The physical properties of clays and micas can be controlled by exchanging ions in the crystal lattice. Atomically thin materials can have superior properties in a range of membrane applications, yet the ion-exchange process itself remains largely unexplored in few-layer clays. Here we use atomic-resolution scanning transmission electron microscopy to study the dynamics of ion exchange and reveal individual ion binding sites in atomically thin and artificially restacked clays and micas. We find that the ion diffusion coefficient for the interlayer space of atomically thin samples is up to 10^4 times larger than in bulk crystals and approaches its value in free water. Samples where no bulk exchange is expected display fast exchange at restacked interfaces, where the exchanged ions can be arranged in islands with dimensions controlled by the moiré superlattice dimensions. We attribute the fast ion diffusion to enhanced interlayer expandability resulting from weaker interlayer binding forces in both atomically thin and restacked materials. This work provides atomic scale insights into ion diffusion in highly confined spaces and suggests strategies to design exfoliated clay membranes with enhanced performance.

C

lays and micas are minerals that consist of aluminosilicate layers with cations both adsorbed on the basal plane surfaces and residing in the space between the layers. The native cations (typically K\(^+\) and Mg\(^{2+}\)) can be exchanged for others when the material is exposed to electrolytes by a process known as ion exchange\(^{-1}\). The crystals are relatively easy to exfoliate along the basal planes, producing high aspect ratio atomically thin sheets. Recent experiments have demonstrated that exchanging the native cations for protons in atomically thin micas yields highly conductive proton transport membranes\(^2\)–\(^4\). Exfoliated two-dimensional (2D) clay or mica crystals can be restacked to produce laminate membranes and composites by similar fabrication methods to those used for graphene oxide\(^5\)–\(^8\). The spaces between the restacked crystallites constitute channels with one of their dimensions comparable with, or narrower than, the Debye length in common electrolytes;\(^9\)–\(^10\) hence, water and ion transport through these channels depends critically on the crystal surface charge\(^10\). This allows for the use of the ion-exchange properties of clays and micas to influence phenomena in the channels such as osmotic power generation\(^1\), selective transport\(^11\)–\(^14\) or solvent filtration.\(^1\) Despite its importance to the different applications of these materials, ion exchange in atomically thin clays and micas remains largely unexplored. In this work, we used advanced aberration-corrected scanning transmission electron microscopy (STEM) to study this phenomenon. STEM, unlike the more commonly used techniques such as atomic force microscopy or X-ray measurements\(^11\)–\(^14\), reveals the local binding environment of exchanged ions with sub-Ångström resolution, enabling understanding of the ion-exchange process.

