters is kept low in comparison to attempts describing the edge sites by all possible types of surface hydroxyl groups present at the edge surface of clay minerals.⁶⁻¹⁰ Chloride anions were assumed to form outer-sphere complexes with positively charged edge surface sites (ion-pair formation) according to reaction (2):

$$\equiv SOH^{0.5-} + H^{\dagger} + CI \rightleftharpoons \equiv SOH_{2} - CI^{0.5-}$$
(2)

with the negative charge of Cl⁻ placed in the 1-plane.¹¹ For the sorption of the divalent cations Ca²⁺, Mn²⁺ and Cd²⁺ to edge sites (reactions (3–8)), distribution of cation charge between 0-plane and 1-plane was allowed. Herein, a cation-to-site ratio of 2:1 was assumed based on fitted surface site densities and known ion sizes.^{12, 13} Ikhsan et al.⁸ showed that the adsorption of five transition metals (Pb²⁺, Cu²⁺, Zn²⁺, Co²⁺ and Mn²⁺) could be described via the formation of a bidentate surface complex on the edge sites. The same model was used by Angove et al.¹⁴ and Lackovic et al.¹⁵ to describe Cd(II) adsorption onto kaolinite resulting in a good description of Cd adsorption data with a bidentate surface species (reactions (5), (6), and (8)) were considered, additionally.

$$2 \equiv SOH^{0.5-} + Ca^{2+} \rightleftharpoons (\equiv SOH)_{2} - Ca^{+}$$
(3)

 $2 \equiv SOH^{0.5-} + CaCI^{\dagger} \rightleftharpoons (\equiv SOH)_2 - CaCI$ (4)

$$2 \equiv SOH^{0.5-} + Mn^{2+} \rightleftharpoons (\equiv SOH)_{-}-Mn^{+}$$
(5)

 $2 \equiv SOH^{0.5-} + MnOH^{+} \rightleftharpoons (\equiv SOH)_{2} - MnOH$ (6)

$$2 \equiv SOH^{0.5-} + CdOH^{\dagger} \rightleftharpoons (\equiv SOH)_{2}-CdOH$$
⁽⁷⁾

For the permanently charged sites Ex⁻ the formation of fully charge-compensated cation complexes was assumed according to reactions (8)–(11):

$$Ex^{-} + H^{+} \rightleftharpoons Ex^{-} H$$
 (8)

$$2 \operatorname{Ex}^{2} + \operatorname{Ca}^{2^{+}} \rightleftharpoons (\operatorname{Ex})_{2} - \operatorname{Ca}$$
(9)

$$2 \operatorname{Ex}^{-} + \operatorname{Cd}^{2+} \rightleftharpoons (\operatorname{Ex})_{2} - \operatorname{Cd}$$
(10)

$$2 \operatorname{Ex}^{-} + \operatorname{Mn}^{2^{+}} \rightleftharpoons (\operatorname{Ex})_{2^{--}} \operatorname{Mn}$$
(11)

Herein, the entire charge of the adsorbing cations was exclusively placed into the 1-plane (Figure S4). By placing the charge of the adsorbing cations exclusively on the 1-plane at the permanently charged site Ex⁻ we approximate the cation exchange models using a TPM.



Figure S4: Schematic representation of the electrical potential Ψ as a function of the distance from the surface h and the location of ions at the surface of clay minerals with the three-plane model (TPM).

Table S2: Surface site densities (SD), surface complexation constants (K) and assignment of ioncharges to model planes Δz used in this study for KGa-1b. Proton and calcium surface complexes wereoptimized to acid-base titration data. Cadmium and manganese surface complexes were optimized tobinary metal sorption data at various CaCl₂ concentrations.Surface complexlog K Δz_0 Δz_1 Δz_d Equation nr.

