A general orientation distribution function for clay-rich media

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The role of the preferential orientation of clay platelets on the properties of a wide range of natural and engineered clay-rich media is well established. However, a reference function for describing the orientation of clay platelets in these different materials is still lacking. Here, we conducted a systematic study on a large panel of laboratory-made samples, including different clay types or preparation methods. By analyzing the orientation distribution functions obtained by X-ray scattering, we identified a unique signature for the preferred orientation of clay platelets and determined an associated reference orientation function using the maximum-entropy method. This new orientation distribution function is validated for a large set of engineered clay materials and for representative natural clay-rich rocks. This reference function has many potential applications where consideration of preferred orientation is required, including better long-term prediction of water and solute transfer or improved designs for new generations of innovative materials.
Clay minerals are one of the fundamental constituents of numerous terrestrial and marine environments on Earth and are systematically present in soils and sedimentary rocks. The sub-micrometric particle sizes of clay particles most often account for a major proportion of the specific surface area of the whole material, leading to strong interactions with organic macromolecules or dissolved cations and anions. Owing to their lamellar shape, the preferred orientation of clay platelets gives rise to anisotropy in the morphology of the pore network. Both effects have considerable influence on retention and anisotropic transfer of water and solutes in clay-rich media, causing clay minerals to play a pivotal role in the exploration and management of critical resources for human beings.

In sedimentary rocks such as mudrocks or shales, clay minerals are common markers for paleoenvironmental reconstructions and the preferred orientation of clay platelets associated with nanometer-sized pores provides low permeability values to the whole clay-rich material. This latter process has a major effect on the development of oil, gas, water reservoirs, and is at the origin of the consideration of these clay-rich media as a natural barrier for CO₂ capture and nuclear waste storage. The omnipresence of clay minerals in soil environments is also involved in the development of thin crusts at the top surface. The significant preferred alignment of clay platelets in this environment and the low permeability of the material exert a key effect on soil erosion and directional dependence of water and pollutant migration. Clay minerals are also used in engineered materials given their low cost, abundance and the availability of natural deposits. Tuning the desirable fluid and gas barrier efficiency of these engineered materials through orientation control of clay platelets offers a variety of innovative sealing solutions ranging from rigid gaskets for high-temperature industrial applications to flexible and transparent films for packaging applications in food and electronic industries.

Although anisotropic features in clay platelet alignment have demonstrated their importance in numerous natural or engineered materials, a general function predicting preferred orientation for clay platelets is still lacking. Preferred orientation is generally studied through the analysis of the orientation distribution (OD) of crystallites by diffraction methods. The extent of anisotropy in clay platelet orientation is then most often illustrated by global descriptors of the experimental orientation distribution function (ODF) or by an adjustable spreading parameter of conventional distribution functions (Gaussian, Bingham, etc.) fitted to the experimental data. Though providing a complete description of the shape of the OD, these latter analyses remain targeted towards a limited number of clay minerals and preparation methods or are restricted to a narrow range of anisotropy degrees. To date, no conventional distribution function has been shown to be applicable for a large set of data. This lack of a reference function describing OD for clay minerals thus leads to significant uncertainties in the prediction of long-term transfers of critical resources in compacted clay-rich systems or for driving the design of high-performance engineered materials.

Herein, our objective is to fill this crucial gap by providing a general reference function of clay platelet alignment in a large number of clay-rich engineered and natural materials. We first develop a large set of laboratory clay-based engineered materials covering the most characteristic clay types (kaolinite, mica, chlorite, vermiculite, and smectite) and a broad panel of preparation methods (compaction, sedimentation, and centrifugation). Experimental orientation distributions of clay mineral platelets are then determined by X-ray scattering (XRS) measurements. Through detailed analysis of the different moments of the experimental data, we unravel, for the first time, the existence of a specific orientation signature independent of the type of clay platelet or preparation method. We also demonstrate that none of the conventional distribution models used so far allows for the reproduction of the overall set of measured ODFs. Based on the maximum-entropy method, we propose a new function that allows a complete description of the experimental OD for clay platelets throughout the whole range of anisotropy degrees. Finally, the efficiency of this new distribution function in modeling the preferred orientation of clay platelets is illustrated for a representative set of engineered samples, as well as for three natural systems, i.e., a shale, a soil crust, and a schist, representative of the main different clay-rich environments on Earth’s surface or subsurface.

