Interlayer energy of pyrophyllite: Implications for macroscopic friction

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Running title: Interlayer energy of pyrophyllite
Abstract

Deformation of phyllosilicate can control the dynamics of the Earth’s crust. The phenomenological relationship between stress and deformation is known for some typical phyllosilicates; however, the underlying physics originating from the crystal structures is poorly understood. In this study, the deformation mechanism of pyrophyllite along basal planes was revealed through density functional theory calculations and atomic-scale theory of friction. The stable and meta-stable interlayer structures formed by interlayer slide were consistent with the experimental results reported previously by high resolution transmission electron microscopy. The difference in potential energies between stable and meta-stable interlayer structures can be interpreted as the difference in stacking of dioctahedral sheets between the adjacent layers. The estimated friction coefficient of the pyrophyllite between adjacent layers was consistent with the results of atomic force microscopy, suggesting that atomic-scale friction can be adequately estimated by this method. The calculated shear stress in our simulations has a linear relationship with the normal stress and has no significant crystallographic dependence on sliding direction along the basal planes. The crystallographic isotropy of interlayer friction is explained by the absence of interlayer cations in pyrophyllite, while muscovite showed crystallographic anisotropy as observed in
The macroscopic friction of a single crystal of pyrophyllite was estimated from atomic-scale friction by using the area of contact. The macroscopic friction coefficient of ideal interlayer sliding was estimated to be 0.134, which was smaller than a reported value (0.276) in shear experiments conducted for wet polycrystalline gouge layers. This difference can be primarily explained by the degree of orientation of pyrophyllite particles in the gouge layers. The friction coefficient estimated by a simple model of randomly oriented pyrophyllite gouge layer was 0.203 ± 0.001, which was similar to the reported value of 0.276 and clearly smaller than the values (0.6–0.85) of common minerals estimated by the empirical Byerlee’s law. These results indicate that weak interlayer friction of phyllosilicates has a large effect on the low frictional strength of gouge layers in natural faults. Our methodology and results are useful for understanding the physics behind the phenomenological friction laws of phyllosilicate gouge. **Keywords:** pyrophyllite, friction coefficient, interlayer friction, gouge layers, density functional theory
Introduction

Deformation of rocks and minerals controls crustal dynamics. The shear strength of rocks can be reduced by the presence of phyllosilicates (Byerlee 1978; Shea and Kronenberg 1993; Wintsch et al. 1995; Jefferies et al. 2006; Mariani et al. 2006; Amiguet et al. 2012). Phyllosilicates have been found in many natural faults and on sliding planes of landslides; therefore, the frictional properties of phyllosilicates are critical for understanding the dynamics of the Earth’s crust.

The stability of gouge-bearing faults have been evaluated in a laboratory using shear tests and through analyses based on a phenomenological rate- and state-dependent friction (RSF) law (Dieterich 1979; Ruina 1983); however, the physics behind the law depends on the materials, is complicated, and it is difficult to extrapolate the results to natural faults. Grain boundary friction, grain-size reduction, grain rolling, and pressure solution are critical parameters affecting granular fault gouges (Bos and Spiers 2001). Recent development of a microphysical model partly reveals the physics behind the macroscopic frictional strength of granular fault gouges (Chen and Spiers 2016; Chen et al. 2017). In their model, the shear strength of the gouge is mainly controlled by porosity and grain boundary friction. However, the model was limited to spherical particles and grain
boundary friction was still expressed by an empirical parameter.

Grain boundary friction of phyllosilicates may be weaker than for other minerals because of two reasons. First, friction can be lubricated by adsorbed and interlayer water in hydrophilic phyllosilicates (Horn and Deere 1962; Morrow et al. 2000; Sakuma et al. 2006; Ikari et al. 2007; Moore and Lockner 2007; Sakuma et al. 2011; Behnsen and Faulkner 2012; Sakuma 2013; Katayama et al. 2015; Kawai et al. 2015; Morrow et al. 2017; Tetsuka et al. 2018). Second, the presence of weak bonding planes in phyllosilicate crystal structures can reduce the frictional force (Moore and Lockner 2004; Kawai et al. 2015; Sakuma et al. 2018; Okuda et al. 2019).

Here, we focused on the second hypothesis during dry conditions by studying hydrophobic pyrophyllite minerals. Recent experimental and theoretical calculations revealed that sub-meter scale frictional strength of a single muscovite crystal along basal planes can be explained by the roughness of the atomic-scale potential energy surface during sliding (Sakuma et al. 2018). The potential energy should depend on the crystal structures; therefore, this mechanism should be tested on various phyllosilicates and sheet-structured minerals. A theoretical calculation of brucite revealed the difference between interlayer friction with muscovite, which would originate from the differences in
interlayer interactions (Okuda et al. 2019).

