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Polytypism in semi-disordered lizardite and amesite by low-dose HAADF–STEM

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Abstract

Serpentine minerals exert important controls on the physical properties of ultramafic rocks and have the potential to influence deformation phenomena in fault zones and to control the release of water in subducted slabs. Sheet serpentine generally, and lizardite and amesite specifically, can adopt alternative crystallographic stacking arrangements called polytypes. Polytypism has been extensively studied in fully ordered crystals, but it remains largely enigmatic in the more common semi-disordered crystals that in long-range analyses such as X-ray diffraction only exhibit random combinations of $0\boldsymbol{b}$ and $\pm 1/3\boldsymbol{b}$ interlayer shifts. To date, atomic-resolution imaging to identify locally ordered polytypes has been precluded by the beam-sensitive nature of this hydrous magnesium silicate mineral. Here, we employed low-dose high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM) to study the polytypic structure of semi-

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disordered lizardite and amesite. Because the electron dose was as low as ~6000 $e^-/Å^2$, it was possible to directly resolve oxygen atomic columns and all the cations with a resolution of ~1 Å and reveal the short-range order. For lizardite, we identified long-period non-standard polytypes, including examples with 3, 4, 8 and 9 layers stemming from the ordering of the octahedral tilt along the **a**-axis. For amesite, we found short-range ordered polytypes with periodicities of up to 42 Å stemming from the ordering of interlayer shifts along the **b**-axis. The resolution was sufficient to determine the relative abundance of $6R_2$, $6R_1$, $2H_1$ and $2H_2$ polytypes in amesite to be 46.1%, 29.6%, 7.7% and 1.9% respectively. This is contrary to the expectation that the most common form of amesite is the $2H_2$ polytype, which may be more likely to form macroscopic crystals suitable for conventional X-ray diffraction-based study. We conclude that HAADF–STEM methods open the way for characterization of beam sensitive minerals and to resolve the structural details of less well ordered (but possibly more abundant) minerals at unit-cell scale.

Keywords: Polytype; HAADF-STEM; Amesite; Lizardite; Serpentine

Introduction

Sheet silicates are a diverse family of minerals that includes serpentine-kaolin group minerals, smectite, chlorite, micas, etc.. They are often produced during thermal and chemical alteration of rocks. Sheet silicates exhibit substantial structural diversity, understanding of which enables us to infer aspects of geological history (Morton 2005; Thiry 2000; Turpault et al. 2008). The structural diversity arises through alternative stacking sequences of the fundamental building blocks, silica tetrahedra (T) and metal-oxide octahedra (O) sheets in a 1:1 or 2:1 ratio, which leads to polytypes analogous to those observed in alloys (Zhang et al. 2018), ceramics (Zhang et al. 2020) and many other layered materials (Trigunayat 1991).

Serpentine is the structurally simplest group among the many sheet silicates. In serpentine, the T- and O-sheets of the TO layers are covalently bonded, and sequential layers are held together mainly by hydrogen bonding (Evans et al. 2013). Because of weak interlayer coupling, the energy difference among various possible stacking configurations is relatively small, generally a few kJ/mol among the energetically favorable structures (Mercier and Yvon 2008). Consequently, various stacking patterns can coexist in ordered or disordered arrangements. The former creates numerous polytypes (Bailey 1969). One polytypic variable is the tilt of octahedra. Change in the tilt direction, denoted as I and II (**Fig. 1**) is equivalent to a ±60° or 180° rotation (Bailey 1969). The most common polytypes have two TO layers with alternating octahedral tilts in one unit cell, but the periodicity can be as long as tens of nanometers due to complicated tilt patterns (Bailey and Banfield 1995). Using selected area electron diffraction (SAED), Banfield et al. reported a series of long-period structures with periodicities of 21 Å, 35 Å, 42 Å, 49 Å and 63 Å (Banfield et al. 1995) that, based on modeled diffraction intensities, were interpreted as structures with the tilt pattern (I,I,II), (I,I,II,II) or (I,I,I,II), (I,II,I,II,II), (II,I,I,I,II,II), (I,II,I,II,II,II,II) or (I,II,I,II,I,II,II), respectively.

Another polytypic variable is the interlayer shift of one TO layer relative to the next, which could be ±1/3b and 1/3a (Bailey 1969; Bailey and Banfield 1995; Plançon 2001). For the structure with alternating octahedral tilt, polytypes with interlayer shifts along the b-axis are most common, **Fig. 1**. The simplest 2-layer polytype, 2H$_1$, has the T- and O-sheets (shaded in gray in **Fig. 1a**) stacked along the c-axis without interlayer shifts along the a- or b-axes (**Figs. 1a,b**). The stacking sequence for 2H$_1$ can be written as (0b^{I}, 0b^{II}, 0b^{I}, 0b^{II}…). In 2H$_2$, the adjacent TO layers in the unit cell are shifted by 1/3b (red arrow in **Fig. 1c**) with a net stacking sequence of (1/3b^{I}, -1/3b^{II}, 1/3b^{I}, -1/3b^{II}…). In 6R$_1$ (**Figs. 1e,f**), the adjacent TO layers are consecutively shifted by 1/3b resulting

in the ($1/3b^{\mathrm{I}}$, $1/3b^{\mathrm{II}}$, $1/3b^{\mathrm{I}}$, $1/3b^{\mathrm{II}}$, $1/3b^{\mathrm{I}}$, $1/3b^{\mathrm{II}}$…) periodic stacking sequence. One another reported polytype is $6R_2$, which has been classified as non-standard due to the intermixing of $0b$ and $1/3b$ in one unit cell (**Figs. 1g,h**) (Bailey and Banfield 1995; Wiewiora et al. 1991) and which can be described as ($1/3b^{\mathrm{I}}$, $0b^{\mathrm{II}}$, $1/3b^{\mathrm{I}}$, $0b^{\mathrm{II}}$, $1/3b^{\mathrm{I}}$, $0b^{\mathrm{II}}$…).