Surface complex	log K	∆z₀	Δz_1	Δz_d	Equation nr.
ExH	5.6	0	1.0	0	(8)
Ex ₂ Ca	4.7	0	2.0	0	(9)
Ex ₂ Cd	6.4	0	2.0	0	(10)
Ex ₂ Mn	6.6	0	2.0	0	(11)
≡SOH ₂ ^{0.5+}	5.4	1.0	0	0	(1)
\equiv SOH ₂ Cl ^{0.5-}	5.8	1.0	-1.0	0	(2)
(≡SOH)₂Ca ⁺	-1.9	1.1ª	0.9 ^a	0	(3)
(≡SOH)₂CaCl	-1.2	1.1 ª	-0.1 ª	0	(4)
(≡SOH)₂Mn⁺	3.8	0.7 ^a	1.3ª	0	(5)
(≡SOH)₂MnOH	7.8	0.7 ^a	0.3 ^a	0	(6)
(≡SOH)₂CdOH	7.6	0.9 ^a	0.1ª	0	(7)
KGa-1b	KGa-1b SD _{edge} (sites/nm ²)		26.1		R ² = 0.999
	SD _{face} (sites/nm ²)		0.7		

^aManually optimized parameters

Table S3: Surface site densities (SD), surface complexation constants (K) and assignment of ion charges to model planes Δz used in this study for Syn-1. Proton and calcium surface complexes were optimized to acid-base titration data. Cadmium and manganese surface complexes were optimized to binary metal sorption data at various CaCl₂ concentrations.

surface complex	log K	Δz_0	Δz_1	$\Delta \mathbf{z}_{d}$	Equation nr.
ExH	5.9	0	1.0	0	(8)
Ex ₂ Ca	5.1	0	2.0	0	(9)
Ex_2Cd	6.3	0	2.0	0	(10)
Ex ₂ Mn	6.7	0	2.0	0	(11)
≡SOH ₂ ^{0.5+}	5.1	1.0	0	0	(1)
\equiv SOH ₂ Cl ^{0.5-}	3.4	1.0	-1.0	0	(2)
(≡SOH)₂Ca ⁺	-0.6	1.0 ^ª	1.0 ^a	0	(3)
(≡SOH) ₂ CaCl	-1.3	1.0ª	0 ^a	0	(4)
(≡SOH)₂Mn⁺	2.5	0.7 ^a	1.3 ^a	0	(5)
(≡SOH)₂MnOH	4.5	0.7 ^a	0.3 ^a	0	(6)
(≡SOH)₂CdOH	5.2	0.8 ^a	0.2 ^a	0	(7)
Syn-1	Syn-1 SD _{edge} (sites/nm ²)		24.2		R ² = 0.998
SD _{face} (sites/nm ²)		tes/nm²)	1.3		

^aManually optimized parameters

4. Acid-base titration

The proton consumption was determined by subtracting the contribution of the electrolyte solution to the proton balance from known amounts of added acid and bases as given in Eq.12. The background electrolyte contribution includes the concentrations of H^+ and OH^- in the bulk as well as the amounts of H^+ and OH^- consumed by the formation of any hydrolysis species in solution such as e.g., CaOH⁺ and Ca(OH)₂.

Proton consumption = $(H_{added} - OH_{added}) - (H_{bulk} - OH_{bulk}) - (-OH_{CaOH} - 2OH_{Ca(OH)2})$ (Eq.12)

Due to the significant amount of clay dissolution, Si and Al species were considered additionally (see Eq.13), including:

- (1) AI(OH)₂, AI(OH)₃, AI(OH)₄, AI(OH)₅, AI₂(OH)₂, AIOH, AI₁₃O₄OH₂₄
- (2) H₂SiO₄, H₃SiO₄, H₄SiO₄, H₆Si₄O₁₂, HSiO₄, AlOH₆SiO, Ca(H₃SiO₄), CaH₃SiO₄, CaH₂SiO₄

 $Proton \ consumption = (H_{added}-OH_{added})-(H_{bulk}-OH_{bulk})-(-OH_{CaOH}-2OH_{Ca(OH)2})-(H_{Al,Si \ species}-OH_{Al \ ,Si \ species})$ (Eq.13)

Silicium and aluminum concentration were fixed to their concentrations as measured at the end of the potentiometric titration of the clay minerals (see Table S2).

Table S4: Percentage Si and Al c	f total solid dissolved (after acid-base titration c	of KGa-1b and Syn-1.
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	KGa-1b	Syn-1
Si (wt % dissolved)	0.04	0.99
Al (wt % dissolved)	0.03	0.36

Including the contribution of aluminum species in the calculation of total proton consumption (Eq. 13) based on dissolved Al at the end of the titration experiment (see Figure S4) resulted in an obvious overcorrection as evidence by the minimum of net proton adsorption at about pH 4.5 (see Figure S5). Therefore, only the correction for Si species included in the data analysis as presented in Figure S6.