Pyrophyllite is a 2:1 type dioctahedral clay mineral and the charge of the layer is neutral. The interlayer bonding energy is characterized by weak van der Waals forces, in contrast to the relatively strong Coulomb forces of micas and hydrogen bonding in hydroxides (Sakuma and Suehara 2015). During atomic-scale friction, a low friction coefficient was observed between a silicon nitride tip and pyrophyllite flakes by using atomic force microscopy (Bucholz et al. 2012). For macroscopic friction under a confining pressure of 100 MPa, the maximum friction coefficient of pyrophyllite was 0.4 for highly aligned pyrophyllite grains within shear planes, while muscovite had a value of 0.55 (Moore and Lockner 2004). It would be difficult to determine the relationship between atomic-scale and macroscopic friction only from these previous studies, because of non-negligible effects of the silicon nitride tip on atomic-scale friction.

Here the change in potential energy of pyrophyllite along six sliding paths on a basal plane was calculated based on the density functional theory (DFT) (Hohenberg and Kohn 1964; Kohn and Sham 1965). The reliability of the DFT calculations were confirmed by comparing the stable and meta-stable structures with high-resolution transmission electron microscopy (HRTEM) observations (Kogure et al. 2006; Kogure and Kameda 2008). The
frictional strength of a single pyrophyllite crystal determined using DFT calculations are discussed and the results were used to understand the origin of macroscopic deformation of pyrophyllite in a frictional regime.

Computational methods

Potential energy surface and frictional force

Atomic-scale friction can be estimated from the roughness of the potential energy surface during sliding (Zhong and Tománek 1990; Schwarz and Hölscher 2016; Sakuma et al. 2018). The computational method to obtain the potential energy profile along a sliding path is the same as in previous studies (Zhong and Tománek 1990; Sakuma et al. 2018). Briefly, the interlayer energy $E_{\text{IL}}$ as a function of sliding distance $x$ and interlayer distance $z$ was calculated as follows.

$$E_{\text{IL}}(x, z) = E_{\text{2layers}}(x, z) - 2E_{\text{1layer}}$$ (1)

Here, $E_{\text{2layers}}$ and $E_{\text{1layer}}$ are the total energy of two pyrophyllite layers and the single layer in the supercell, respectively. The interlayer distance $z$ depends on the applied load $f_{\text{ext}}$ as
follows.

\[ f_{\text{ext}} = -\frac{\partial E_{\text{IL}}(x,z)}{\partial z} \quad (2) \]

Potential energy \( V \) as a function of \( x \) and \( f_{\text{ext}} \) can be obtained by considering the interlayer energy and the work against the applied load as follows.

\[ V(x, f_{\text{ext}}) = E_{\text{IL}}(x,z) + f_{\text{ext}}z \quad (3) \]

The potential energy difference is only required for calculating the frictional force; therefore, \( V \) was expressed as the difference from the minimum potential energy in this study. The frictional force \( f_{\text{friction}} \) as a function of \( x \) and \( f_{\text{ext}} \) can be obtained by the derivative with respect to \( x \) of the potential energy as follows.

\[ f_{\text{friction}}(x, f_{\text{ext}}) = \frac{\partial V}{\partial x} \quad (4) \]

To obtain the frictional force, the potential energy surface can be estimated from
DFT calculations.

Density functional theory calculations

The relaxed structure and potential energies of pyrophyllite layers under shear were derived from the DFT calculations. The exchange and correlation energy were calculated using the generalized gradient approximation of the Perdew-Burke-Ernzerhof (GGA-PBE) method (Perdew et al. 1996). Valence electrons in atoms were explicitly considered in the calculations using a pseudopotential method (Garrity et al. 2014). A semiempirical dispersion force correction (DFT-D2) (Grimme 2006; Barone et al. 2009) was included in the calculations for reproducing weak van der Waals forces among atoms. The reliability of the corrections were confirmed in our previous study by comparing the results with several dispersion-correction methodologies (Sakuma and Suehara 2015). All DFT calculations were performed using QUANTUM ESPRESSO (Giannozzi et al. 2009, 2017).