The polytypes have been extensively studied in fully ordered crystals. For example, in lizardite, the most common form of serpentine, $2H_1$ and $1T$ are the dominant structures. In amesite, $(Mg_2Al)(SiAl)O_5(OH)_4$, which is structurally similar but compositionally distinct from lizardite, $(Mg_3)Si_2O_5(OH)_4$, the polytypes show clear locality dependence. The amesite crystals from Saranovskoye chromite deposit and Antarctica predominantly take $2H_2$ structure, although $2H_1$, $6R_1$ and $6R_2$ polytypes are also present (Anderson and Bailey 1981; Hall and Bailey 1976). In contrast, $2H_1$ and $6R_2$ are the dominant polytypes in the crystals from Postmasburg deposit (South Africa) (Zheng and Bailey 1997) and Sobotka Mountains (Poland) (Wiewiora et al. 1991), respectively.

Different polytypic preferences likely result from chemical differences, like lizardite versus amesite. When the composition is not a significant variable, the distribution of cations may play a vital role. The amesite crystals, except for those from Saranovskoye, exhibit alternating enrichments of Al and Si in the tetrahedral sheets, but they all possess different particular patterns of Al^{3+} ordering within the T- and O-sheets (Anderson and Bailey 1981; Hall and Bailey 1976; Hall and Bailey 1979; Wiewiora et al. 1991; Zheng and Bailey 1997). These cation distributions are suggested to be driven, at least in part, by the cation-cation interactions within T- and O-sheets, and those between the T- and O-sheets (Palin et al. 2014), but the balance of short- and long-range interactions controlling stacking energetics is poorly understood. Imaging the constituent atoms is one, yet maybe the most important, step towards uncovering the underlying mechanism of

polytypic preference. What makes the problem more complicated is that most natural samples, both lizardite and amesite, are far away from fully ordered. They are semi-disordered in most cases with random interlayer shifts along the **b**-axis (Bailey 1988; Brindley et al. 1951; Steadman and Nuttall 1962) from the long-range and average perspective. For those semi-disordered crystals, the only available option is atomic-scale imaging with transmission electron microscopes (TEM).

High-resolution transmission electron microscopy (HR-TEM) has been used for the characterization of polytypes in sheet silicates (Banfield et al. 1994; Banfield and Kogure 1998; Dódony and Buseck 2004; Inoué and Kogure 2016; Ji et al. 2018; Kogure et al. 2002; Kogure et al. 2006; Kogure et al. 2008; Wang et al. 2019). HR-TEM is based on the phase-contrast technique, where the interpretation of the image contrast is nontrivial without image simulation. An alternative approach, high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), provides a more direct image mode in which the contrast is directly proportional to $\overline{Z^\alpha}$ (the average of Z^α for all the atoms along the projection direction), where Z is the atomic number and the exponent is an imaging-condition and materials dependent constant (Hartel et al. 1996; Nellist and Pennycook 2000), $1 < \alpha < 2$. Atomic resolution identification of high-Z elements has been achieved in Cs-bearing phlogopite (Okumura et al. 2014) and Fe-rich celadonite (Kogure and Drits 2010). However, a key challenge for applying these methods to study hydrous minerals such as lizardite and amesite is that they are very electron-beam sensitive. In recent years, the development of low-dose TEM methods has transformed our ability to analyze beam-sensitive materials including hydrous minerals. Kogure used low-dose HR-TEM to reveal the structure of tubular halloysite with a total dose of ~300 e$^-$/Å^2 (Kogure 2016). This is important because halloysite damage starts and completes at electron doses of ~1950 and ~8800 e$^-$/Å^2, respectively (Kogure 2016). Recently, our group used low-dose HR-TEM to image

montmorillonite along [001] with a total electron dose of less than ~100 $e^-/Å^2$ and achieved a resolution of 1.2 Å (Whittaker et al. 2018; Whittaker et al. 2019).

Here, we hypothesized that low-dose HAADF–STEM could directly resolve stacking arrangements and used it to study the short-range ordered structures in semi-disordered lizardite and amesite. Our results show that, indeed, polytype domain size and polytypism can be resolved and the volumetric proportions of the ordered polytypes were determined. Further, we compare the energies of the serpentine polytypes calculated by *ab initio* and classic molecular dynamics (MD) simulations, considering, for simplicity, the substitution-free lizardite end member.

Experiment and simulation

The Cr-containing amesite, $(Mg_{2.01}Ca_{0.01}Al_{0.92+x}Fe_{0.03-x}Cr_{0.06})(Si_{1.01}Al_{0.99-x}Fe_x)O_5(OH)_{3.93}$ with $0 \leq x \leq 0.03$, and lizardite, $(Mg_{0.877}Cr_{0.069}Al_{0.034}Fe_{0.018})_3(Si_{0.827}Al_{0.173})_2O_5(OH)_4$, was taken from Saranovskoye mine (Russia) and Woods Chrome Mine (Pennsylvania, USA) (Banfield et al. 1995), respectively. Cr resides in the octahedral sites in mica, smectite and halloysite, and is expected to reside in the octahedra in amesite and lizardite as well (Brigatti et al. 2001; Mitsis et al. 2018).

Sample preparation, electron microscopy and image simulations

TEM foils were prepared by ion milling and coated with carbon to mitigate the charging. Electron diffraction patterns and HAADF–STEM images were collected on the Thermo Fisher Themis and double-Cs-corrected TEAM1 (Ercius et al. 2012) operating at 300 kV with a probe convergence semi-angle of 17.1 mrad. Since the minerals are very beam-sensitive, the electron dose was kept around 10^4 $e^-/Å^2$ or lower. For the structural analysis, the HAADF–STEM images were taken with an inner collection semi-angle of 58 mrad and a dose of ~11000 $e^-/Å^2$. Images recorded with an inner collection semi-angle of 48 mrad and a dose of ~6000 $e^-/Å^2$ were compared with image simulations. To reduce the electron irradiation as much as possible, all the images were

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collected from the region near the area used for sample and microscope alignment. All the atomic-scale HAADF–STEM images were processed using an average background subtraction filter in Gatan DigitalMicrograph.