Results

Basics of the orientation distribution function and its determination from X-ray scattering experiments. The orientation of a clay platelet in an orthogonal framework Oxyz is determined by the orientation of its normal Oζ, which is defined by its spherical coordinates θ and φ (Fig. 1a). Clay systems are transverse isotropic media with the z-axis as the unique symmetry axis. The orientation distribution function f(θ, φ) thus only depends on the angle θ where:

\[ f(\theta) \geq 0 \] (1)

![Fig. 1 Experimental measurement of the orientation distribution function.](image)

a) Spherical coordinates (θ, φ) defining the orientation of an individual clay platelet (in yellow) with respect to the laboratory frame. b) Schematic representation of an X-ray scattering experiment. The sample is studied in transmission, and scattered intensities are recorded on a planar detector where the color scale ranges from dark blue for the smallest intensity values to red for the largest values. The image here corresponds to a kaolinite sample. The rings corresponding to 00l Bragg reflections and hk reflections (i.e., 02 and 11 reflections) have maximum intensities along the vertical z direction and the horizontal x direction, respectively. c) A typical experimental ODF deduced from the angular scan of the 001 diffraction ring using Eq. (4), with the calculated \( P_0 \), \( P_1 \), and \( P_2 \) order parameter values from Eq. (10).
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θ

, φ

+ 0.0 0.2 0.4 0.6 0.8 1.0

θ

〈P4cosθ) 〉= \int_0^\pi P_4cosθf(θ)sinθdθ  

(10)

Analysis of orientation anisotropy most often relies on the
value of the second momentum \( P_2 \). This parameter is known as
H, the Hermans parameter in polymer and composites sciences
or \( S \), the nematic order parameter in colloid science. This
parameter has a value of 0 for isotropic organization and 1 for
perfectly aligned particles. However, \( P_2 \) also has a null value
when all particles are oriented at the magic angle \( \theta = acos(1/3) \)
\( \approx 54.7° \). This specificity illustrates the limit of using only the \( P_2 \)
order parameter to characterize the anisotropy. The actual
fingerprint of the shape of the ODF and the whole set of
momenta \( P_l \) are accessible from XRS analysis according to Eqs.
(4) and (10). This contrasts with other vibrational techniques
such as infrared or Raman spectroscopies, which provide only
\( P_2 \) or \( P_0 \) \( P_4 \) momenta, respectively, thus limiting the
number of Legendre polynomials to the fourth rank order in
Eq. (5).

In an effort to obtain information that is as general as possible
on the ODF for clay-rich media, a large set of different clay types
(kaolinite, mica, chlorite, vermiculite, and smectite) and prepara-
tion methods (compaction, sedimentation, and centrifugation)
are considered here. These different clay types represent the most
ubiquitous clay minerals on the Earth’s subsurface. The three
preparation protocols are considered here to be representative of
the main different formation mechanisms of clay-rich natural or
engineered materials. These protocols include the compaction
process in dried conditions (i.e., compaction method), the settling
of clay particles in suspension (i.e., sedimentation method), and a
coupled sedimentation-compaction method in water saturated
conditions mimicking the early diagenesis process of minerals
(i.e., centrifugation method). A total of 100 XRS analyses,
complemented by recent anisotropy measurements on four
sedimented artificial clay samples, provide a large experimental
dataset for the analysis of ODF and a wide range of anisotropy
degrees (i.e., order parameter values). Among the whole set of
\( P_l \) order parameters accessible by XRS analysis, Fig. 2 shows
the first momenta \( P_4 \) and \( P_6 \) as a function of \( P_2 \) for all samples

\[
f(\theta) = f(\pi - \theta)  
\]

(2)

Any distribution function is positive and can be normalized to
unity, which yields Eqs. (1) and (3), respectively. The platelet
orientation is equivalently characterized by a unit vector parallel
to \( Oz \) and by its opposite, defined by the spherical coordinates
(\( \theta, \varphi \)) and (\( \pi - \theta, \varphi + \pi \)) from Eq. (2). In the XRS experiments
performed here, scattered intensities are recorded on a planar
detector (Fig. 1b). Due to the preferred orientations of the
platelets, the intensity of the 001 diffraction ring is modulated
angularly. Assuming that the angle \( \tau \) on the detector is equal to
the spherical coordinate \( \theta \) (see Supplementary Note 1, Supple-
cimentary Figs. 1–3), the ODF \( f(\theta) \) (Fig. 1c) can be fully determined
from the angular distribution of intensity \( I \) along the 001
diffraction ring:

\[
f(\theta) = \frac{I(\theta)}{\int_0^\pi I(\theta) sin(\theta)d\theta}  
\]

(4)

Momenta analysis of the experimentally determined orienta-
tion distribution functions for clay platelets. The ODF \( f(\theta) \)
can be developed as an infinite series of Legendre’s polynomial
functions \( P_l(\cos\theta) \) as:

\[
f(\theta) = \sum_{l=0}^{\infty} \frac{2l + 1}{2} (P_l(\cos\theta))P_l(\cos\theta)  
\]

(5)

The sum can be restricted to even values of \( l \) as Eq. (2) leads to
null values of odd terms of the series. The first Legendre
polynomials in the expansion are expressed as follows:

\[
P_0(\cos\theta) = 1  
\]

(6)

\[
P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)  
\]

(7)

\[
P_4(\cos\theta) = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)  
\]

(8)