Bulk calculations. To test the reliability of the employed computational method, pyrophyllite lattice constants were calculated under various input parameters in DFT calculations. The initial structure of pyrophyllite was set to that reported by an X-ray
diffraction (XRD) method (Lee and Guggenheim 1981). The supercell includes 40 ions composed of two \( \text{Al}_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \) units. Convergence thresholds on the total ion energies in the supercell, forces, and stresses were \( 1 \times 10^{-6} \) Ry (=0.0136 meV), \( 1 \times 10^{-4} \) Ry/bohr/ion (=1.36 meV/bohr/ion), and 0.5 kbar, respectively. Kinetic energy cutoffs for wavefunction and charge density were chosen to be 40 Ry (=544.2 eV) and 320 Ry (= 4353.6 eV), respectively, by confirming the energy and structural convergences. These cutoff energies were fixed for subsequent calculations on slab geometry. Sampling of k-points in the Brillouin zone was established using \( 4 \times 2 \times 2 \) in Monkhorst-Pack grids (Monkhorst and Pack 1976), which was sufficient to achieve energy and structural convergences.

**Slab calculations.** Interlayer energy was calculated using the total energy of two layers in the supercell subtracted by two single layers in the supercell, as calculated in our previous studies (Sakuma and Suehara 2015; Sakuma et al. 2017, 2018). The size of the supercell was determined to be \( a = 5.17539 \) Å, \( b = 8.98879 \) Å, \( c = 46.78165 \) Å, \( \alpha = 90.97^\circ, \beta = 100.58^\circ, \gamma = 89.83^\circ \) based on the relaxed structures in bulk calculations, except for length \( c \). Length \( c \) was elongated to include vacuum space. Sampling of k-points in the Brillouin zone was set to \( 4 \times 2 \times 1 \) in Monkhorst-Pack grids. A dipole correction (Bengtsson 1999) was applied perpendicular to the basal plane of pyrophyllite to remove an
artifact arising from periodic boundary conditions. In this supercell, the size of $a$-$b$ plane was equal to the area in only one crystallographic unit cell. A comparison of calculated elastic constants and shear modulus with experimental values may be a clue for understanding the effect of system size, though it is difficult to obtain precise values in experiments. A DFT study on kaolinite (Weck et al. 2015) revealed that calculated shear constants and shear modulus using a small supercell of $a = 5.18$ Å, $b = 8.98$ Å, and $c = 7.33$ Å were consistent with experiments. These results imply that the small system size used in our study has insignificant effect on shear deformation. Atomic relaxations were conducted for ions in the supercell except Al ions in octahedral sites. Fixing the position of these Al ions is required to fix the interlayer distance. Convergence thresholds on the total ion energies in the supercell and forces were $1 \times 10^{-6}$ Ry (=0.0136 meV) and $1 \times 10^{-4}$ Ry/bohr/ion (=1.36 meV/bohr/ion), respectively.

### Results and discussion

**The bulk structure of pyrophyllite**

Calculated lattice constants of pyrophyllite are listed in Table 1. The differences between and the calculated and experimental lattice constants were less than 0.3% for all
parameters.

**Interlayer energy along six sliding paths**

Six sliding paths parallel to the basal plane were tested by considering crystallographic symmetry as shown in Fig 1. The length of sliding paths $L$ depends on the sliding directions, because crystallographic equivalent positions to the initial positions are required for averaging the frictional forces. The interlayer energies $E_{IL}$ were calculated every ~0.5 Å along the paths. The results along path 1 are shown in Fig. 2. Horizontal sliding of the top layers can be confirmed by analyzing the top views of the interfacial tetrahedral sheets. The triangle indicating the same SiO$_4$ tetrahedron in the top layer moved from left to right along path 1 as shown in Figs. 2 (A), (B), and (C). The interlayer energy was calculated at various $x$ displacements in the top layer by moving the top layer up and down perpendicular to the basal plane as shown in Fig. 2 (D). The interlayer energies at various $x$’s were plotted in Fig. 2 (E). The lowest energy was obtained at $x = 0$ which corresponds to the stacking structure reported by the single-crystal X-ray measurements of pyrophyllite (Lee and Guggenheim 1981). The energy increased as the two layers approached each other indicating the repulsion between the layers. The $z$ positions of lowest energies in the profiles changed depending on the displacement $x$. The interlayer
energies were fitted to an eighth- or seventh-degree polynomial equation and analytically calculated derivatives were used to derive the $z$ position balanced with applied normal forces. All interlayer energies along the six sliding paths are available in the supplemental figure S1.