STEM imaging of ion exchange

Atomic-resolution STEM investigations of Cs\(^+\) ion exchange were performed for atomically thin clays and micas\(^15\)–\(^16\) (Supplementary Section 1). Cs\(^+\) was chosen for this study because diffusion of radioactive caesium (\(^{137}\)Cs) in clay soils is of environmental relevance following nuclear incidents\(^17\) and because its large atomic number provides bright contrast in annular dark field (ADF)-STEM images. To characterize the ion-exchange process, we obtained three-dimensional lattice images by combining both cross-sectional (Fig. 1a,c,e) and plan-view STEM imaging (Fig. 1b,d,f). For cross-sectional imaging, the crystals were mechanically exfoliated onto oxidized silicon substrates and immersed in CsNO\(_3\) electrolyte (0.1 M aqueous solution) for a period from one second to several months to enable ion exchange (Extended Data Fig. 1). The crystals were then covered by a graphite flake and a Pt protective strap, so that thin slices of this assembled stack could be extracted by focused ion beam (FIB) milling\(^18\) (Extended Data Fig. 1, Supplementary Section 2 and Supplementary Figs. 1–6). To probe plan-view specimens, mechanically exfoliated mono-(1L), bi- (2L) and tri-layer (3L) crystals were transferred over holes in SiN\(_x\) transmission electron microscopy (TEM) grids and immersed in CsNO\(_3\) electrolyte, as described above. For further information on sample preparation, see Supplementary Section 2 and Extended Data Fig. 1. In the following three sections, we describe our observations of ion exchange in the interlayer spaces of natural and twisted specimens as well as on the crystal basal plane surface. In each section, we exploited the differences in crystal chemistry\(^15\)–\(^16\) and the related ion-exchange behaviour for one of three crystals—muscovite mica, biotite mica.
Fig. 1 | Interlayer cations in exchanged clays and micas. a, Cross-sectional atomic model of a typical pristine bilayer (2L) clay or mica viewed along the layers. The aluminosilicate tetrahedral–octahedral–tetrahedral (TOT) layers are connected by exchangeable ions (for example, K⁺ and Mg²⁺). The weakly bonded surface cations are omitted for clarity. b, Plan-view atomic model showing the interlayer ions with adjacent top and bottom T layers consisting of aluminosilicate (Al–Si–O) hexagonal rings. The exchangeable interlayer ions form a quasi-hexagonal lattice (marked with a green hexagon). c, e, Cross-sectional ADF-STEM images of Cs-exchanged bilayer (c) and trilayer (3L) (e) vermiculite (Ver). The interlayer ions are exchanged with Cs⁺, visible as rows of bright dots between the aluminosilicate layers. The atomically thin vermiculite is encapsulated between graphite (Gr) and SiO₂ to enable atomic-resolution imaging. d, f, Plan-view ADF-STEM images of Cs-exchanged bilayer (d) and trilayer (f) vermiculite. A single interlayer of Cs⁺ ions forms a quasi-hexagonal lattice (marked with a green hexagon in d), while the offset between two superimposed planes of interlayer Cs⁺ ions creates a linear pattern (offset of the second plane is illustrated by the blue hexagon) (f). Scale bars, 1 nm.

Ion exchange in the interlayer spaces of vermiculite clay

For the study of interlayer ion exchange as a function of crystal thickness we employ vermiculite, which has attracted attention in few-layer form for application in proton-conducting membranes. In bulk form the material is exchanged in time frames measured in hours to days (depending on the ion), timescales that are readily accessible to investigation by STEM imaging. Fig. 1 shows ADF-STEM images taken from typical samples of Cs-exchanged atomically thin vermiculite. Cs⁺ ions are visible as one and two rows of bright spots between the aluminosilicate layers in bilayer and trilayer cross-sectional specimens, respectively (Fig. 1c,e, Extended Data Fig. 2). These observations can be complemented with plan-view imaging, which resolves the lateral distribution of the ions (Fig. 1d,f). In a trilayer sample, the projected arrangement of the two Cs⁺ layers appears as a linear pattern formed by a superposition of two of these quasi-hexagonal Cs⁺ lattices (Fig. 1f and Supplementary Fig. 7). These images confirm that the exchanged ions form fully occupied interlayer planes—one in 2L samples and two in 3L samples—with each layer having quasi-hexagonal symmetry (in-plane Cs⁺ lattice constant of 5.3 Å). This uniform lateral distribution of Cs⁺ suggests that the ion diffusion in the interlayer is not driven by in-plane defects like dislocations. In our samples, we see no preferential direction for ion penetration within the basal plane, indicating that ion diffusion is the result of uniform ion penetration into the interlayer space through the entire length of exposed crystal edges (see also Extended Data Fig. 3).