Fig. 2 Relationships between the experimental \( \langle P_2 \rangle \), \( \langle P_4 \rangle \), and \( \langle P_6 \rangle \) order parameters. Momenta of the experimental ODF for kaolinite, mica, chlorite,
vermiculite, smectite, and artificial clay samples made of disc packings are depicted by squares, circles, and diamonds, respectively. Sample
preparation based on compaction, centrifugation, and sedimentation methods are depicted by squares, circles, and diamonds, respectively. Experimental
preparation protocols are considered here to be representative of
the main different formation mechanisms of clay-rich natural or
engineered materials. These protocols include the compaction
process in dried conditions (i.e., compaction method), the settling
of clay particles in suspension (i.e., sedimentation method), and a
coupled sedimentation-compaction method in water saturated
conditions mimicking the early diagenesis process of minerals
(i.e., centrifugation method). A total of 100 XRS analyses,
complemented by recent anisotropy measurements on four
sedimented artificial clay samples, provide a large experimental
dataset for the analysis of ODF and a wide range of anisotropy
degrees (i.e., order parameter values). Among the whole set of
\( P_l \) order parameters accessible by XRS analysis, Fig. 2 shows
the first momenta \( P_4 \) and \( P_6 \) as a function of \( P_2 \) for all samples
investigated (with ODF determined from Eq. (4) and order parameters from Eq. (10)) to assess a potential common signature of ODFs. Regardless of the nature of the clay mineral (i.e., kaolinite, mica, chlorite, vermiculite, and smectite) or the preparation method (i.e., compaction, sedimentation, or centrifugation), univocal relationships are evident for the three order momenta of the ODF, revealing a specific signature for the preferred orientation of clay platelets.

For simplicity, experimental OD profiles are commonly fitted in the literature with conventional distribution models. For clay minerals, the most commonly used distribution functions are the Gaussian, Lorentzian and Fisher functions, the Bingham or Maier-Saupe distribution model, and the mechanical compaction models, taking the following form:

\[ f_G(\theta) = k_G(m) \exp\left(-\frac{\theta^2}{m}\right) \]

\[ f_L(\theta) = k_L(m) \frac{m}{\theta^2 + m} \]

\[ f_F(\theta) = k_F(m) \exp(m \cos\theta) \]

\[ f_{B/MS}(\theta) = k_{B/MS}(m) \exp(m \cos^2\theta) \]

\[ f_{MC}(\theta) = k_{MC}(m) \frac{m}{(\cos^2\theta + m \sin^2\theta)^{1/2}} \]

Note that to satisfy the symmetry of the ODF stated in Eq. (2), the Gaussian, Lorentzian and Fisher functions \( f_i(\theta) \) with \( i = G, L, F \) are summed up with \( f_i(\pi - \theta) \). The prefactor \( k_i(m) \), with \( i = G, L, F, B/MS, \) or \( MC \), is a normalization constant to satisfy Eq. (3), and \( m \) is the parameter governing the ODF spread.

For each function and by varying the parameter \( m \), we calculated order parameters for \( l = 2, 4, \) and \( 6 \). The calculated \( \langle P_2 \rangle - \langle P_4 \rangle \) and \( \langle P_0 \rangle - \langle P_2 \rangle \) curves are reported in Fig. 2. It is clear that none of the standard models are able to correctly reproduce our experimental dataset. The Lorentzian and mechanical compaction distributions indeed clearly overestimate the \( \langle P_2 \rangle \) and \( \langle P_4 \rangle \) order parameters through the entire range of \( \langle P_2 \rangle \) values. The Gaussian and Fisher models provide good agreement with experimental data for small and large \( \langle P_2 \rangle \) values, i.e., below 0.2 and above 0.9, but they significantly underestimate the \( \langle P_2 \rangle \) and \( \langle P_4 \rangle \) order parameter values in the intermediate range of \( \langle P_2 \rangle \) values. Finally, the Bingham or Maier-Saupe distribution model provides the closest agreement with our data but still fails to account for \( \langle P_4 \rangle \) and \( \langle P_0 \rangle \) contributions in the \( 0.4 < \langle P_2 \rangle < 0.9 \) region. The present results clearly demonstrate the limitations of conventional distribution models in reproducing the full signature of the clay mineral ODFs across the whole range of anisotropy degrees.

**Determination of a general orientation distribution function based on the maximum-entropy method.** To describe the entire ODF for clay-rich media, an alternative to the limitation of existing distribution models is to consider the maximum-entropy method (MEM) for reconstructing the full orientation function. The MEM relies on information theory (in statistics) and provides the most probable ODF that is consistent with a set of few known \( \langle P_i \rangle \) values. One estimates the equilibrium ODF and thus the entire range of \( \langle P_2 \rangle \) parameters by maximizing the information entropy defined as:

\[ S(f(\theta)) = -\int_0^\pi f(\theta) \ln(f(\theta)) \sin(\theta) d\theta \]

