Two-Step Delamination of Highly-charged, Vermiculite-like Layered Silicates via Ordered Heterostructures

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Supporting Information

Content:

1. Supporting Data

Scanning Electron Microscopy.

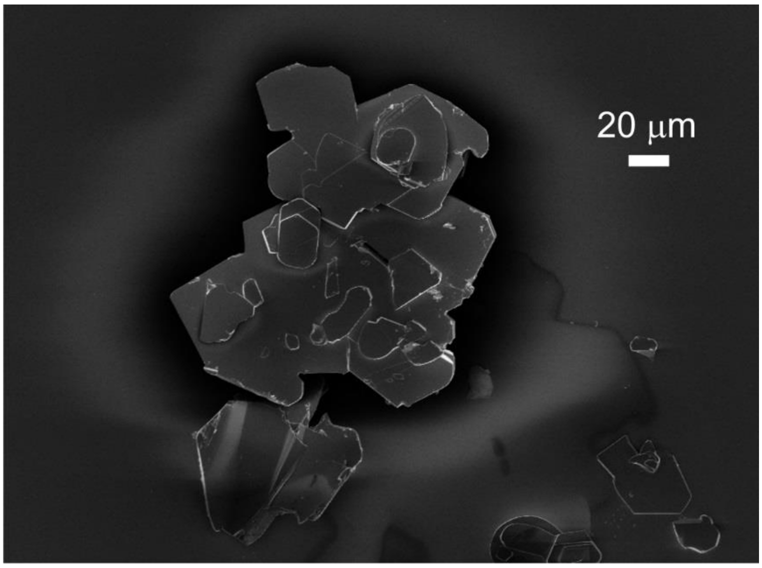
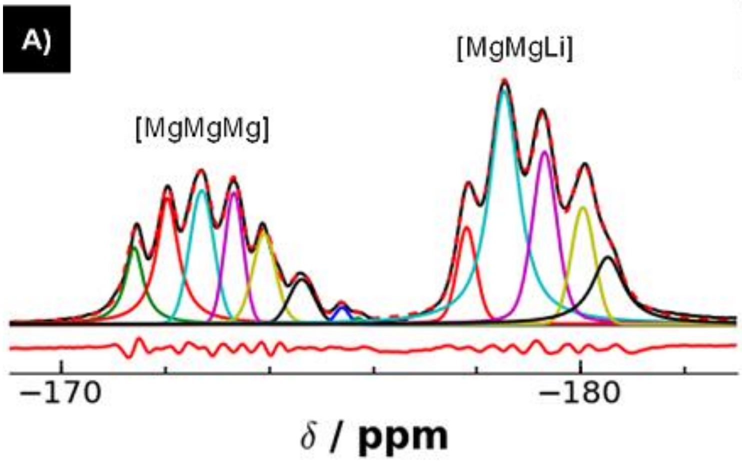


Figure S1. SEM of a Na-Hec agglomerate as obtained from melt synthesis.

^{19}F-NMR-Spectroscopy.



B)

peak	summed intensities
[MgMgMg]	1.541
[MgMgLi]	2.277

Figure S2. (A) shows the ^{19}F-NMR of Na-Hec with two separated bands that can be assigned to [MgMgMg]- and [MgMgLi]-environments of ^{19}F in the octahedral layer.[1] As no other fluorine sites were detected, the obtained Na-Hec is therefore perfectly trioctahedral. Deconvolution was performed using Pseudo-Voigt-functions with the same FWHM for Gaussian- and Lorentzian-part. Part (B) of the same figure shows the summed intensities of the two peaks.

Calculations of the composition of the octahedral layer based on these integrals are explained in the following.