The image simulations were performed with a multi-slice algorithm embedded in Prismatic (Pryor et al. 2017) using the experimental microscope parameters. For simplicity, we only consider Al and Cr substitution in octahedra and Al substitution in tetrahedra and ignore Fe and Ca because of their low concentrations. The experimental images used for the comparison with simulated images were recorded in regions with thicknesses of ~35 nm, as estimated from the electron energy loss spectrum (EELS). The models for 35 nm thick regions were sliced into ~1 Å thick slabs and 30 frozen phonon configurations were used to account for the thermal diffuse scattering.

Molecular simulations

We used plane-wave density functional theory (DFT) calculations and classical MD simulations to predict the relative energetics of 1:1 layer silicate polytypes using a supercell composed of six layers of a 2 × 2 unit cell slab, each layer shifted relative to the neighbor along the **b**-axis. The DFT calculations were carried out using the CASTEP code (Clark et al. 2005) with PBE exchange-correlation functional (Perdew et al. 1996) and Grimme's van der Walls correction (Goerigk and Grimme 2010). We found that the energy cutoff of 340 eV was optimal for a final supercell composed of 846 atoms if ultrasoft pseudopotentials were used, while 900 eV for norm-conserving pseudopotentials. The geometry optimization was carried out using the Broyden–Fletcher–Goldfarb–Shanno algorithm (Broyden 1970; Fletcher 1970; Goldfarb 1970; Shanno 1970). The MD calculations were carried in canonical (NVT) and isothermal-isobaric (NPT) ensembles at ambient conditions. The interatomic interactions were described using the ClayFF force fields (Cygan et al. 2004). Identical input configurations are used in the DFT and MD calculations. We

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used the Nosé-Hoover (Hoover 1985; Nosé 1984) thermostat-barostat, with velocity Verlet integration scheme (Verlet 1967) and smooth particle Mesh Ewald (Essmann et al. 1995) treatment of electrostatic interactions. The relative energies are reported as averages over 10 ns simulations.

Results

HAADF–STEM imaging is generally conducted with an electron dose of ~10^7 e$^-$/Å^2, which was found to damage the amesite and lizardite samples within a few seconds. To make atomic-resolution imaging possible, the critical electron dose that can be tolerated by our samples was estimated by the loss rate of diffraction intensity, as shown in **Fig. 2**. The diffraction spots in the SAED patterns chosen for analysis correspond to a real-space distance of ~1 Å (**Fig. S1**). The relative intensity decreases quickly in a nearly linear manner and drops by 50% after irradiated by 14000 e$^-$/Å^2. Balancing the electron damage effect and signal-to-noise performance, we chose ~11000 e$^-$/Å^2 and ~6000 e$^-$/Å^2 for the structural analysis and comparison between experimental and simulated images.

1. Semi-disordered structure

Before we dive into the atomic scale, the general structural features of amesite and lizardite are introduced. **Fig. 3a–d** show the SAED patterns recorded along [001], [100], and [010]. The pseudo-hexagonal symmetry of the TO layers results in six-fold rotation symmetry in the [001] pattern in **Fig. 3a**. The (0kl) diffraction rows with k=6n±2 are significantly (**Fig. 3b)** and near-completely (**Fig. 3c)** streaked, which generally indicates that the interlayer shifts are semi-random or random combinations of 0b and ±1/3b. Sharp separate diffraction spots in the [010] SAED pattern indicates that the stacking along the a-axis is much more ordered (**Fig. 3d**). All the four low-index patterns can be indexed with a pseudo-orthogonal cell with a=5.3 Å, b=9.2 Å, c=14.1 Å, α=90.3°, β=90.1° and γ=90.0° (Anderson and Bailey 1981).

In the HAADF–STEM images (**Fig. 4)**, the brightest spots are octahedral cationic columns whereas the darker spots are tetrahedral cationic columns. The oxygen columns that are associated with cations are observed for the first time (**Fig. 4b)**. Based on the visualization of oxygen, the tilts of the octahedra are unequivocally determined, layer by layer (**Fig. 4a)**. **Fig. 4a** reveals stacking with the octahedral tilts alternating along the *a*-axis (I, II, I, II, etc., as shown by the green parallelograms), and with no interlayer shifts along the *a*-axis (horizontal line).

When viewed along [100], the oxygen columns are less clearly resolved than the cation columns (**Fig. 5**). Nevertheless, the streaking of the intensity from the octahedral cation columns along the *c*-axis is a strong indication of the location of the oxygen columns, as indicated by the yellow arrows in the inserted simulation image. By viewing the tetrahedral sheet structure along [100] the sequence of interlayer shifts along the *b*-axis can be inferred directly. In **Fig. 5**, adjacent TO layers have interlayer shifts of $|1/6b|$ or $|0b|$ in the projection direction, corresponding to shifts of $1/3b$ and $0b$ in the 3D structure. The observed interlayer shifts, however, show no long-range periodicity, as expected based on the SAED patterns (**Figs. 3b,c**). It is important to note that L1 and L2 in the experimental image are 1.321 Å and 3.099 Å, respectively, while 1.560 Å and 2.920 Å in the model and simulated image. A 15.5% smaller L1 indicates that the structure is more severely distorted than the model reported by Anderson et al. (Anderson and Bailey 1981), however, it remains unknown what causes this large discrepancy at present.