The ODF can then be written as:

\[ f_{MEM}(\theta) = k_{MEM} \exp\left(\sum_{i=2}^n \lambda_i P_i(\cos\theta)\right) \]

where \( n \) is the index of the higher order parameter used as a constraint (the sum over \( i \) in Eq. (17) runs on even numbers between 2 and \( n \)), \( \lambda_i \) represents the Lagrange multipliers, and \( k_{MEM}(\lambda_2, ..., \lambda_n) \) is the normalization constant that satisfies the relation in Eq. (3). The index 'MEM' refers to the maximum-entropy method. The MEM approach has been proven to be very efficient when only a few order parameters are known. Indeed such a reduced knowledge yields Eq. (5) inoperable for high degree of anisotropy. The situation differs here as XRS analysis provides the full \( f(\theta) \) ODF and thus the entire set of order parameters. The objective in the present work is to benefit from MEM theory to derive a reference distribution function based on a minimum number of parameters (i.e., \( \lambda_i \) coefficients) so that the whole set of \( \langle P_i \rangle \) moments would be automatically accounted for. By limiting the reconstruction of the \( f_{MEM}(\theta) \) function to the two first \( \lambda_i \) parameters (i.e., \( n = 4 \)), the ODF takes the following form:

\[ f_{MEM}(\theta) = k_{MEM}(\lambda_2, \lambda_4) \exp(\lambda_2 P_2(\cos\theta) + \lambda_4 P_4(\cos\theta)) \]

with Lagrange multipliers \( \lambda_2 \) and \( \lambda_4 \) calculated to satisfy the experimental constraints:

\[ \int_0^\pi P_2(\cos\theta) f_{MEM}(\theta) \sin(\theta) d\theta = \langle P_2 \rangle \]

\[ \int_0^\pi P_4(\cos\theta) f_{MEM}(\theta) \sin(\theta) d\theta = \langle P_4 \rangle \]

According to MEM theory, each pair \( (\lambda_2, \lambda_4) \) defines a full set of \( \langle P_2 \rangle \) moments. Figure 3 reports the interrelation between Lagrange multipliers and the first \( \langle P_2 \rangle \) or \( \langle P_4 \rangle \) moments and illustrates the associated shapes of ODFs.
Prep. method:

Notations as Fig. 2) are compared to calculated momenta using the general ODF for clay minerals (\( \langle f_{\text{MEM}}(\theta) \rangle \)) function. For \( \lambda_2 = 0 \), the ODF in Eq. (18) is identical to the Bingham/Maier-Saupe distribution in Eq. (14), which was successfully applied in liquid crystals to describe the condensation of the nematic phase within a mean-field theory\(^{42}\). Herein, the comparison between the \( f_{\text{MEM}}(\theta) \) (or Eq. (18)) with \( \lambda_4 = 0 \) and the experimental dataset of order parameters in Fig. 2 calls for a positive contribution of \( \lambda_4 \), especially in the \( 0.4 < \langle P_2 \rangle < 0.9 \) region. In contrast, in the case of rod-like organic 4,4'-dimethoxyazoxybenzene compound, Humphries et al.\(^{43}\) proposed an alternative model leading to an ODF similar to that in Eq. (18), with a negative contribution of \( \lambda_4 \). Moreover, these authors considered a fixed ratio between \( \lambda_2 \) and \( \lambda_4 \) in their model. For the clay minerals studied here, the correlation between \( \lambda_1 \) and \( \lambda_4 \) is achieved by first extracting the exact values of \( (\lambda_2 - \lambda_4) \) pairs associated with each experimental \( \langle P_2 \rangle \) – \( \langle P_4 \rangle \) pair and then by deriving the \( \lambda_4 - \lambda_2 \) relationship (see Supplementary Note 2, Supplementary Fig. 4). A good fit is obtained for \( \lambda_4 = 0.005(\lambda_2)^3 \), and the general ODF for clay platelets becomes:

\[
f_{\text{CM}}(\theta) = k_{\text{CM}}(\lambda_2)\exp[\lambda_2 P_2(\cos\theta) + 0.005(\lambda_2)^3 P_4(\cos\theta)]
\]

where \( \lambda_2 \) is a single parameter controlling the spreading parameter of the ODF and \( k_{\text{CM}}(\lambda_2) \) is the normalization constant that satisfies Eq. (3). The index ‘CM’ refers to clay minerals, whereas \( P_2(\cos\theta) \) and \( P_4(\cos\theta) \) are the first two orders of the Legendre polynomial series reported in Eqs. (7) and (8), respectively. We show in Fig. 4 that the \( f_{\text{CM}}(\theta) \) ODF based on the MEM well reproduces the correlation between the \( \langle P_2 \rangle \) and \( \langle P_4 \rangle \) order parameters for our experimental OD dataset. Such an excellent agreement does not guarantee, however, that the entire set of other \( \langle P_i \rangle \) momenta are correctly accounted for by this new function. The adequacy of our model for the prediction of the \( \langle P_i \rangle \) order parameter (Fig. 4) provides, however, good indications that a cut-off of \( n = 4 \) in Eq. (17) is relevant and that \( \lambda_i \) parameters for \( i \geq 6 \) are null. A crucial test for the validation of the \( f_{\text{CM}}(\theta) \) function through its capacity to reproduce the full set of \( \langle P_i \rangle \) order parameters is performed below on the basis of a direct comparison between the experimental and predicted ODF curves.