To characterize the speed of the ion penetration into the interlayer space, we imaged >30 samples with thicknesses ranging from 2 to 70 layers that were subject to the CsNO₃ solution treatment for different lengths of time (t). These images effectively provide ‘snapshots’ of the exchange process. Cross-section images reveal the penetration distance of Cs⁺ into the crystal, ∆P (Fig. 2), which allows for the estimation of the ion diffusion coefficient $D = \frac{\Delta P^2}{2t}$ (Supplementary Section 6), with $\langle \Delta P^2 \rangle$ the mean square penetration distance averaged from measurements of all the individual interlayer spaces in the sample. Taking the 5L sample in Fig. 2b as an example ($t=10$s), for each interlayer space (1, 2, 3, 4), we measured the Cs⁺ penetration distance $\Delta P = \left( \Delta P_1^2 + \Delta P_2^2 + \Delta P_3^2 + \Delta P_4^2 \right)$, which allows for the estimation of the mean square displacement of Cs⁺ as $\langle \Delta P^2 \rangle = \frac{\sum_i \Delta P_i^2}{4} = 0.3 \mu^2$ and the Cs⁺ diffusivity $D_{\text{bulk}} \approx 0.15 \mu^2 \text{s}^{-1}$. Following this method, we performed a systematic study of ion diffusion in vermiculite clays with thickness ranging from 2–70 layers. To our surprise, 2L samples showed Cs⁺ exchange with large penetration distances of around 15 µm after only one second of CsNO₃ solution treatment (Fig. 2c, Supplementary Fig. 8, Supplementary Section 6). This exceptionally fast exchange yields the diffusion constant of Cs⁺ in bilayer vermiculite as $\approx 10^{-3} \mu^2 \text{s}^{-1}$, only ~10 times lower than the diffusion coefficient of Cs⁺ in water. This behaviour was reproducible across 3 different 2L samples and statistical analysis of these data revealed $D_{\text{bulk}} = 60 \pm 40 \mu^2 \text{s}^{-1}$. Similar measurements for 3L vermiculite showed a slower interlayer diffusivity with a value of $D_{\text{bulk}} = 15 \pm 12 \mu^2 \text{s}^{-1}$. Repeating this experiment for different crystal thicknesses revealed that $D$ decreases exponentially with crystal thickness, reaching the literature values for Cs⁺ diffusion in bulk vermiculite $^{16,21}, D_{\text{bulk}} = (7 \pm 3) \times 10^{-3} \mu^2 \text{s}^{-1}$ (Fig. 2a,d), for all specimens thicker than ~10 layers. The measured dependence of $D$ on the number of layers, $N$, can be described by the formula $D = D_0 \left[ 1 + \exp(-\alpha(N-N_c)) \right]$, where $\alpha = 1.17$, a material-specific coefficient, $D_0 = 5 \times 10^{-3} \mu^2 \text{s}^{-1}$ and $N_c = 10$. The fast exchange was confirmed using vermiculite lamellae made from exfoliated thin flakes, which showed a similar enhancement of the ion-exchange speed compared to the bulk non-exfoliated crystal (Supplementary Section 7 and Extended Data Fig. 4).

To understand these findings, we note that diffusion of interlayer ions in bulk clays depends strongly on interlayer expandability $^{16,22}$. This suggests that this property could be responsible for the fast exchange observed in thin (<10 layer) clays. To investigate this hypothesis, we measured the swelling of our samples in a liquid environment (0.1 M NaCl solution) using an atomic force microscope.
Fig. 2 | Measuring the interlayer Cs⁺ diffusivity for vermiculite flakes of different thickness. a. Left panel, cross-section ADF-STEM image taken from a 33L vermiculite exchanged for 10 s. ΔP_{\text{max}} denotes the largest penetration distance among interlayers (for detailed penetration distances, see Supplementary Tables 3.1–3.15). Scale bar, 200 nm. Right panel, corresponding high magnification image. Scale bar, 5 nm. b. Top panel, low magnification cross-section ADF-STEM image of a 5L vermiculite (t = 10 s), with the left side showing the end of the flake where the Cs⁺ penetration starts. Scale bar, 200 nm. Bottom panels, magnified images from the regions marked by dashed rectangles in the top panel. Scale bar, 5 nm. c. Top panel, cross-section ADF-STEM image of 2L vermiculite (t = 1 s). For this specimen (35 μm wide), ΔP ≈ 14.5 μm (see Supplementary Fig. 8 for optical image), which is too long to display in this STEM figure. Scale bar, 20 nm. Bottom panel, magnified view showing a bright line of Cs⁺ ion columns. Scale bar, 5 nm. d. D as a function of N, measured from over 30 vermiculite flakes. Error bars represent the standard deviation from the mean calculated for at least three different samples. Inset, D(N) data for N ≤ 7. Dashed lines, analytical formula described in the main text.