First the site intensities belonging to Mg (S_{Mg}) and to Li (S_{Li}) are calculated from the integrals (I):

$$S_{Mg} = 3 \cdot I_{[MgMgMg]} + 2 \cdot I_{[MgMgLi]} = 9.177 \quad (1)$$

$$S_{Li} = 1 \cdot I_{[MgMgLi]} = 2.277 \quad (2)$$

The total intensity is obtained by summation:

$$S_{total} = S_{Mg} + S_{Li} = 11.454 \quad (3)$$

As there are three octahedral positions surrounding each structural F ion which are fully occupied for trioctahedral clay minerals, the stoichiometry of the octahedral layer (O) can be calculated:

$$O_{Mg} = \frac{3}{S_{total}} \cdot S_{Mg} = 2.40 \quad (4)$$

$$O_{Li} = \frac{3}{S_{total}} \cdot S_{Li} = 0.60 \quad (5)$$

Hence the layer charge per formula unit $Si_4O_{10}F_2$ according to the obtained octahedral composition $[Mg_{2.40}Li_{0.60}]^{okt.}$ is 0.60.

CHN-Analysis and Distribution Equilibrium.

Carbon content was determined by CHN-analysis. The molar mass of the partial exchanged phase $[Na_{0.6\text{-}y}C4_y]^{inter.}$ varies with the amount of n-butylammonium intercalated. Carbon content therefore has to be calculated iteratively. By this means y is varied till the molar mass of $[C4_yNa_{0.60\text{-}y}]^{inter.}[Mg_{2.4}Li_{0.6}]^{okt.}\langle Si_4\rangle^{tetr.}O_{10}F_2$ is equal to the experimentally determined carbon content.

Example: OI-Hect (Addition of 74% CEC) features an experimental carbon content of 3.288 wt% as determined by CHN. y=0.2741 leads to a carbon content of 3.288 wt% which is in line with the experimentally determined one. Therefore OI-Hect features a formula of $[Na_{0.33}C4_{0.27}]^{inter.}[Mg_{2.4}Li_{0.6}]^{oct.}Si_4O_{10}F_2$. Hence 46 % of interlayer ions are exchanged (0.2741:0.60=45.7 %). As 75 % of CEC of Na-Hect have been added, 39 % of n-butylammoniumions are remaining in solution (100 % - 45.7 % : 75 % = 39.1 %).

Data following this calculation for all partial exchanged products (15 to 200% of CEC) are given in Table S1 along with the carbon content of C4-Hec. This table is plotted in Figure S2.

Table S1. Distribution equilibrium for partial exchange of Na-Hec with n-butylammonium (C4) as determined by CHN-analysis.

Addition C4 [% of CEC]	C-content [Gew.%]	Na [p.f.u.]	C4 [p.f.u.]	C4 intercalated [% of CEC]	C4 remaining in solution [% of addition]
15	0.696	0.54	0.06	9	37
30	1.366	0.49	0.11	19	38
45	1.999	0.44	0.16	27	39
60	2.842	0.36	0.24	39	35
74	3.288	0.33	0.27	46	39
90	3.815	0.28	0.32	53	41
105	4.105	0.26	0.35	58	45
125	5.139	0.16	0.44	73	42
150	6.099	0.08	0.53	88	42
200	6.632	0.03	0.57	96	52
C4-Hec, complete exchange	6.935	0.00 (-0.003)	0.60 (0.603)		