**Comparison between experimental and predicted orientation distribution functions.** The full validation of the general \( f_{\text{CM}}(\theta) \) function for reproducing the entire signature of the experimental OD profiles is shown in Fig. 5 for representative engineered clay samples. To do so, the parameter \( \lambda_2 \) in the \( f_{\text{CM}}(\theta) \) function is chosen so that the calculated \( \langle P_2 \rangle \) value is equal to the experimental value. The experimental and calculated ODFs are then compared without further adjustments (Fig. 5). The improvement provided by the \( f_{\text{CM}}(\theta) \) function compared to standard models is also highlighted. This comparison is limited to the Fisher (\( f_{\text{F}}(\theta) \)), Bingham/Maier-Saupe (\( f_{\text{MEM}}(\theta) \)), and mechanical compaction (\( f_{\text{MC}}(\theta) \)) distribution models, which provided the closest \( \langle P_2 \rangle \) – \( \langle P_4 \rangle \) relations with respect to our experimental order parameters (Fig. 2). Here again, calculations are performed by adjusting the variable \( m \) in Eqs. (12–14) to fit the experimental \( \langle P_2 \rangle \) value. As expected from Fig. 2, all these standard models reproduce rather satisfactorily the experimental OD profile for \( \langle P_2 \rangle \) = 0.2 (Fig. 5a). For the Bingham/Maier-Saupe model at \( \langle P_2 \rangle \) = 0.4 (Fig. 5b), the calculated \( \langle P_4 \rangle \) value is consistent with the measured value in Fig. 2. However, a systematic discrepancy is observed near \( \theta = 0 \) (or \( \theta = \pi \)) for higher degrees of anisotropy (Fig. 5c, d). Benefitting from the MEM theory, we attribute the excellent agreement between our experimental and predicted OD dataset to the consideration of the \( \lambda_4 \) contribution in the general \( f_{\text{CM}}(\theta) \) ODF.

**Extension to natural clay-rich systems.** To go further, we investigate whether the proposed general ODF could be extended to the analysis of the anisotropy of clay platelet orientation in three complex natural systems, i.e., a shale, a soil crust, and a schist. These selected samples are representative of different clay-rich environments on Earth’s surface or in the subsurface\(^4\) where orientation of clay minerals is of particular interest. Preferred orientation of clay minerals in soils and shales plays indeed a key role on water and solutes migration\(^5\), whereas anisotropy in clay particle orientation in schists is a marker of strains during metamorphism\(^{44–46}\). Compared to previous samples used to determine the shape of the general \( f_{\text{CM}}(\theta) \) function, the organization of clay platelets in these three samples originates from extremely contrasted conditions in terms of depth, temperature, or pressure. Moreover, these samples display a complex assemblage of both clay and non-clay particles, as well as a wide range of particle sizes. Because of this complexity, the collected experimental XRS diagrams (Fig. 6) appear noisier than the monomineralic clay samples (Fig. 5). However, fitting the experimental ODFs (extracted from the 001 reflection of mica or illite clay minerals) with the general \( f_{\text{CM}}(\theta) \) function leads to a very good agreement for the three natural samples investigated (Fig. 6). Such an agreement further confirms the ability of the new \( f_{\text{CM}}(\theta) \) reference function to describe anisotropy in clay platelet orientation for complex natural media. The robustness of this function is evidenced for clay minerals formed under extremely different natural conditions and leading to a wide range of
Discussion

This work provides evidence for the existence of a reference function describing the ODF of clay platelets and is applicable for a large set of clay types, anisotropy ranges, and formation processes in both engineered and natural materials. Our methodology based on the MEM to derive this new numerical function contains, within experimental precision, all relevant information on the ODF (i.e., the full set of \( \langle P \rangle \) order parameters) from the coupling between \( \lambda_2 \) and \( \lambda_4 \) parameters. By relating both entities, the unique general function \( f_{CM}(\theta) \) in Eq. (21), with only one variable parameter, can be applied to describe the whole range of anisotropy degrees. Accordingly, this new function provides clear
improvements compared to conventional distribution models (Gaussian, Bingham/Maier-Saupe, etc.), which are limited to certain anisotropy domains. Furthermore, this general $f_{CM}(\theta)$ function paves the way for unifying the various global descriptors of the experimental OD profiles (e.g., maximum intensity or width of the distribution) used in the literature to interpret the preferred orientation of clay platelets.

One of the important aspects of this approach is that the $f_{CM}(\theta)$ function relies on the consideration of homogeneous samples. In the case of highly heterogeneous samples, the difference between experimental and predicted ODF should help in elucidating the coexistence of spatial regions (or particle populations) with contrasted anisotropic features. Another important property of the $f_{CM}(\theta)$ function relies on its construction through the coupling between the $\lambda_2$ and $\lambda_4$ parameters. Here, a positive contribution of the $\lambda_4$ parameter is required to satisfy the $(P_2)$ relation for clay platelets, whereas a negative $\lambda_4$ contribution was considered in the case of rod-like organic compounds. One may thus tentatively hypothesize that $(\lambda_2, \lambda_4)$ coupling may be somehow linked to the shape of the particle. Future work could thus aim at assessing the extent of the $f_{CM}(\theta)$ function for other lamellar materials (e.g., graphene, MXenes, MoS$_2$, and layered double hydroxides) as well as for other types of grain morphologies (tubes, rods, and wires) in an effort to generalize the methodology developed here to improve the design of engineered materials for the electronics, energy, or catalysis fields (e.g., ZnO, Co$_3$O$_4$, carbon nanotubes, halloysite, or imogolite). Beyond this fundamental knowledge, a better description of the preferential orientation of clay platelets, as proposed here on the basis of the $f_{CM}(\theta)$ function, represents a key parameter for driving the design of new generations of innovative engineered materials in the field of packaging or high-temperature industrial applications with improved mechanical resistance and drastic fluid and gas permeability reduction.