**Figures Distributions: Cs⁺**

(AFM, see also Methods, Extended Data Fig. 5, Supplementary Section 8). The interlayer expansion was found to be largest for bilayer flakes (~5 nm) and decayed rapidly with the number of layers, such that a stable value was reached for N ≥ 7 layers (<0.5 nm expansion per interlayer). This strong thickness-dependent swelling behaviour mirrors that found in our diffusivity data and is consistent with previous swelling studies using other clays[1,2]. From a theory perspective, the interlayer expansion of clays has been proposed to depend on a balance of short-range Coulomb repulsion and long-range van der Waals attraction between the aluminosilicate layers[1,2]. The long-range interaction depends on the number of layers in the crystal, so this force decreases with decreasing N. This leads to a weaker attraction force between the layers, larger interlayer expandability and faster ion diffusivity in atomically thin samples. Our calculations of these van der Waals interactions for our samples are consistent with this interpretation (see Supplementary Section 12.1).

**Cs⁺ ion superlattices in twisted biotite mica**

Laminate materials composed of atomically thin crystals will contain a large proportion of ‘restacked’ interfaces, where the crystal lattices of two neighboring aluminosilicate planes are misaligned or ‘twisted’ with respect to each other (Fig. 3a,b). In few-layer vermiculite, fast interlayer ion exchange obscures STEM imaging of ions in the twisted interface. Therefore, to investigate ion-exchange behaviour in twisted interlayers, we have employed biotite as a layered aluminosilicate mineral that displays negligible interlayer ion exchange even in atomically thin samples exposed for many hours (see Extended Data Fig. 3b). Unexpectedly, we find that within the interface of twisted samples, the exchanged ions arrange in an unusual pattern when observed at atomic resolution. Figure 3 shows plan-view characterization results from two Cs⁺-exchanged biotite samples, each consisting of two monolayer crystals restacked with a small rotational misorientation. The twist angle between the upper and lower crystals, θ, can be measured from the electron diffraction patterns (Fig. 3c,d) and was determined as θ ≈ 9.5 and 2.6° for specimens shown in the top and bottom panels of Fig. 3, respectively. We find that the Cs⁺ ions (bright dots shown in Fig. 3e–h) exchanged at the interface between these twisted bilayers arrange with the same in-plane interionic separation of 5.3 Å seen in the aligned bilayer samples. However, unlike in the arrangement seen in the aligned samples (Fig. 1b,d), these Cs⁺ ions form groups of 7 ± 2 and 130 ± 15 atoms per island for θ ≈ 9.5 and 2.6°, respectively (Fig. 3g,h, Supplementary Figs. 9–11). Outside these islands, Cs⁺ ions are rarely observed. The islands occur periodically with periods of L = 3.2 ± 0.2 nm for θ ≈ 9.5° and 11.7 ± 0.7 nm for θ ≈ 2.6° (Fig. 3e,f). Interestingly, the found L corresponds to the moiré periodicity of the underlying twisted aluminosilicate bilayers, Lₘₐₜ. This latter
Fig. 3 | Interlayer Cs⁺ islands in twisted biotite bilayers. a, b. Schematic atomic models of moiré patterns from twisted biotite monolayers for twist angles of θ ≈ 9.5° and θ ≈ 2.6°, respectively. The two twisted aluminosilicate layers are shown in green and magenta, respectively, with red balls showing the location of interlayer Cs⁺ (AA sites). The high-symmetry sites in this rigid lattice model are labelled as AA and AB according to the stacking sequence of aluminosilicate rings adjacent to interlayer ions. AA corresponds to the same stacking type as pristine bilayer biotite. c, d. Experimental selected area electron diffraction patterns from twisted biotite bilayer samples, showing that the twist angles between the two biotite monolayers are 9.5 and 2.6°, respectively. Scale bars, 2 nm. e, f. Plan-view ADF-STEM images taken from the Cs-exchanged twisted biotite (Bio) bilayer samples for θ ≈ 9.5° and θ ≈ 2.6°, respectively. The Cs⁺ ions form islands visible as brighter regions in the micrographs (see Supplementary Fig. 6 for simulated image). The moiré unit cells are marked by the yellow dashed obliques and the periodicities, L, are indicated. Scale bars, 10 nm. g, h. Magnified views from panels e and f, respectively. Interionic separation marked with white lines. Ion bridges between islands are marked by yellow and blue dashed lines respectively, depending on their lattice orientation alignment. Scale bars, 5 nm.