As shown in **Fig. 5**, the atomic columns between the tetrahedral cation pairs, marked by small black arrows, are on the same vertical line with the tetrahedral cations in the experimental image. The contrast indicated by the short black arrows cannot be due to oxygen atoms as the simulation image shows the oxygen contrast (red arrows) is offset from that due to tetrahedral cations. Although there may be some distortion of the tetrahedral sheets (Brigatti and Guggenheim 2002;

Brigatti et al. 2011), placement of the oxygen columns so that they are coplanar with the Si tetrahedral cations that they coordinate is impossible (**Fig. 6a**). As shown in **Fig. 6b**, the tetrahedral sheet is shifted by 1/3b in one region (crystal 2) compared to the next (crystal 1). In the projection along [100], this will place some Si atoms between the Si pairs in crystal 1, giving rise to the contrast between tetrahedral cation pairs in the HAADF–STEM image (**Fig. 6c**). The intensity of those sites will vary with the thickness of crystal 2 along [100], leading to intensity variation observed in **Fig. 5**. The ±1/3b shift creates domains separated by boundaries marked by the green line in **Figs. 6b,c**.

2. Ordered interlayer shift

Regions containing within-sheet shifts, as discussed above, were rare, and most regions showed only interlayer shifts. Regions with short-range stacking orders were often intergrown at the nanoscale (**Fig. 7**). This microstructure is as predicted based on the streaking in SAED patterns, which sample micrometer-scale areas (**Figs. 3b,c**). Since polytypes of well-ordered amesite have been extensively investigated (Anderson and Bailey 1981; Hall and Bailey 1976; Hall and Bailey 1979; Wiewiora et al. 1991; Zheng and Bailey 1997), our analyses focused on short-range ordered regions to complement the prior literature. However, our analyses also included short-range order in lizardite for comparative purposes.

Fig. 7a shows amesite with intergrown regions with different stacking patterns. We classify the continuous stacking with an interlayer shift of 1/3b as $6R_1$-stacking, and that of 0b as $2H_1$-stacking. As the enantiomorphic of $6R_1$-stacking (-1/3b^I, -1/3b^{II}, -1/3b^I, -1/3b^{II}, -1/3b^I, -1/3b^{II}…) can exist, we designate those sequences $6R_1'$. These coexist in **Fig. 7a**. **Fig. 7b** shows the co-existence of $6R_1$-, $2H_2$- and $6R_2$-stacking. Statistics from ~360 TO layers indicate that the abundance of $6R_2$-, $6R_1$-, $2H_1$- and $2H_2$-stacking is 46.1%, 29.6%, 7.7% and 1.9% respectively (14.7% were not

sufficiently well-resolved). Most stacking patterns persist only for 2~3 unit cells along the c-axis, with the exception being $6R_2$-stacking. The $6R_2$ is a nonstandard polytype, as it contains two types of interlayer shifts (Bailey and Banfield 1995), but as shown in **Fig. 8a,** regions extend over tens of nanometers. A comparison of the distribution of diffraction spots in a simulated SAED pattern with that in the fast Fourier transform (**Fig. 8b**) confirms the $6R_2$ polytype identification (crystal structure information is listed in **Table S1)**. We also observed all the four stacking patterns in semi-disordered lizardite, but the most abundant polytype was $2H_1$.

3. 3-, 4-, 8- and 9-layer structures based on ordered octahedral tilt patterns

Although the structures with alternating octahedral tilts (**Figs. 4, 5, 7, 8**) are those of the most common serpentine minerals (Bailey 1969), longer period polytypes stemming from more complex tilt patterns occur in the lizardite from Woods Chrome Mine (Banfield et al. 1995). Thus, we visualized this lizardite sample to further test the utility of our approach and to extend knowledge about serpentine polytypism. We found that some regions display a 3-layer repeat based on octahedral tilts (I,II,II) (**Fig. 9a**), which gives rise to a 22.4 Å periodicity along the c-axis (**Fig. 9b**). The pattern of octahedral tilts is clearly resolved in the higher magnification image (**Fig. 9c**). We also imaged 4-layer lizardite (**Fig. 10a**), with a c-axis periodicity of 30.2 Å (**Fig. 10b**). The higher magnification image in **Fig. 10c** shows that the tilt pattern in a unit cell is (II,II,I,I).

Fig. 11a shows a region of lizardite with 8-layer periodicity that arises from the pattern of octahedral tilts. The periodicity is so large that it is hard to measure directly in the fast Fourier transform (**Fig. 11b**). A line profile was made from the array highlighted by the red arrow (**Fig. 11c**) and enlarged to determine that the periodicity is 60.1 Å (**Fig. 11d**), as expected for eight TO layers in one unit cell. From the high magnification image, it is clear that the octahedral tilt pattern is (II,II,I,II,II,I,II,I) (**Fig. 11e**). Although the majority of 8-layer structure is lizardite, two layers

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(arrows in **Fig. 11a**) are chlorite. We also found regions comprised of a 9-layer polytype, the periodicity for which is 68.1 Å (**Figs. 12b,c**). The tilt pattern is (II,II,I,II,I,II,I,II,I) (**Fig. 12d**). Within this, most lizardite layers are partially transformed to chlorite (arrows in **Fig. 12a**).

4. Energetics of polytypes

The micrometer-scale disorder observed in amesite and lizardite (**Fig. 3**) arises from the long-range irregular interlayer shifts along the **b**-axis. Short-range ordered interlayer shifts and octahedral tilts were imaged at the nanoscale by HAADF–STEM. Those ordered structures include both standard and nonstandard polytypes. To shed light on the energetics of the polytypes, classical MD and DFT calculations were performed to predict the relative energies of the polytypes. Because of the high computational cost of considering multiple aluminum (the main substitution species) distributions and long-period octahedral tilts, this work considers the polytypes with alternating tilts and substitution-free lizardite composition. It is well established that aluminum content is an essential aspect of serpentine minerals (Caruso and Chernosky 1979; Mellini 1982; Wicks and Whittaker 1975). In the structural studies of lizardite, the observed 1T (Brigatti et al. 2011; Mellini 1982; Mellini and Zanazzi 1987) and the $2H_1$ (Mellini and Zanazzi 1987) polytypes contain low aluminum contents, the single observed $2H_2$ polytype (Brigatti et al. 1997) contains approximately half the Al content of amesite, emphasizing the relationship between composition and polytypism. Although the present calculations cannot accurately predict the energetics of the polytypes in amesite and lizardite they provide a foundation for future work.