We demonstrated here that the $f_{CM}(\theta)$ function is not only valid for pure clay-based samples but also mimics well the OD of clay platelets in three natural media (i.e., soil, shale, and schist). This result provides evidence for the applicability of this reference function to clay minerals in the case where these minerals are not the major mineralogical components. Accordingly, one may thus consider that this generic function represents a good proxy for the quantitative description of preferred orientation in the main different superficial environments of the Earth where clay minerals are found. In that regard, the $f_{CM}(\theta)$ function in Eq. (21) could be incorporated into current predictive models of caprock transport properties for oil, gas, or water resources. As far as clay barriers for waste repositories are concerned, the obtained diffusion coefficient for water can vary by a factor of 3–4 when considering either purely isotropic or perfectly anisotropic orientation of clay platelets. Correctly accounting for the actual preferred orientation using the numerical function determined can be expected to considerably improve the predictive power of these transport models.

Methods

Samples. Two types of sample series were considered in this study, i.e., mono-mineralic reference clay samples and clay-rich natural polymineralic samples. The selected reference clay minerals (i.e., kaolinite, mica, chlorite, vermiculite, and smectite) represent the most common different types of clay minerals in natural environments. Kaolinite KGA-2 with $[\lambda_{Al\cdot Mg_{0.5}}Te_{0.3}Fe^{3+}_{0.14}(Si_{5.66}Al_{2.34})O_{20}(OH)_{4}]^{8+}$ as structural formula was obtained from the Source Clays Repository of the Clay Minerals Society. Large monocrystals of mica clay minerals (i.e., muscovite) from the Structural Formula 57. The two other smectites correspond to hydrothermally synthesized fluorohydroxylated and fluorinated hectorite endmembers with a generic structural formula $[(Mg_{12}Al_{12}O_{20})(OH)_{4}]^{8+}$ for pure clay minerals (mainly mica-type and kaolinite) after rainwater. The second sample is a shale from the eastern Paris basin, France, extracted from the EST104 borehole at 453 m depth and belonging to the Callovo-Oxfordian formation. This claystone contains approximately 25–50% clay minerals (mainly mica-type and smectite) resulting from an original sedimentation event followed by a compaction process under soft lithostatic pressure conditions. The third sample is a schist from Les Sables-d’Or, France, located in the south Armoric-Hercynian belt. This sample was formed under Barrowian metamorphic conditions corresponding to a folding process at a temperature up to 300 °C and leading to crystallization of mica-type clay minerals.

Preparation of pure clay samples with different organizations. Different preparation methods (compaction, centrifugation, and sedimentation) were considered to maximize the range of anisotropy degree in particle orientation for monomineralic engineered clay samples investigated here. All powders were first dried at 60 °C overnight and then sieved through <50 μm to limit the size of particle aggregates. The compaction method involved uniaxial compression of a given amount of powder in polytetrafluoroethylene (PTFE) cylinders with a diameter of 0.64 cm. The centrifuged samples were obtained using the following procedure: dispersion of clay particles in water by sonication, centrifugation of the suspension directly in the PTFE cylinders under gravitational fields ranging from 4500 to 18,000 × g, and drying of the settled sample at 60 °C overnight. For the sedimentation procedure applied to the smectites that allowed thin, self-standing clay films to be obtained, the clay particles were first dispersed in water by sonication and then allowed to settle and dry at room temperature on a flat polyester substrate.

Resin induction and sample slice cutting. For resin impregnation, all self-standing samples were first dried overnight at 60 °C and placed in a cell under a primary vacuum to remove the water. Porosity was then filled with Methyl MethAcrylate (MMA) over a time span ranging from 3–14 days at a temperature up to 300 °C and leading to crystallization of mica-type clay minerals and up to 1 month for natural samples. The MMA resin was then polymerized in a 55 °C bath for at least 24 h using benzoyl peroxide (BPO) as a thermal initiator (BPO/MMA ratio of 0.5 wt%). The impregnated clay samples were then sawed perpendicularly to the main stratigraphic direction (i.e., longitudinally to the PTFE cylinders), and the thickness of the obtained lamellas was then reduced to <50 μm by a successive polishing procedure before XRS analysis.