Figure S5: Proton adsorption to KGa-1b (a) and Syn-1 (b) at three different CaCl₂ concentrations (0.01, 0.03 and 0.1 mM) as a function of pH. Data on net proton adsorption shown here were corrected for proton and hydroxide consumption by Ca, Al, and Si species.

CaCl₂ was used as the background electrolyte in the acid-base titrations in this study. In the two-site TPM, Ca²⁺ adsorption was in a first attempt described by the exclusive formation of outer-sphere surface complexes on both the face sites and the edge sites, i.e. placing Ca²⁺ charges exclusively into the 1-plane for both site. This approach resulted in an unsatisfactory description of proton adsorption in the alkaline pH range for both clay minerals (Fig. S6a,b). The fits of the experimental data were substantially improved by distributing the charge of Ca²⁺ sorbing to the edge sites between the 0- and the 1-plane (R²= 0.999 and R²= 0.998 for KGa-1b and Syn-1 respectively, see Fig. S6c and d). In the best fits, the charge placed on the 0-plane (= Δz_0) equaled 1.1 for KGa-1b and 1.0 for Syn-1 (Tab. S3 and S4).



Figure S6: Proton adsorption to KGa-1b (a,c) and Syn-1 (b,d) at three different CaCl₂ concentrations (0.01, 0.03 and 0.1 M) as a function of pH. Solid concentration was 50 g/L for KGa-1b and 18.75 g/L for Syn-1. Symbols correspond to data points obtained from acid-base titrations (KGa-1b: n = 96 and Syn-1: n=96). Lines represent best-fit description (KGa-1b: $R^2 = 0.999$ and Syn-1: $R^2 = 0.998$) with a two-site TPM (see Table S3 and S4 for parameter values). The fits depicted in panels a and c correspond to best fits when placing the Ca²⁺ charge on edge sites exclusively into the 1-plane to form only outer-sphere surface complexes. In panels b and d, best fits including charge distribution for Ca²⁺ on edge sites are shown (Δz_1 (=SOH-Ca) = 1.1 for KGa-1b and 1.0 for Syn-1) (b,d). Data and fits are plotted as net proton adsorption relative to the point of zero net proton charge of edge surfaces.



5. Cd²⁺ and Mn²⁺ sorption on KGa-1b and Syn-1

Figure S7: Sorption of Cd^{2+} (a,c) and Mn^{2+} (b,d) on KGa-1b as function of pH at $CaCl_2$ concentration. Total metal concentrations were 0.5 and 5 μ M for Cd^{2+} and 0.1 and 5 for Mn^{2+} , respectively. All samples were prepared with a solid concentration of ~1 g/L and were equilibrated for 1 day. In the samples equilibrated with DDI water, the dissolved Ca concentration was about 1 μ M after the 1 day equilibration. Lines represent the best-fit for Cd^{2+} ($R^2 = 0.974$, n = 187) and Mn^{2+} sorption ($R^2 = 0.974$, n = 192) described with the two-site TPM, calibrated with the protonation data.



Figure S8: Sorption of Cd^{2+} (a,c) and Mn^{2+} (b,d) on Syn-1 as function of pH at $CaCl_2$ concentration. Total metal concentrations amounted to 1 μ M and 50 μ M were for Cd^{2+} and 1 μ M and 10 μ M for Mn^{2+} . All samples were prepared with a solid concentration of ~1 g/L and were equilibrated for 1 day. In the samples equilibrated with DDI water, the dissolved Ca concentration was about 0.1 mM after the 1 day equilibration. Lines represent the best-fit for Cd^{2+} (R^2 =0.982, n = 252) and Mn^{2+} sorption (R^2 =0.909, n = 120) described with the two-site TPM, calibrated with the protonation data.