Starting from the published atomic coordinates for the $2H_1$ (Zheng and Bailey 1997), $2H_2$ (Anderson and Bailey 1981; Hall and Bailey 1976), $6R_1$ (Bailey 1969) and $6R_2$ (Wiewiora et al. 1991) polytypes, we relaxed the structures and found negligible structural differences between the polytypes relaxed by MD and DFT. However, the two simulation approaches gave markedly

different predictions in the relative polytype stabilities (**Table 1**). Relative to the $2H_1$ polytype, the DFT simulations predict $2H_2$ to be significantly more stable, by ~200 kJ/mol, than $2H_1$, $6R_2$ and $6R_1$. The predicted energy differences among $2H_1$, $6R_1$ and $6R_2$ are relatively small, around 5 kJ/mol, equivalent to ~$2R$T, where R is Boltzmann's constant and T is temperature. In contrast, the MD simulations predicted $2H_1$ to be the most stable phase with only ~20 kJ/mol difference with $2H_2$. Also listed in **Table 1** are the reported relative abundances of the amesite polytypes from literature and this study.

Discussion

In this work, we resolved individual oxygen columns along amesite and lizardite [010] (**Fig. 4**) for the first time and show that high-resolution oxygen atom imaging can provide direct insights into the polytypic structure. For example, the visualization of oxygen atoms directly distinguishes the long-period tilt patterns of the octahedra. We anticipate that this capability can be extended to obtain further structural information. In particular, resolving oxygen atoms might reveal the structural distinction underpinning different polytypes. Single-crystal X-ray diffraction studies indicate that the positions of tetrahedral oxygens are displaced among polytypes by up to ~0.2 Å due to intersheet strain and interlayer hydrogen bonding (Brigatti and Guggenheim 2002; Brigatti et al. 2011). Given the theoretical resolution of HAADF–STEM (Cui et al. 2017) it may seem possible to detect this by imaging oxygen columns along [100]. However, this was not possible, likely due to electron-irradiation damage. Further reduction in electron-beam damage via lowering electron dose resulted in poor signal-to-noise ratio (SNR). For example, the SNR decreases by 3/4 when the electron dose is reduced from 700 to 200 e$^-$/Å^2 (Sader et al. 2010). We achieved a resolution of 1 Å (**Fig. S2**) with ~6000 e$^-$/Å^2, but lowering the electron dose decreased the SNR to the extent that atomic resolution was not possible. We anticipate that dose-efficient techniques like

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4D–STEM ptychography (Stevens et al. 2018a) and the sub-sampled approach (Stevens et al. 2018b) could circumvent this limitation and resolve all of the oxygen atoms.

One major challenge for polytype determination is to record the images of multiple zone axes from the same region without obvious beam damage (Kogure 2020). Lizardite and amesite retain their structures up to ~14000 e$^-$/Å^2 and imaging with ~6000 e$^-$/Å^2 can give good images. Therefore, collecting [100] and [010] images from the same regions is feasible if an automatic tilt program, for example k-space navigator (Duden et al. 2009), is used.

Despite the electron dose limitations, we were able to observe domains with short-range periodic stacking in amesite and lizardite. The fact that these domains occurred sequentially (**Fig. 7**) and not intermixed within randomly stacked materials, argues that even few-layer long blocks with regular stacking did not occur by random chance. Thus, our data support the energetic preference for polytypic order over random stacking in 1:1 trioctahedral silicates.

Our results support the expectation that structures with alternating octahedral tilts (i.e., I,II) are absolutely the most frequent, regardless of the interlayer shifts along the **b**-axis in lizardite and amesite. In lizardite, where longer period polytypes were observed, the next most common structure has a 3-layer periodicity in the pattern of octahedral tilts (I,II,II). Lizardite with structure arising from octahedral tilts with a four-layer periodicity was significantly less frequently observed than that with a three-layer periodicity but more common than those with 8- or 9-layer periodicities.

Lizardite has two most common polytypes in nature, 2H$_1$ (Mellini and Zanazzi, 1987) and 1T (Mellini 1982; Mellini and Zanazzi 1987) with octahedral tilt patterns of (I,II) and (I,I), respectively. By analysis of very large regions we determined that sequential layers in which octahedral tilt I is followed by II or II by I (as would occur in the 2H$_1$ polytype) accounts for 2/3 of the 3-layer polytype, 1/2 of the 4-layer polytype, 3/4 of the 8-layer polytype and 8/9 of the 9-

layer polytype. Assuming that the polytypes with different tilt patterns interconvert by the shift of the terminal OH plane by $+a/3$ and octahedral cations by $+2a/3$, these long-period structures may be intermediate products of the transformation between the most commonly observed 1T and $2H_1$ polytypes. The atomic-scale structural rearrangements may be triggered by macroscopic deformation. However, why the interconversion of I and II octahedral tilts would occur in a regular way to form long-period lizardite structures remains a mystery.

A clue to the origin of long-period sheet-silicate structure may come from prior work on chlorite. It has been shown by SAED that the stacking of dioctahedral chlorite, cookeite, dramatically varies with the pressure in geological settings (Jullien et al. 1996). These authors proposed that semi-random stacking dominates up to a pressure of 0.5 GPa, structures with 14 Å and 28 Å appear in the domains with a pressure of 0.5~1 GPa, super-long period structures with 42 Å, 56 Å, 84 Å, 112 Å, 140 Å, and 196 Å form in the domains with a pressure higher than 1 GPa. Thus, like chlorite, the long-period serpentine polytypes involving ordered interlayer shift along the b-axis or octahedral tilt along the a-axis may have formed under specific very high-pressure conditions. The findings do not address the mystery how the periodicity is imposed.