X-ray scattering measurements. The XRS experiments were carried out at the Laboratoire de Physique des Solides at Orsay, France. The X-ray beam is delivered by a copper rotating anode generator (RU H3R, Rigaku Corporation, Japan) and monochromatized ($\lambda_{CuK\alpha}=1.5418 \AA$) by a multilayer W/Si mirror (Osmic), providing a monochromatic beam of 600 × 600 μm$^2$ at the sample position. Two-dimensional XRS patterns were collected on a MAR345 detector (marXperts GmbH, Germany), with a 150 μm pixel size, placed at a sample-to-detector distance $D$ of 250 mm or 350 mm. The beam stop was placed 30 mm behind the sample. This setup allows us to reach a scattering vector modulus down to $Q_{min} = 0.2 \AA^{-1}$ (i.e., $4\pi\sin(\theta)/\lambda$, where $\lambda$ is the incident wavelength and $2\theta$ is the scattering angle), i.e., $Q$-spacing up to 31.5 A (where $\lambda = 2\theta$). The sample slices were mounted on a goniometer head so that the axis of the main stratigraphic direction was perpendicular to the incident X-ray beam. The assumption regarding the cutting of sample slices longitudinally to the main stratigraphic direction was verified on several selected samples (Supplementary Note 3, Supplementary Fig. 5). The ODFs were deduced from the angular modulation of intensity I along the 001 diffraction ring (Eq. (4)) after background subtraction.

Data availability. The data that support the findings of this study are available on request from the corresponding authors.