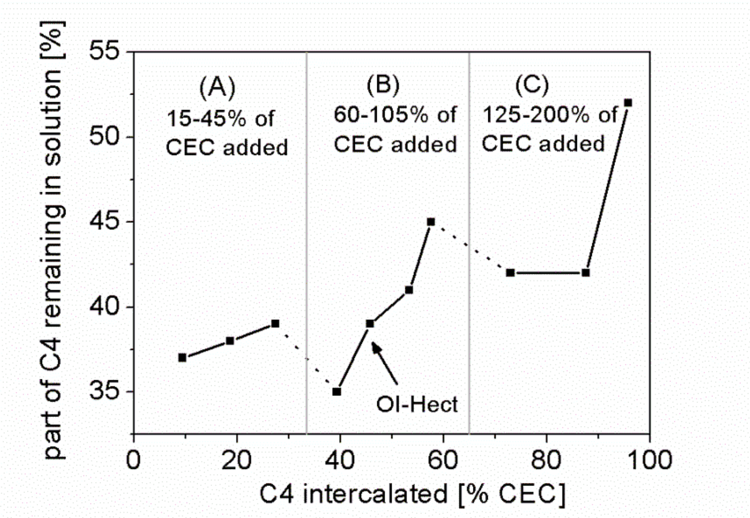


Figure S3. Distribution equilibrium of the partial exchange of Na-Hec with n-butylammonium. The part of n-butylammonium remaining in solution is plotted over the amount intercalated for different amounts of CEC added to the neat hectorite.

PXRD of Partial Ion-Exchange.

Table S2. *00l*-series and coefficient of variation (cv) for different stages of partial exchange in % of CEC of Na-Hect (at 43 % r.h.).

00l	d(*00l*) for different additions of C4 in % of CEC of Na-Hect						
	60 %	67 %	70 %	72 %	74 %	76 %	90 %
001	25.282	25.000	25.078	25.120	25.392	24.845	24.861
002	12.663	12.616	12.650	12.644	12.745	12.615	12.724
004	6.346	6.336	6.344	6.344	6.367	6.338	6.372
005	5.103	5.098	5.093	5.086	5.105	5.069	5.041
006	4.234	4.230	4.233	4.233	4.243	4.234	4.243
007	3.636	3.641	3.639	3.635	3.642	3.625	3.616
008	3.175	3.174	3.176	3.176	3.183	3.174	3.180
009	2.834	2.832	2.831	2.830	2.835	2.824	2.816
0011	2.317	2.316	2.316	2.316	2.320	2.314	2.308
0012	2.119	2.118	2.119	2.119	2.121	2.118	2.119
0013	1.961	1.961	1.961	1.959	1.963	1.958	1.953
0014	1.815	1.816	1.816	1.816	1.819	1.816	1.821
0016	1.588	1.589	1.589	1.590	1.591	1.590	1.594
average d(*00l*)·*l* [Å]	25.42	25.39	25.40	25.38	25.48	25.32	25.37
cv [%]	0.27	0.55	0.44	0.39	0.14	0.65	0.68

Humidity-dependent d-spacings.

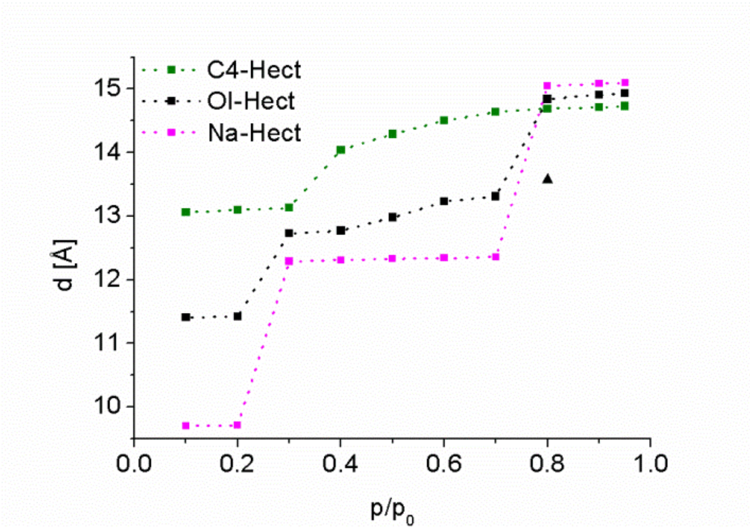


Figure S4. Humidity dependent d-spacings of C4-Hect (d_{001}), OI-Hect (d_{002}) and Na-Hect (d_{001}) measured in a humidity chamber. For the homoionic phases d_{001} is shown. In case of OI-Hec d_{002} is shown that corresponds to the averaged d-spacing of the superstructure. A slight shoulder at about 13.6 Å ($p/p_0 = 0.8$) is marked by a triangle. D-spacings at $p/p_0 = 0.98$ did not deviate from the d-spacings measured under a drop of ethanol/water (1:1).