Ion exchange on the basal surface plane of muscovite mica

Ions within twisted interlayer spaces could be considered as a bonding situation part-way between the pristine interlayer and a free surface. Characterizing basal plane surface ions by STEM is experimentally more demanding and such studies have remained conspicuously absent in the literature. Nonetheless, here we demonstrate that ultra-thin muscovite samples now allow for atomic-resolution investigations of single surface ions. Muscovite is preferred as the sample for surface ion study since it displays no measurable interlayer ion exchange, even in few-layer samples after months of electrolyte treatment (Supplementary Section 9). We found that ADF-STEM of our cross-sectional samples can characterize the out-of-plane distance for surface ions when the samples are encapsulated between graphite and SiO₂. Comparing native and exchanged materials we found that the out-of-plane spacing was ~1 Å larger for Cs⁺ than for the native ions (Fig. 4a, b, Supplementary Fig. 13).
Fig. 4 | Cations adsorbed on the surface basal plane of muscovite. a,b, Schematic (a) and corresponding cross-sectional ADF-STEM image (b) of a 3L muscovite sample (see Supplementary Fig. 13b for raw image). The distance between the surface K⁺ (Cs⁺) ions and the outer aluminosilicate layer is marked with green (red) horizontal lines. Superscripts ‘S’ and ‘I’ refer to surface and interlayer ions, respectively. Scale bar, 5 Å. c,d, Cross-sectional (c) and plan-view (d) schematics of a monolayer of muscovite with K⁺ and Cs⁺ ions adsorbed on opposite surfaces. In the aluminosilicate TOT layers the top (T¹) and bottom (T²) tetrahedral sheets are coloured blue and magenta, respectively, emphasizing that the layers are not vertically aligned. For clarity, in d only two partially overlapping T sheets are shown, with the O sheet entirely omitted. Type I and Type II refer to the different adsorption sites of K⁺ and Cs⁺ ions. e,f, ADF-STEM image (e) and ABF-STEM image (f) of the same area of Cs-exchanged monolayer muscovite. Atomic positions are bright in the ADF image and dark in the ABF image. Higher magnification images (insets) show example positions for Cs⁺ and K⁺ ions, with red and green circles respectively. Note that the K⁺ ions are not identifiable in ADF-STEM due to low atomic number, so their positions were obtained from the ABF image. Scale bar, 2nm.

Complementary plan-view STEM imaging allows us to characterize with sub-Ångström resolution the in-plane ordering of surface Cs⁺ ions and, crucially, the relative positions of the ions with respect to the aluminosilicate backbone. To achieve this, we employ simultaneous ADF-STEM and annular bright-field (ABF)-STEM imaging. The ADF image captures the heavy Cs⁺ ions while the ABF image captures the lighter cations and the atoms in the aluminosilicate layer. Figure 4e shows that surface Ca⁺ ions, visible as bright spots in the ADF image, form a quasi-hexagonal lattice. The ABF image of the same area is shown in Fig. 4f. Here, atomic positions are clearly visible as dark spots, which indicates that the specimen remained crystalline during imaging (see also Supplementary Figs. 14 and 15). This image shows the expected Al–O and Si–O ring structures, known in the literature as hexagonal or ditrigonal rings (coloured blue and magenta in Fig. 4c,d). Correlation of the ADF- and ABF-STEM images reveals that K⁺ and Cs⁺ ions are adsorbed on different sites within these rings and, in this sample, on opposite surfaces. K⁺ ions adsorb in the centre of the hexagonal rings (Type I site) on the top surface (T¹); whereas, statistically, Cs⁺ ions are found to overwhelmingly (76%, see Supplementary Fig. 14) adsorb on the vertex of the hexagonal rings (Type II site on T², Fig. 4c,d). The difference between in-plane and out-of-plane coordinates observed here for Cs⁺ compared to the native K⁺ cations is attributed to the presence of multiple hydration complexes for Cs⁺ ions6,25–27. These lead to different favourable adsorption sites during the exchange process in solution that are preserved when imaging (see Supplementary Fig. 16 and Supplementary Section 12.2).