To investigate the respective contributions of the two types of sites present on the clay surface, namely the edge and face sites, to the total proton adsorption of both clay minerals, acid-base titration data were modelled with a two-site TPM as presented in section 4. Optimized model parameters corresponding to best fits of acid-base titration data as shown in Figure S6c,d are listed in Table S3 and S4. Subsequently the optimized surface parameters of the clay minerals, namely the site densities of \equiv SOH^{0.5-} on edge and Ex⁻ on face surfaces and the protonation and surface complex formation constants for Ca²⁺ and Cl⁻ were fixed and surface complex formation of Mn²⁺ and Cd²⁺ onto the clay minerals were optimized using the metal adsorption data.

Sorption of Mn^{2+} and Cd^{2+} to KGa-1b and Syn-1 as function of pH and $CaCl_2$ concentrations was well described ($r^2 > 0.90$) by the two-site TPM (see lines in Fig. 1, S7 and S8). In order to obtain a good fit for both Mn^{2+} and Cd^{2+} , charge distribution between 0-plane and 1-plane had to be allowed for surface complexes on edge sites similarly to Ca^{2+} (see Table S3 and S4). In addition, metal cation hydroxide surface complexes had to be included on the edge sites to obtain good fits in the alkaline pH range. In case of Cd^{2+} , only two types of surface complexes were needed to best describe the whole metal sorption dataset, (i) an outer-sphere surface complex on the permanently charged face sites, predominating in Cd adsorption in the acidic pH range, and (ii) a cadmium-hydroxo complex on the edge sites, predominating in Cd adsorption in the alkaline range (Fig. S9a, c and S12a, c). For Mn^{2+} , three complexes were required to best describe the whole metal sorption dataset, (i) an outer-

sphere complex on the permanently charged face sites, being dominant in the acidic pH range, (ii) a manganese surface complex on the edge sites, quantitatively prevailing between pH 7 and 9, and (iii) a mangenese-hydroxo complex on the edge sites, predominating in the alkaline range (Fig. S9b, d and S12b, d).



Figure S9: Sorption isotherm of Mn^{2+} at pH 7.5 ±0.1 (a) and Cd^{2+} at pH 7.5 ±0.1 (b) on ~1 g/L Syn-1 montmorillonite as a function of dissolved metal concentration at different $CaCl_2$ concentrations. All samples were equilibrated for 1 day. Dissolved Ca after equilibration amounted to about 0.1 mM in samples prepared with DDI water. Lines represent predictions based on the optimized two-site TPM. The isotherms were constructed by selecting data points from pH-dependent experiments.



Figure S10: Sorption isotherm of $Mn^{2+}(a)$ and $Cd^{2+}(b)$ at pH 6.5 ±0.1 on ~1 g/L KGa-1b as a function of dissolved metal concentration at different CaCl₂ concentrations. Dissolved Ca after equilibration amounted to about 0.1 μ M in samples prepared with DDI water. Lines represent predictions based on the optimized two-site TPM. The isotherms were constructed by selecting data points from pH-dependent experiments.



Figure S11: Calculated speciation of surface complexes for Cd^{2+} (a, c) and Mn^{2+} (b, d) adsorbed to KGa-1b (a, b) and Syn-1 (c, d) as a function of pH in DDI water (1 μ M Ca for KGa-1b and 0.1 mM Ca for Syn-1) for selected total metal concentrations of 0.5 and 1 μ M Cd^{2+} and 0.1 and 1 μ M Mn^{2+} . For comparison, experimental data points and fits corresponding to the sum of plotted species are shown, additionally.



Figure S12: Speciation of surface complexes for Cd^{2+} (a, c) and Mn^{2+} (b, d) adsorption to KGa-1b (a, b) and Syn-1 (c, d) as a function of pH in 10 mM CaCl₂ as calculated with the optimized two site TPM model for selected total metal concentrations of 0.5 and 1 μ M Cd²⁺ and 0.1 and 1 μ M Mn²⁺. For comparison, experimental data points and fit corresponding to the sum of plotted species are shown, additionally.



6. Competitive sorption

Figure S13: Sorption of Cd^{2+} (0.001 mM) to Syn-1 (a) and KGa-1b (b) in 10 mM $CaCl_2$ with various Mn^{2+} concentrations (0 mM, 0.05 mM and 0.5 mM) as a function of pH. The solid concentration was ~1 g/L. Lines show the predicted effect of Mn^{2+} on Cd^{2+} sorption assuming that competition for adsorption sites is the dominant type of interaction in a competitive system.