Static Light Scattering.

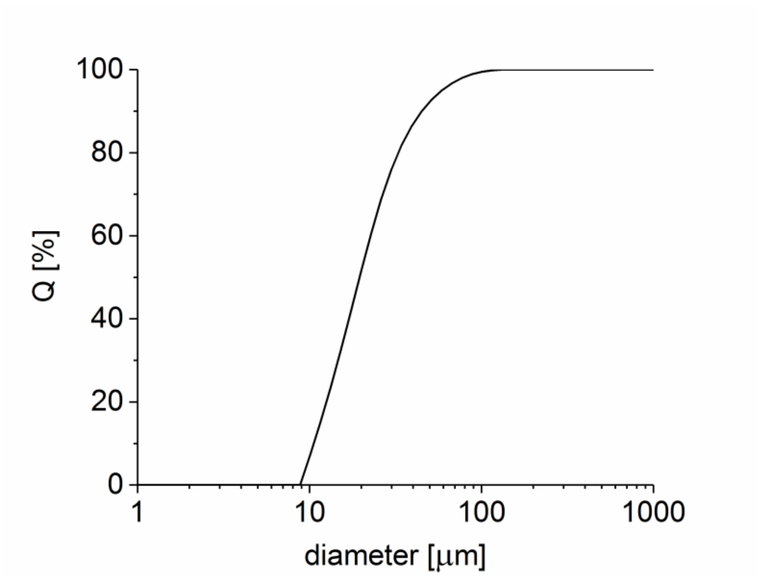


Figure S5. Particle size distribution as determined by SLS, the number weighting yields an average diameter of 24 μm.

C4-Vermiculite at 95% relative humidity.

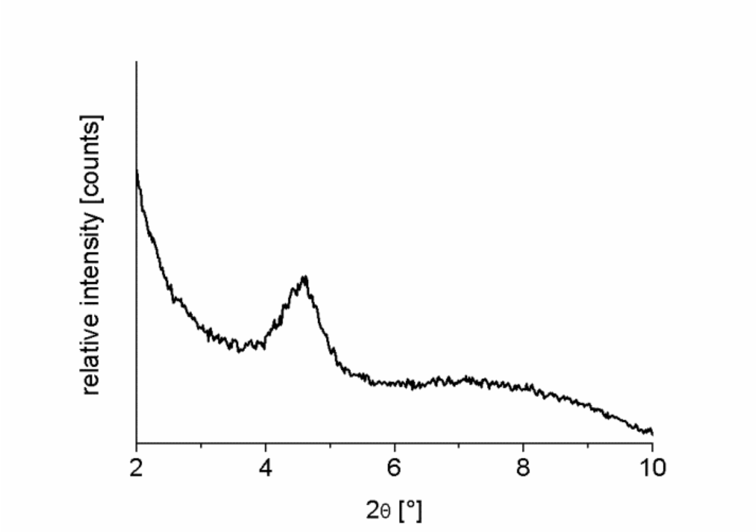


Figure S6. PXRD of a n-butylammonium exchanged vermiculite (Eucatex) measured in a humidity chamber at 95% relative humidity with a d-spacing of 19.2 Å.

Calculations: d-spacing of a Gel.

The d-spacing of a homogeneously swollen gel can be calculated via the volume fraction ϕ using the thickness of a single lamella D:

$$\phi = \frac{m_{Hec}/\rho_{Hec}}{m_{Hec}/\rho_{Hec} + m_{water}/\rho_{water}} \tag{1}$$

$$d = \frac{D}{\phi} \tag{2}$$

2. Supporting References

(1) Huve, L.; Delmotte, L.; Martin, P.; le Dred, R.; Baron, J.; Saehr, D. 19F MAS-NMR Study of Structural Fluorine in some Natural and Synthetic 2:1 Layer Silicates. *Clays Clay Miner.* **1992,** *40*, 186-191.