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References

1. Ito, A. & Wagai, R. Global distribution of clay-size minerals on land surface in a biogeochemical and climatological studies. Sci. Data 4, 170103 (2017).
2. Backberg, N. R. et al. Quantifying the anisotropy and tortuosity of permeable pathways in clay-rich mudstones using models based on X-ray tomography. Sci. Rep. 7, 14838 (2017).
3. Biscaye, P. E. Mineralogy and sedimentation of recent deep-sea clay in the Arctic ocean area and adjacent seas and oceans. GSA Bull. 76, 803–832 (1965).
4. Iacoviello, F., Giorgietti, G., Nieto, F. & Memmi, I. T. Evolution with depth from detrital to authigenic smectites in sediments from AND-2A drill core (McMurdo Sound, Antarctica). Clay. Miner. 47, 481 (2018).
5. Kampman, N. et al. Observational evidence confirms modelling of the long-term integrity of CO2-reservoir caps. Nat. Commun. 7, 12268 (2016).
6. Busch, A. et al. Carbon dioxide storage potential of shales. Int. J. Greenh. Gas Control 2, 297–308 (2008).
7. Charlet, L., Alt-Epping, P., Wersin, P. & Gilbert, B. Diffusive transport and water quality issue. Adv. Water Resour. 106, 39–59 (2017).
8. Wenk, H.-R. & Vasin, R. Preferred orientation patterns of phyllosilicates in surface clays. Clays Clay. Miner. 65, 329–341 (2017).
9. Valentín, C. & Bresson, L.-M. Morphology, genesis and classification of surface crusts in loamy and sandy soils. Geoderma 55, 225–245 (1992).
10. Mahato, N., Banerjee, A., Gupta, A., Omar, S. & Balani, K. Progress in material science and composition. J. Struct. Geol. 69, 1641–1662 (2013).
11. Podsiadlo, P. et al. Ultrastrong and Stiff Layered Polymer Nanocomposites. Science 318, 80 (2007).
12. Aulin, C., Salazar-Alvarez, G. & Lindström, T. High strength, flexible and transparent nanofibrillated cellulose–nanoclay biobased films with tunable oxygen and water vapor permeability. Nanoscale 4, 6622–6628 (2012).
13. Pollo, H. R. et al. Forming clay minerals. for biogeochemical and climatological studies.
14. Hubert, F. et al. Investigating the anisotropic features of particle orientation in synthetic clay porous media. Clays Clay. Miner. 61, 397–415 (2013).
15. Cebula, D. J., Thomas, R. K., Middleton, S., Ottewill, R. H. & White, J. W. Neutron diffraction from clay-water systems. Clays Clay. Miner. 27, 59–72 (1979).
16. Hubert, F. et al. Investigating the anisotropic features of particle orientation in synthetic clay porous media. Clays Clay. Miner. 61, 397–415 (2013).
17. Voltoni, M., Wenk, H., Monol, N., Bjorlykke, K. & Jähn, J. Anisotropy of experimentally compressed kaolinite-illite-quartz mixtures. Geophysics 74, D13–D23 (2008).
18. Lutterotti, L., Wenk, H.-R., Voltoni, M., Bandyopadhyay, K. & Vanorio, T. Texture analysis of a turbosourced disordered Ca-montmorillonite. Am. Mineral. 95, 98–103 (2010).
19. Voltoni, M., Wenk, H., Mondol, N., Bjorlykke, K. & Jähn, J. Anisotropy of experimentally compressed kaolinite-illite-quartz mixtures. Geophysics 74, D13–D23 (2008).
20. Hubert, F. et al. Investigating the anisotropic features of particle orientation in synthetic clay porous media. Clays Clay. Miner. 61, 397–415 (2013).
21. Cebula, D. J., Thomas, R. K., Middleton, S., Ottewill, R. H. & White, J. W. Neutron diffraction from clay-water systems. Clays Clay. Miner. 27, 59–72 (1979).
22. Hubert, F. et al. Investigating the anisotropic features of particle orientation in synthetic clay porous media. Clays Clay. Miner. 61, 397–415 (2013).
23. Meheust, Y., Knudsen, K. D. & Fossum, J. O. Inferring orientation distributions in anisotropic powders of nano-layered clay minerals from a single two-dimensional WAXS image. J. Appl. Crystallogr. 39, 661–670 (2006).
24. Arne Johansen, T., Ole Ruud, B. & Jakobsen, M. Effect of grain scale formation on crystalline swelling of montmorillonite. J. Chem. Soc. Faraday Trans. 1 79, 1687–1700 (1983).
25. Manseau, A., Chateigner, D. & Gates, W. P. Polarized EXAFS, distance-valence least-squares modeling (DVLS), and quantitative texture analysis approaches to the structural refinement of Garfield nontronite. Phys. Chem. Miner. 25, 347–365 (1998).
26. Dohrmann, R., Rüping, K. B., Kleber, M., Ufer, K. & Jahn, R. Variation of preferred orientation in oriented clay montmorillonite as a result of sample preparation and composition. Clays Clay. Miner. 57, 686–694 (2009).
27. Méheust, Y., Knudsen, K. D. & Fossum, J. O. Inferring orientation distributions in anisotropic powders of nano-layered clay minerals from a single two-dimensional WAXS image. J. Appl. Crystallogr. 39, 661–670 (2006).
28. Arne Johansen, T., Ole Ruud, B. & Jakobsen, M. Effect of grain scale formation on crystalline swelling of montmorillonite. J. Chem. Soc. Faraday Trans. 1 79, 1687–1700 (1983).
29. Manseau, A., Chateigner, D. & Gates, W. P. Polarized EXAFS, distance-valence least-squares modeling (DVLS), and quantitative texture analysis approaches to the structural refinement of Garfield nontronite. Phys. Chem. Miner. 25, 347–365 (1998).
30. Chai, X. & Pumera, M. Characteristics and performance of two-dimensional nanomaterials for electrochemical applications. Nat. Catal. 1, 909–921 (2018).
31. Schmidt-Mende, L. & MacManus-Driscoll, J. L. ZnO-nanostuctures, defects, and devices. Mater. Today 10, 40–48 (2007).
32. Xie, X., Li, Y., Liu, Z.-Q., Haruta, M. & Shen, W. Low-temperature oxidation of CO catalysed by Co3O4 nanorods. Nature 458, 746 (2009).
33. De Volder, M. F. L., Tawfick, S. H., Baughman, R. H. & Hart, A. J. Carbon nanotubes: present and future commercial applications. Science 339, 535 (2013).
34. Pichot, V. et al. Structural and mechanical properties of single-wall carbon nanotube fibers. Phys. Rev. B 74, 245416 (2006).
35. Zhang, Y., He, X., Ouyang, J. & Yang, H. Palladium nanoparticles deposited on silanized hallowy stanene: synthesis, characterization and enhanced catalytic property. Sci. Rep. 3, 2948 (2013).
36. Paineau, E. et al. A liquid-crystalline hexagonal columnar phase in highly-dilute suspensions of imogolite nanotubes. Nat. Commun. 7, 10271 (2016).
37. Mermut, A. R. & Cano, A. F. Baseline studies of the clay minerals society source clays: chemical analyses of major elements. Clays Clay. Miner. 49, 381–392 (2001).
38. Reinholdt, M. X. et al. Morphological properties of vermiculite particles in size-selected fractions obtained by sonication. Appl. Clay Sci. 77–78, 18–32 (2013).
39. Ferrage, E. et al. Cation site distribution in clinochlores: a NIR approach. Clay. Miner. 38, 329–338 (2003).
40. Marcos, C., Argüelles, A., Ruiz-Carreño, A., Sánchez-Soto, P. J. & Blanco, J. A. Study of the dehydration process of vermiculites by applying a vacuum pressure formation of interstratified phases. Mineral. Mag. 67, 1253–1268 (2003).
41. Devineau, K. et al. In situ neutron diffraction analysis of the influence of geometric confinement on crystalline swelling of montmorillonite. Appl. Clay Sci. 31, 76–84 (2006).
42. Davis, B. et al. Smectite flocculation and its impact on interlayer water content and structure: a way to fine tune the hydrophilicity of clay surfaces? Microporous Mesoporous Mater. 181, 233–247 (2013).
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Author contributions
F.H. and E.F. conceived the project. T.D., F.H., C.L., B.G., B.D. and E.T. designed and prepared the samples. T.D. and E.P. performed the XRS experiments. T.D., P.L., E.P., F.H., A.D. and E.F. analyzed the data and interpreted the results. All authors contributed to the discussion and to the writing or review of the paper.

Competing interests
The authors declare no competing interests.

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