7. Pourbaix diagram for manganese



Figure S14: Pourbaix diagram for manganese displaying the predominant dissolved and solid manganese species as calculated for Mn^{2+} activities of $10^{-0.3}$, Ca^{2+} activity of $10^{-1.7}$ and C⁺ activity of $10^{-0.34}$ (25°C) using the Geochemist's Workbench software and the NIST 46.7 database. The selected activities correspond to the conditions of batch experiments prepared for XAS analysis.

8. Saturation indices

Table S5: Saturation indices for potential minerals forming in XAS samples at the beginning of anoxic equilibration. Displayed pH values correspond to the pH measured at the end of the equilibration period for each sample.

рН	[Mn ²⁺]	[Cd ²⁺]	[Ca ²⁺]	[Cl ⁻]	Saturation index ^a					
	(mM)	(mM)	(mM)	(mM)						
					Cd(OH)2 (s)	CdCl ₂ (s)	CdOHCl (s)	MnCl ₂ :4H ₂ O (s)	Ca(OH)₂	Mn(OH)₂
									(Portlandite)	(Pyrochroite)
7.8		0.25	50	100.5	-2.825	-6.344	-1.629			
8.1		0.25	50	100.5	-2.225	-6.344	-1.329			
8.1	2.5		50	105.0				-8.048	-8.323	-2.096
8.7	2.5		50	105.0				-8.089	-7.123	-0.937
8.2	2.5	0.25	50	105.5	-2.026	-6.347	-1.231	-8.051	-8.123	-1.897
8.4	2.5	0.25	50	105.5	-1.626	-6.347	-1.031	-8.055	-7.723	-1.502

^aSaturation Index = (log IAP – log K_{sp}), IAP (= Ion activity product), K_{sp} (= Stoichiometric solubility product). Note: a 100% N₂ atmosphere is assumed for all calculations.

9. Protocols to ensure anoxic conditions

The oxygen sensitivity of Mn^{2+} required all batch sorption experiments and XAS sample preparation to be performed under strict anoxic conditions. All experiments were executed in an anoxic glovebox with a 100% N₂ atmosphere, equipped with copper catalyst (MBraun) attached to a fan box to scavenge trace O₂ and with an O₂-meter to monitor oxygen level during experiments. The O₂ meter reading remained at < 10 ppm during the entire experimental period. Water used for sample and reagent preparation was boiled and purged with pure nitrogen gas for at least 3 hours outside the glovebox, and then transferred inside to cool down and degas for at least 24 hours before use. All sample containers were wrapped in aluminum foil to minimize any possibility of oxidation by photochemistry. All labware used in the experiments, including bottles, tubes, filters, syringes and pipette tips, were brought into glovebox at least one day before use to remove adsorbed oxygen.

10. Batch experiments for solid phase analysis

Table S6: Amounts of sorbed Mn^{2+} and Cd^{2+} (mol/kg) for batch experiment with KGa-1b and Syn-1 prepared for solid phase analysis. All samples were equilibrated for 1 day under anoxic conditions with a solid-to-solution ratio of ~5 g/L.

Syn-1	sorbed Cd ²⁺	Syn-1	sorbed Mn ²⁺
	(mol/kg clay)		(mol/kg clay)
No Mn ²⁺	0.0097	No Cd ²⁺	0.1425
With Mn ²⁺	0.0150	With Cd ²⁺	0.1312
KGa-1b		KGa-1b	
No Mn ²⁺	0.0026	No Cd ²⁺	0.1915
With Mn ²⁺	0.0229	With Cd ²⁺	0.1683



Figure S15: Sorption of Mn^{2+} (2.5 mM) to Syn-1 and KGa-1b in 50 mM CaCl₂ in absence and presence of Cd²⁺ (0.25 mM) at pH ~8. The solid concentration was ~5 g/L. Samples were equilibrated for 1 day under anoxic conditions. Displayed pH values correspond to the pH measured at the end of the equilibration period for each sample. The error bars indicate the standard deviation of duplicates.



11. Si released in XAS batch experiments

Figure S16: Dissolved Si released from (a) KGa-1b and (b) Syn-1 (\sim 5 g/L) in 50 mM CaCl₂ after 1 day equilibration.