The long-period polytypes can be envisaged as the spiral growth of the simplest polytype $2H_1$ if they are formed through the dissolution-precipitation process. For example, assuming a screw dislocation creates a ledge with (II,I,II) in $2H_1$, the spiral activity produces repeated stacking of (II,I,II), and results in the stacking sequence of 3-layer polytype (I,II,II). Likewise, a ledge with (II,I,II,I,II,I,II,I,II) creates 9-layer polytype. For 4-layer and 8-layer polytypes, it could be explained with the faulted stacking in the ledge (Pandey et al. 1982). A more detailed description of the spiral growth model can be found in micas (Baronnet 1975; Baronnet and Amouric 1986). However, there are two major problems with the application of the spiral growth model in our case.

First, the Burgers vector is very large, roughly $7n$ Å (n is the number of layers needed for the ledge of the spiral growth). That's 21 Å for 3-layer and 63 Å for 9-layer polytype. It is unclear where those dislocations could come from and how they are stabilized. Second, the spiral growth model does not apply to solid-state transformation. Our unpublished data clearly show that some lizardite and amesite crystals transform to chlorite or long-period lizardite-chlorite interstratification via solid-state transformation, it is reasonable to assume the long-period polytypes are formed via solid-state transformation as well.

For the structure with alternating octahedral tilts, the interlayer shifts along the b-axis can be ordered over short distances in overall semi-ordered lizardite and amesite and result in the coexistence of $2H_1$-, $2H_2$-, $6R_1$- and $6R_2$-stacking at the nanoscale. In lizardite, $2H_1$-stacking was dominant. In amesite, whose polytypes have been more extensively studied compared to lizardite, we found relative abundances of the polytypic stacking different from that reported in a prior study of fully ordered crystals from the same location. The $2H_2$-stacking was reported to dominate ordered amesite from Saranovskoye (Anderson and Bailey 1981) but this polytypic stacking accounted for only ~2% in our semi-disordered sample, whereas the $6R_2$-stacking forms the largest domains and has an overall abundance of ~46%.

The average elemental compositions measured for the semi-disordered sample are very similar to those reported for the ordered amesite from Saranovskoye. Thus, we suspect that small chemical differences cannot account for polytypic differences in amesite. Further, we detected no significant difference in the composition of different amesite samples with different polytypic structure. In principle, the observation of multiple polytypes in a single sample offers the opportunity to test for cation composition variation among polytypes likely formed under very similar geochemical conditions. However, we did not detect any intensity differences in the HAADF–STEM images

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that could indicate uneven distributions of heavy cations Cr and Fe in regions with different polytype structures. It remains possible that differences in Al distributions among ordered and semi-ordered amesite may be correlated with the different polytype abundances. However, due to their similar Z, Al cations are indistinguishable from Si and Mg in HAADF–STEM images. Chemical mapping using EELS or energy dispersive spectroscopy may permit variation in Al concentration in materials with sufficiently large regions of the same polytypes. However, if small regions with different polytypes differ in cation distributions or cation concentrations, atom-resolved EELS would be required to detect them.

Although advanced low-dose electron imaging methods continue to have great promise for directly determining composition and structure for beam-sensitive materials such as amesite and lizardite, molecular simulations could explore cation and polytype parameter space. Based on the comparison between DFT and MD simulations, we conclude that MD with ClayFF is unsuited to predictions of sheet silicate polytype stability. ClayFF considers only electrostatic and van der Waals interactions between atoms—essentially treating clay minerals as ionic solids—with the exception of the semi-rigid bond between hydrogen and oxygen in the hydroxyl group or water molecule. In the context of polytypism, this approach can capture electrostatic interactions, such as hydrogen-bonding, and the interlayer hydrogen bonding energy estimated by ClayFF and DFT simulations are similar here and close to prior studies (Larentzos et al. 2007; Pouvreau et al. 2019). However, the plane-wave DFT calculations predict that the electron density redistributes significantly between polytypes, an aspect that cannot be captured by the same values of charge assigned to clay atoms by ClayFF irrespective of the polytype.

The DFT prediction that the $2H_2$ polytype is strongly favored in aluminum-free lizardite is surprising based on prior single-crystal studies. Lizardite with low Al concentrations normally

possesses 1T and $2H_1$ polytypes (Mellini and Zanazzi 1987), while the $2H_2$ polytype has only been observed for lizardite with 17.3% Mg and 29.5% Si substituted by Al (Brigatti et al. 1997). In our semi-disordered lizardite, $2H_1$ is the dominant structure. With high Al concentrations, lizardite-like amesite, $2H_1$, $2H_2$ and $6R_2$ have been observed to be dominant depending on the locality of the minerals (**Table 1**). The discrepancies between experimental observations and DFT simulations raise questions about the applicability of the DFT method at present. However, and more importantly, they may also highlight the possible importance of cation substitution, especially Al, and geological conditions (e.g., temperature and pressure) in the polytypic preference.

Implications

A key conclusion from this study is that low-dose annular dark-field scanning transmission electron microscopy can provide 1-Å resolution of highly beam sensitive clay materials. Using this method, we visualized oxygen atomic columns, revealed within-sheet shifts, determined the prevalence of regular alternating octahedral tilts in lizardite and amesite, and resolved the ordered structure with long-period complex octahedral tilts in lizardite. Surprisingly, for the structures with alternating octahedral tilts, the normally rare non-standard $6R_2$ polytype dominates in semi-disordered amesite. The observed polytypic preference could not be reproduced by *ab-initio* calculations with substitution-free models at zero temperature and pressure, which highlights the importance of substitution and geological conditions. The research lays the foundation for atomic and nano-scale characterization of the structures and microstructures of a wide variety of clays and other beam sensitive materials.