Outlook for atomically thin minerals

Altogether, our results provide atomic-scale insights into surface ion adsorption and interlayer ion diffusion in micas and clays. This is of relevance for optimizing clay-membrane designs for specific applications24–26 and for understanding the limited movement of heavy metal ions in contaminated land27. Beyond this, our STEM ‘snapshots’ method and complementary AFM studies provide fundamental insights into ion transport in highly confined spaces, of interest following recent developments28. Given the wide research interest in the electronic and optical properties of 2D metals29 and in the heterostructures of twisted 2D materials30, our observations suggest opportunities for fabricating mica-encapsulated 2D metal ion superlattices31. Finally, our demonstration of enhanced ion-exchange speed and capacity in low-layer crystals and their laminates provides evidence that exfoliated clays and micas can be used to produce membranes, filters and adsorption products with enhanced performance.

Online content

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Methods

**STEM and TEM imaging.** A probe-side aberration-corrected FEI Titan G2 80–200 S/TEM ChemiSTEM microscope was used for ADF-STEM. This microscope was operated at 200 kV with a probe current of ~6–15 pA, a convergence angle of 21 mrad and an ADF detector with inner (outer) collection angles of 48 (196) mrad. For STEM energy dispersive X-ray spectroscopy (EDS), we used a Super-X EDS detector with a beam current of ~6 pA, a per pixel dwell time of 50 µs, a total acquisition time of 100 s and a pixel size of 0.05 nm. Selected area electron diffraction patterns were obtained using the same microscope operated in TEM mode. For the FIB lamellae, selected area electron diffraction patterns were used to orientate the specimen along the low-index zone axis using low-electron-fluence in order to achieve atomically resolved high-resolution STEM image data. A JEOL ARM300CF double aberration-corrected microscope was used to acquire ADF- and ABF-STEM images simultaneously. This instrument has a cold FEG electron source and was operated at 80 kV with a probe current of ~6–15 pA and a convergence angle of 24.8 mrad. Images were acquired with an ADF detector having a collection angle of 50–150 mrad and an ABF detector having a 12–24 mrad collection angle. In Figs. 1 and 2, Extended Data Fig. 3 and Supplementary Figs. 5, 7, 9 and 13, greyscale STEM images have been false-coloured with a standard colour look-up table to enhance contrast, using Gatan’s Digital Micrograph software or the open-source Python package Matplotlib\(^2\). Multislice image simulation for high-resolution STEM images was conducted using atomic models created under the Atomic Simulation Environment\(^3\), together with the QSTEM software\(^4\), with the above experimental parameters and a source size of 0.8–1 Å. See Supplementary Section 2 for detailed TEM sample fabrication methods and Supplementary Section 11 for details on STEM imaging of adsorbed surface ions.

**Comparison of Cx exchange speed in bulk and exfoliated vermiculites.** Exfoliated vermiculite laminites were prepared using the method reported in previous work\(^5\). In brief, 100 mg of bulk Mg vermiculite was mixed with a saturated solution of NaCl (3 g ml\(^{-1}\)) and heated under reflux conditions for 24 h. The vermiculite was then filtered and washed thoroughly using de-ionized (DI) water and mixed with 2 M LiCl under reflux conditions for 24 h. The vermiculite was then filtered and washed thoroughly using DI water to remove any residual salt. After washing, vermiculite crystals were dispersed in 50 ml DI water and sonicated for a period of 30 min to facilitate exfoliation. The solution thus obtained was centrifuged at 4,000 rpm until no sediments were observed. The supernatant was collected and used for further experiments. Few-layer vermiculite laminites, consisting of ~30% bilayer and ~15% trilayer crystallites (Li-vermiculite, thickness distribution shown in Extended Data Fig. 4), were obtained using the above-mentioned method. These were then filtered through porous alumina substrate, using vacuum-assisted self-assembly to create a laminate membrane. The 2D laminate membranes thus obtained were dried and the interlayer cations were exchanged with Mg\(^{2+}\) ions by treating with 2 M MgCl\(_2\) for a period of 3 h (Mg-vermiculite membranes). The membranes were dried and used for further ion-exchange experiments. For comparison, similar ‘bulk’ samples were also made from an equal quantity of bulk Mg vermiculite powder.