Figure S17: Released Si for sorption batch experiment of Mn^{2+} and/or Cd²⁺ with KGa-1b (a) and Syn-1 (b) at pH ~8 with CaCl₂ concentration of 50 mM. All samples were equilibrated for 1 day under anoxic conditions with a solid concentration of ~5 g/L. Average Si release between pH 6 and 8 for KGa-1b and Syn-1 is given with a red dashed line. Displayed pH values correspond to the pH measured at the end of the equilibration period for each sample.

12. X-ray absorption spectroscopy

Samples for XAS measurements were prepared by homogenizing the dried solids with a mortar and pestle. The homogenized powder samples were pressed into 13-mm pellets. The pellets were subsequently sealed between Kapton[®] tape and sealed in two doubly sealed aluminum bags under N₂ gas for transport to the synchrotron. Two samples were additionally prepared as oriented clay films and measured with polarized–XAS (α = 10°, 35°, 55°, and 80°). The oriented samples were prepared by collecting the clay on a cellulose nitrate filter, stacking the filters with the solid, and sealing them between Kapton® tape. All our measurements were conducted at 25 K to avoid beam damage and oxidation of oxygen sensitive samples. The Mn K-edge (6539 eV) XANES and EXAFS spectra of the sorption samples (~0.5 mmol Mn/kg clay) were measured in transmission mode. The Cd K-edge (26711 eV) XANES and EXAFS spectra of the sorption samples (~0.05 mmol Cd/kg clay) were collected in fluorescence mode using a 36-element array Ge detector (Canberra). For polarized EXAFS spectra of the clay films were recorded at 10°, 35°, 55°, and 80° in fluorescence detection mode. A Helium cryostat was used to minimize beam-induced redox changes of Mn during measurements. Monochromator (Si(220)) was calibrated to the first-derivative maximum of the K-edge absorption spectrum of a metallic Mn-foil (6540 eV) and Ag-foil (25514 eV) for the Mn and Cd K-edge, respectively. The Mn- or Ag-foil were continuously measured to account for small energy shifts (< 1 eV) during the sample measurements.

All spectra were energy calibrated, pre-edge subtracted, and post-edge normalized in Athena.¹⁶ LCF analyses of Mn K-edge XANES spectra were performed over an energy-range of 6530-6650 eV with the E_0 of all spectra and reference compounds set to 6551 eV (Mn). No constraints were imposed on all LCF fits, and initial fit fractions (99.3–99.5%) were recalculated to a compound sum of 100%. Suitable Mn references that were considered for LCF analyses were: birnessite, nsutite, ramsdellite, Mn^{2+} sorbed on illite, Mn(II)-hydroxide, hausmannite, rhodonite, feitknechtite and manganite.



Figure S18: Derivative of normalized Mn K-edge XANES spectra of Mn^{2+} (2.5 mM) was reacted with KGa-1b and Syn-1 in 50 mM CaCl₂ in absence (blue lines) and presence of Cd²⁺ (0.25 mM) (green lines) at pH 8. The solid concentration was ~5 g/L. Samples were equilibrated for 1 day under anoxic conditions.



Figure S19: LCF of Mn K-edge XANES spectra of sorption samples. Mn^{2+} (2.5 mM) was reacted with KGa-1b and Syn-1 in 50 mM CaCl₂ in absence (blue lines) and presence of Cd²⁺ (0.25 mM) (green lines) at pH 8. The solid concentration was ~5 g/L. Samples were equilibrated for 1 day under anoxic conditions. Points indicate experimental data and solid lines show the model fits.

KGa-1b	Mn(OH)₂	MnAl-LDH	Sum	R-factor	red. χ^2 (10 ⁻³)	% Mn(II)
No Cd ²⁺	34	66	99.5	0.0025	0.3058	100
With Cd ²⁺	38	62	99.5	0.0033	0.4104	100
Syn-1	Rhodonite	MnAl-LDH	Sum	R-factor	red. χ² (10 ⁻³)	% Mn(II)
No Cd ²⁺	60	40	99.3	0.0052	0.5948	100
With Cd ²⁺	42	58	99.4	0.0055	0.6447	100

Table S7: The two-components LCF of XANES of Mn K-edge for Mn-containing sorption samples.