Acknowledgments

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Figure captions

Figure 1. Illustration of four common polytypes of sheet serpentine. (a,b) $2H_1$, (c,d) $2H_2$, (e,f) $6R_1$, (g,h) $6R_2$. The projections in (a), (c), (e) and (g) are along [100], while those in (b), (d), (f) and (h) are along [010]. The oxygen atoms, hydroxyl groups, octahedral and tetrahedral cations are represented by red, green, yellow and blue balls respectively. The 1/3*b* interlayer shifts of the

TO layer (relative to its lower layer) are indicated by red arrows. The adjacent TO layers without the indicating arrows have no interlayer shifts relative to each other (0*b*). The representation of octahedral tilts is sketched on the right side in (b), (d), (f) and (h), where triangles and parallelograms with dots at the centroid are tetrahedra and octahedra respectively, and I and II denote the tilts towards *a* and -*a*, respectively.

Figure 2. Intensity evolution with accumulated electron dose. The intensity is normalized to the value in the SAED pattern recorded before the irradiation experiment. The data shown were for an amesite sample, but the results apply for lizardite as well.

 Figure 3. Amesite SAED patterns along (a) [001], (b,c) [100] and (d) [010]. The patterns were indexed with a pseudo-orthogonal unit cell. Strong streaks were observed at $(0kl)$ with $k=6n\pm2$, where k and n are integers. The presence of $(00l)$ diffraction spots for odd l in (c) and (d) is caused by multiple diffractions, as verified by tilting the sample 6°~10° away from the zone axis along the $(00l)$ Kikuchi lines. The SAED patterns of lizardite were similar, so not shown here.

Figure 4. HAADF–STEM images viewed along [010]. In (a), the tilts of octahedral sheets in each TO layer are sketched with green parallelograms. The tetrahedral cations in adjacent TO layers are located at the same horizontal line, indicating no interlayer shifts along the *a*-axis. The framed region is enlarged and shown in (b), where the simulated image is superimposed. Black arrows mark the oxygen columns. The basic features in the images of amesite and lizardite are the same, so only the images of amesite are presented here.

Figure 5. (a) HAADF–STEM image viewed along [100]. Cation pairs in the tetrahedral sheets are highlighted by green boxes and relative interlayer shifts between two TO layers are illustrated by long black arrows. The inset at the center is a simulation image. Green, red and yellow arrows mark the contrast due to different oxygen atomic columns in the simulation image. However, the

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contrast due to these oxygen atoms cannot be resolved in the experimental image. Interestingly, for the columns between tetrahedral cation pairs, there is contrast variation in the experimental image, as indicated by the short black arrows. The greater contrast indicated by the arrow on the left is because shifts of $\pm1/3\boldsymbol{b}$ bring more tetrahedral atoms there, as shown in **Fig. 6**. The basic features in the images of amesite and lizardite are the same, so only the images of amesite are presented here.

Figure 6. (a) Projection of one TO layer along [100]. Si, Mg, O and hydroxyls are represented by blue, yellow, red and green balls. For the oxygen columns to locate at the same level of Si would completely disrupt the tetrahedral sites. (b) Tetrahedral sheets viewed along [001]. Red balls with crosses are apical oxygen atoms of the tetrahedra. Red balls and those with crosses are below and above the projection plane (Si balls), respectively. The same tetrahedral sheet in crystal 2 is shifted by $1/3\boldsymbol{b}$ ($-1/3\boldsymbol{b}$ also works) relative to that in crystal 1. Green line illustrates the interface. To guide the eye, projection of Si atoms along [100] onto the HAADF–STEM image is illustrated by the long black arrows.

Figure 7. HAADF–STEM images showing co-existence of (a) $2H_1$- and $6R_1$-, (b) $6R_2$-, $6R_1$- and $2H_2$-stacking in amesite. The region denoted as C in (a) is a chlorite layer. Small black boxes mark the tetrahedral cation pairs and arrows denote the interlayer shifts. A false-color temperature map is used for clearer visualization. The stacking layers of the regions denoted as $6R_1$ and $6R_1$' in (a) are less than one unit cell, but they are designated as $6R_1$- and $6R_1$'-stacking still because they are the only simple polytypes having those stacking sequences.

Figure 8. (a) HAADF–STEM images of $6R_2$ amesite. The ordered $6R_2$-stacking extends over tens of nanometers (only several unit cells are shown). Small boxes mark the tetrahedral cation pairs, and arrows denote the interlayer shifts. A false-color temperature map is used for clearer