For ion-exchange experiments, the as-fabricated membranes (inset of Extended Data Fig. 4c) were cut into several samples of the same lateral size (~5 mm × 5 mm). Both the exfoliated and ‘bulk’ membrane samples were then exposed to 1 M CoCl\(_2\) for a specified period, followed by an extensive wash with DI water and sonication in 100 ml of DI water for 2 days to remove any excess ions. The exchanged samples were then dried at 50 °C for 24 h prior to X-ray diffraction (XRD) analysis. XRD data of both the exfoliated membrane and the bulk samples were collected using a Rigaku SmartLab thin-film XRD system (Cu Kα radiation) operated at 1.8 kW.

**AFM measurement.** To investigate the possible effect of crystal thickness on interlayer expandability, we measured the height profile of vermiculite flakes in ambient conditions and in liquid using a Bruker Dimension FastScan AFM with ‘ScanAsyst Fluid+’ probes (Extended Data Fig. 5). Swelling values for a certain flake were extracted from the difference in height measured in ambient air and in a liquid environment. To ensure that the difference in height was not due to water intercalation between the vermiculite flake and the substrate, we modified our sample preparation with respect to the TEM sample recipe described in Supplementary Section 2. Prior to flake exfoliation, the SiO\(_2\)/Si substrates were coated with an adhesion layer of SU-8 3005 epoxy and then photo-cured under an ultraviolet source. Vermiculite samples were then mechanically exfoliated onto the as-prepared substrates. The samples were ‘hard baked’; typically at 60°C for 10 min, to further promote polymer/clay adhesion. For measurements in ambient air, AFM scans were taken in ambient conditions in a class 1,000 clean room environment at ~50% relative humidity and a temperature of ~21 °C. For the measurement of flakes immersed in liquid, we used a 0.1 M NaCl aqueous solution.

**Data availability**

All raw data are available from the corresponding authors on request.

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**Author contributions**

S.J.H., M.L.-H. and Y.-C.Z. designed the project. Y.-C.Z., L.M., N.C. and G.-P.H. conducted the sample preparation under the supervision of S.J.H., R.G. and M.L.-H. The (S)TEM experiments, image processing and analysis were performed by Y.-C.Z., S.J.H., Y.-C.W. and N.C. STEM image simulations were conducted by Y.-C.Z. and D.G.H. Theoretical support was provided by F.M.P., C.B. and S.M. Synthesis of vermiculite laminites and measurement of their ion-exchange behaviour was performed by R.R.-N. and V.S. The manuscript was written by Y.-C.Z., M.-L.H. and S.J.H. S.S., R.G. and K.S.N. commented on the manuscript and interpretation of results. All authors contributed to discussions.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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**Correspondence and requests for materials**

Correspondence and requests for materials should be addressed to M.L.-H. or S.J.H.

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Extended Data Fig. 1 | Schematic illustrating the procedure of TEM sample preparation. 

**a–d.** Steps used in the preparation of cross-sectional samples. **a.** Mechanical exfoliation of mica(clay) flakes. **b.** Ion exchange processes for the selected flakes: electrolyte immersion; then drying in a N₂ gas environment and quality inspection by optical microscopy. **c.** Cover the target flakes with thin graphite to avoid surface damage or contamination. **d.** FIB lift out of the graphite/SiOₓ/mica(clay) stack, followed by FIB thinning and S/TEM imaging. 