Figure S20: Mn K-edge k^3 -weighted EXAFS spectra of sorption reacted with 2.5 mM Mn²⁺ in absence (blue lines) or presence (green lines) of Cd²⁺ (0.25 mM). Additionally, relevant Mn K-edge EXAFS spectra of Mn(II) and Mn(III)- reference compounds were shown (black lines). Sorption samples were equilibrated for 1 day under anoxic condition at pH 8 with a solid concentration of ~5 g/L of KGa-1b or Syn-1.



Figure S21: Cd K-edge k^3 -weighted EXAFS spectra of sorption samples (grey lines) reacted with 0.25 mM Cd²⁺ in absence (blue lines) or presence (green lines) of Mn²⁺(2.5 mM). Sorption samples were equilibrated for 1 day under anoxic condition at pH 8 with a solid concentration of ~5 g/L of KGa-1b or Syn-1.

Shell-fit analyses of the fourier transform of the extended X-ray absorption fine structure (EXAFS) spectra were performed in order to obtain information about the short range local coordination environment of Mn and Cd. Fourier transforms of k³-weighted EXAFS spectra were calculated over a k-range of 3–8 Å⁻¹ and 3–10 Å⁻¹ using a Kaiser-Bessel window function and a frequency cut-off parameter for Cd and Mn, respectively. The Rbkg set to 1.2 for the FT of both Cd and Mn EXAFS spectra. The edge-energy, E₀, was defined as the highest maximum in the XANES spectra. The shell-fit analyses of all k³-weighted Mn and Cd K-edge EXAFS spectra were performed in R-space R + Δ R-range of 1.2–3.5 Å with software Artemis¹⁶ for the exception of Cd sorption samples without Mn²⁺ for which shell-fit analysis was performed in R-space R + Δ R-range of 1.1–2.5 Å. Theoretical phase-shift and amplitude functions were calculated with FEFF v.6^{17, 18} based on the structures of pyrochroite (Mn(OH)₂)¹⁹ and CdO.²⁰



Figure S22: High-resolution WT analyses of the second shell (r 2.3 – 3.6 Å), with Morlet parameters of $\eta = 5.8$, $\sigma = 1$, shown for reference compounds (a) Mn(OH)₂, (b) MnAl-LDH, and (c) rhodonite.



Figure S23: High-resolution WT analyses of the second shell (r 2.3 – 3.6 Å), with Morlet parameters of $\eta = 5.8$, $\sigma = 1$ for (a) KGa-1b equilibrated with Mn^{2+} (b) Syn-1 equilibrated with Mn^{2+} (c) KGa-1b equilibrated with Mn^{2+} and Cd²⁺ (d) Syn-1 equilibrated with Mn^{2+} and Cd²⁺.

14. P-EXAFS of Mn and Cd K-edge XAS

In P-EXAFS neighbouring atoms along the electric field (or along polarization direction of the X-ray beam) are preferentially probed, and atoms located in a plane perpendicular to this electric field direction are attenuated. Applying this method to clay mineral self-supporting films has the advantage of minimizing the contribution of cations from the tetrahedral sheets by orienting the layer ab plane to electric field and conversely, the contributions of cations from the octahedral sheet is extinguished in the perpendicular orientation of the electric field.

P-EXAFS of the self-supporting film of Mn sorption sample are given in Figure S25 and S26. The $k^{3}\chi(k)$ spectra contained isosbestic points for which $\chi(k)$ is independent of k over the whole k range and the spectra displayed a large dependence of the $k^{3}\chi(k)$ spectra upon orientation in the regions between the isosbestic points.



Figure S24: k^3 -weighted Mn K-edge EXAFS spectra of a Mn and Cd-sorbed clay film at angles of 10°, 35°, 55° and 80°. Mn²⁺ (0.5 mol/kg) and Cd²⁺ (0.05 mol/kg) were sorbed onto KGa-1b (a) and Syn-1 (b) at pH 8 and equilibrated for 1 day under anoxic conditions.



Figure S25: k^3 -weighted Cd K-edge EXAFS spectra of a Mn and Cd-sorbed clay film at angles of 10°, 35°, 55° and 80°. Manganese (0.5 mol/kg) and cadmium (0.05 mol/kg) were sorbed onto KGa-1b (a) and Syn-1 (b) at pH 8 and equilibrated for 1 day under anoxic conditions.

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