visualization. (b) Fast Fourier transform of the HAADF–STEM image in (a). Spots were indexed based on the $6R_2$ structure.
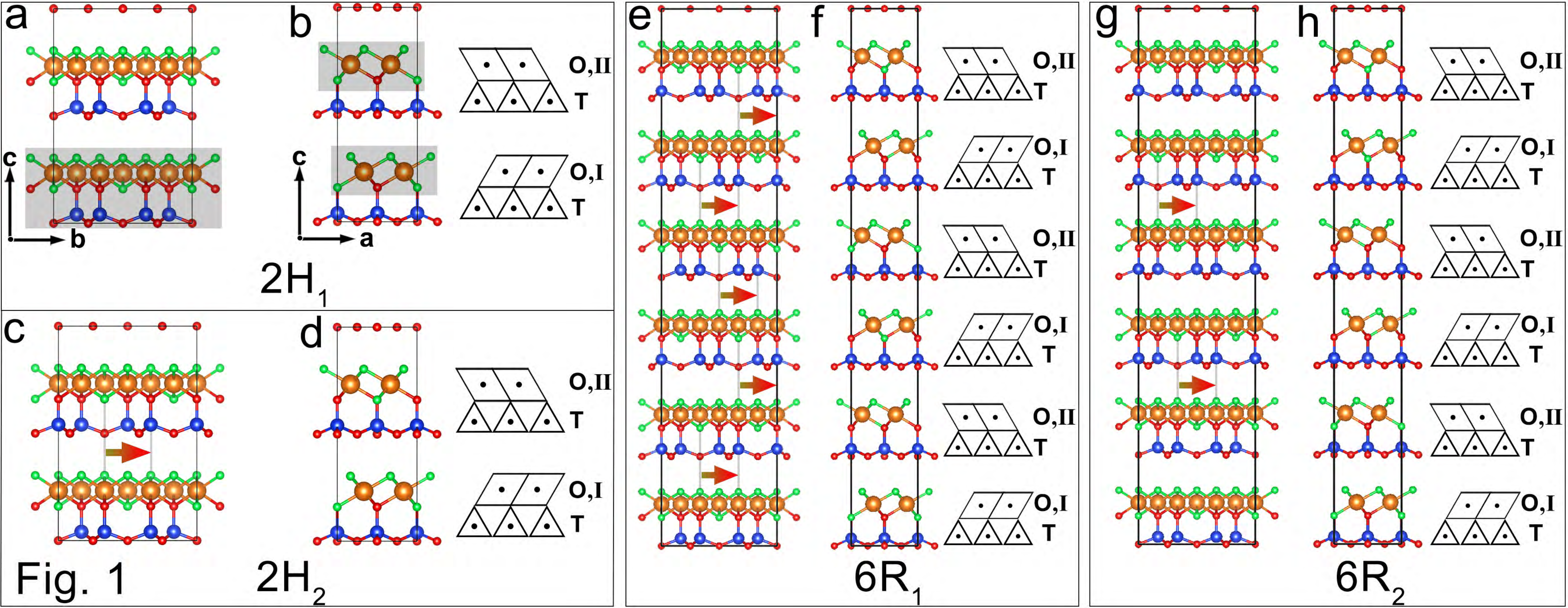
Figure 9. (a) HAADF–STEM image of 3-layer lizardite. A zoom-in image is shown in the inset. Red lines denote the tilt of octahedra. Green boxes indicate the 3-layer repeat of the tilt pattern. (b) Fourier transformation of (a) showing the 22.4 Å periodicity. (c) shows a higher magnification view of a region in (a), in which the (I,II,II) tilt pattern is clearly resolved. Triangles and parallelograms with dots at the centroid illustrate the tetrahedra and octahedra, respectively. A unit cell is highlighted with a black rectangle.

Figure 10. (a) HAADF–STEM image of 4-layer lizardite. A zoom-in image is shown in the inset. Red lines denote the tilt of octahedra. Green boxes indicate the 4-layer repeat of the tilt pattern. (b) Fast Fourier transformation of (a) in which arrows indicate spots representing 30.2 Å periodicity. (c) Higher magnification of a region from (a), showing two stacking units with the (II,II,I,I) tilt pattern. Triangles and parallelograms with dots at the centroid illustrate the tetrahedra and octahedra, respectively. A unit cell is highlighted with a black rectangle.

Figure 11. (a) HAADF–STEM image of 8-layer lizardite. A zoom-in image is shown in the inset. Red lines denote the tilt of octahedra. Green boxes indicate the 8-layer repeat of the tilt pattern. (b) Intensity profile along the arrow in the fast Fourier transformation in (c). (d) is enlarged from (b). Red arrows mark five peaks. (e) is a higher magnification view of a region in (a), showing one stacking unit with the (II,II,I,II,II,I,II,I) tilt pattern. The triangles and parallelograms with dots at the centroid illustrate the tetrahedra and octahedra, respectively.

Figure 12. (a) HAADF–STEM image of 9-layer lizardite. Many lizardite layers have transformed to chlorite layers. A zoom-in image is shown in the inset. Red lines denote the tilt of octahedra. Green boxes indicate the 9-layer repeat of the tilt pattern. (b) Fast Fourier transformation of (a).

(c) is enlarged from the framed region in (b). Red arrows mark five spots used for periodicity calculation. (d) is zoomed from (a), showing one stacking unit with the (II,II,I,II,I,II,I,II,I) tilt pattern. The triangles and parallelograms with dots at the centroid illustrate the tetrahedra and octahedra, respectively.

Table 1. The relative abundance of various polytypic stackings in amesite and the calculated relative energy. In this work, there are 14.7% TO layers not resolved well enough for polytype analysis. The uncertainty of the assignment of the TO layer near the boundary between different regions causes ~1% error.

Polytype	Energy relative to $2H_1$ (kJ/mol)		Abundance	
	DFT	ClayFF	This work	Literature
$2H_1$	0.00	0.00	7.7%	Dominant in Postmasburg deposit, South Africa (Zheng and Bailey 1997)
$2H_2$	-193.31	19.64	1.9%	Dominant in North Urals mountain, Russia (Anderson and Bailey 1981) Pensacola Mountains, Antarctic (Hall and Bailey 1976)
$6R_2$	5.39	27.97	46.1%	Dominant in Sobotka Mountains, Poland (Wiewiora et al. 1991)
$6R_1$	10.98	28.73	29.6%	Rare in North Urals mountain, Russia (Anderson and Bailey 1981) Pensacola Mountains, Antarctic (Hall and Bailey 1976)

Fig. 1

a, b — 2H$_1$

c, d — 2H$_2$

e, f — 6R$_1$

g, h — 6R$_2$

Fig. 2

Fig. 3

Fig. 4

a

b

OT OT OT OT OT OT OT OT OT OT OT OT OT OT OT OT

1 nm

Fig. 5

a

O

b

c

b

T

b

a

crystal 1

crystal 2

c

T OT OT OT

crystal 2

b

a

c

crystal 1

Fig. 6

HAADF-STEM

a

2H$_1$ 2H$_1$ 6R$_1$ 2H$_1$ 6R$_1$ 6R$_1$' C 6R$_1$' 6R$_1$ 6R$_1$ 2H$_1$ 6R$_1$

2 nm

b

6R$_2$ 2H$_2$ 6R$_1$ 6R$_2$ 2H$_2$ 6R$_2$ 6R$_1$ 6R$_2$

b

c

Fig 7

2 nm

Fig. 8

Fig. 9

a

b Fig. 10   2 1/nm

c   II
II
I
I
II
II
I
I

5 nm

Fig. 11

Fig. 12

5 nm

2 1/nm