**e–h.** Steps used in the preparation of plan-view samples. **e.** Mechanical exfoliation of mica(clay) crystals onto a PVA/PPC coated SiOₓ/Si substrate, followed by dissolving PVA in water to leave a floating PPC/mica(clay) stack. **f.** Transfer of the PPC/mica(clay) stack by micromanipulation onto a SiNx/Si TEM grid, followed by removal of PPC in solvent to leave a clean and suspended flake. **g.** Ion exchange and cleaning of the mica(clay) flake on TEM grid. **h.** STEM and TEM imaging.
Extended Data Fig. 2 | EDS characterization for beam sensitive clay/mica samples. a, ADF-STEM cross-sectional image taken from a Cs exchanged 2L vermiculite sample. Scale bar, 1 nm. b, c, Consecutively acquired EDS elemental line profiles along the line I to II (summed vertically for the whole ADF region shown in a). b, EDS line profile from t=0 to t=100 s with t being the EDS acquisition time, total electron fluence of ~1.6×10^7 e·Å^-2. c, EDS line profile collected from t=100 to t=200 s with material having experienced a total electron fluence of ~3.2×10^7 e·Å^-2. The peak values for Cs⁺ counts are marked by red dashed lines. The lower peak Cs concentration for the second measurement shows that Cs⁺ diffuses away from the region of interest during STEM imaging (Cs⁺ counts in b > c). A similar decrease is seen in the Mg concentration. Note that the total dose required for high-resolution STEM EDS elemental mapping is >10^8 e·Å^-2, much larger than the total electron fluence that would amorphize the Cs-vermiculite crystals (10^6 e·Å^-2), and hence it is not possible to perform atomic-scale chemical mapping or quantitative atomic analysis in these clay samples.
Extended Data Fig. 3 | Plan-view ADF-STEM images taken from the edge of ion exchanged few-layered muscovite and biotite. a, Muscovite (Mus), b, Biotite (Bio), both Cs-exchanged for 300 h. Cs$^+$ ions are visible as the brightest yellow dots. The largest penetration depth of Cs$^+$ from the edge into the interlayer space in the crystal ($\Delta P$) is indicated, yielding $D_{\text{Mus}} \approx 10^{-11} \mu\text{m}^2\text{s}^{-1}$, and $D_{\text{Bio}} \approx 10^{-10} \mu\text{m}^2\text{s}^{-1}$. Scale bars, 5 nm.
Extended Data Fig. 4 | Exchange speed characterization of vermiculite samples with different exposure times for Cs⁺ ion exchange, analysed using XRD. 

a, XRD taken from bulk crystals (t being the CsCl solution treatment time). 

b, XRD taken from the laminates made from exfoliated nanosheets. A right shift of (002) peaks can be observed with increasing exposure time due to the contraction of interlayer spacing caused by Cs⁺ incorporation. 

c, Flake thickness distribution in the laminates measured by AFM. Inset, optical image of a typical Mg-vermiculite laminate (membrane). Scale bar, 5 mm.
Extended Data Fig. 5 | Comparison of the swelling behaviour for vermiculite crystals of different thicknesses in NaCl solution. a–d. AFM results for a 2L vermiculite region (outlined by red dashed lines) and a local 1L region (outlined by black dashed lines). a, AFM height image taken in ambient air and b, in aqueous 0.1 M NaCl. c, Corresponding height profiles in air and liquid extracted from the positions of the lines (I, II, III, IV) for c, 2L region and d, 1L region. e–h. AFM results for a 3L vermiculite (green dashed lines) containing a local 1L region (black dashed lines). e, AFM height image taken in ambient air, and f, in aqueous 0.1 M NaCl. g, Corresponding height profiles extracted from the positions of the lines (V, VI, VII, VIII) for g, 3L region, and h, 1L region. i, Statistical results showing the AFM measured height ($z$) values for vermiculite as a function of $N$, in ambient air (magenta) and liquid NaCl (blue). Swelling values ($\Delta z$) are extracted as height difference in liquid and ambient, with the standard deviation extracted from at least three different measurements. j, Mean swelling values per interlayer as a function of $N$, calculated as $\Delta z \times (N-1)^{-1}$ using $\Delta z$ values shown in i. Error bars represent the standard deviation (s.d.) from the mean for at least 3 different samples. Dotted line is a guide to the eye. Scale bars in a, b, e, f are all 200 nm.