Potential energy profiles along six sliding paths and experimentally observed interlayer structures

Potential energy changes along six sliding paths are plotted in Fig. 3. The difference between the lowest and highest potential energies increased as the applied normal stress $\sigma_n$ increased from 0 to 10.7 GPa. The most common interlayer structures determined by XRD measurements correspond to the lowest potential energy at $x = 0$ and $\sigma_n = 0$ GPa for all sliding paths. Similar low potential energy configurations were derived for paths 1, 3, and 5 at $x = 3.1$, 5.9, and 2.8 Å, respectively. Several meta-stable configurations appeared for paths 1 (\text{<010>}) and 3 (\text{<310>}) at $x = 6.2$ and 3.1 Å, respectively. These stable and metastable layered structures viewed at right angles to the basal plane are shown in Fig. 4. The overlap between the interfacial tetrahedral sheets at right angles to the basal planes are almost identical for these three structures. The difference between the stable and metastable structures were clear when considering the overlap of octahedral and tetrahedral sheets near
the interface. The stable structures seem to avoid overlap, while the metastable structure overlaps between the tetrahedra and octahedra as shown in Fig. 4. Such overlap would render repulsive interactions owing to the electrostatic interactions among oxygen atoms and among cations.

These interlayer structures were compared to actual pyrophyllite crystals with stacking disorder, and observed using HRTEM (Kogure et al. 2006; Kogure and Kameda 2008). The HRTEM image in Fig. 5 was interpreted as pyrophyllite and observed along [−110]. The dark spots in the tetrahedral sheets and octahedral sheets correspond to a pair of Si tetrahedra and Al octahedra, respectively. The stacking sequence is represented as a black solid line connecting the dark spots, to act as a visual guide. There are three types of interlayer structures. A structure indicated by asterisks in Fig. 5, which correspond to the metastable structures found in our study, is rare. On the other hand, the other two interlayer structures that are abundant in the image correspond to stable structures in our study. Therefore, the occurrence of these three stacking structures in natural pyrophyllite probably corresponds to their stability derived by our simulation.

**Frictional forces along six sliding paths**

The distance derivative of potential energy profiles provides the frictional force
along the sliding paths. The shear stress is plotted in Fig. 6. Assuming that the energy to reduce the potential energy is dissipated via surface phonons (Cieplak et al. 1994), the negative shear stress cannot contribute to the friction (Zhong and Tománek 1990). The positive shear stress increases with increasing normal stress for all sliding paths. The average shear stress, which may correspond to steady-state friction, can be calculated by integrating the positive shear stress along $x$ and dividing by the path length. The average shear stress $\tau$ as a function of normal stress $\sigma_n$ is plotted in Fig. 7. The average gradient $\mu$ among six paths obtained by fitting a simple linear equation of $\tau = \mu \sigma_n + C$ was $\mu = 0.078$ which is consistent within an order of magnitude of that (0.03) measured for atomic-scale friction between a pyrophyllite surface and a silicon nitride Si$_3$N$_4$ tip (Bucholz et al. 2012).

It should be noted that the shear and normal stresses are the values at the real contact area; therefore, these values are not equal to the macroscopic shear and normal stresses applied in macroscopic experiments. Shear stresses are required even when $\sigma_n = 0$ GPa and a linear relationship can be obtained for all six sliding directions. The differences among sliding directions reflect the degree of overlap of SiO$_4$ tetrahedra and AlO$_6$ octahedra during sliding. Shear stresses were smaller than those calculated for muscovite basal planes (Sakuma et al. 2018). The large shear stress for muscovite is due to the strong electrostatic
repulsion between positive potassium ions in the interlayer space and cations in tetrahedral sheets during sliding. In contrast, the basal plane of pyrophyllite does not have an interlayer cation, resulting in low shear stresses.

A possible uncertainty to compare our results with real material would be the presence of defects and/or isomorphic substitutions of cations which were neglected in our study. We cannot estimate the potential energy change due to the presence of such defects and substitutions without further additional simulations. These effects should be discussed combined with the density of defects and impurities in future works.

Implications for macroscopic frictions

Friction coefficient of basal plane

Most observable macroscopic frictional forces have a linear relationship with applied loads according to Amontons’s law (Amontons 1699). This relationship can be interpreted as the change in the real contact area as observed at the μm to mm scale (Abe et al. 2002) and the real contact area $A_r$ can be described as a function of the normal load $L$ as follows (Dieterich and Kilgore 1996).
Here \( p \) is the indentation hardness of the material. In this expression, the possible finite real contact area at \( L = 0 \) was ignored. In the previous section, the shear stress at the real contact area was calculated using the DFT method; therefore, macroscopic shear stress \( \tau_{\text{macro}} \) of pyrophyllite can be obtained as follows.

\[
\tau_{\text{macro}} = \frac{A_p}{A} \tau = \frac{A_p}{A} (\mu \sigma_n + C) = \left( \mu + \frac{C}{p} \right) \sigma_{n,\text{macro}} 
\]

Here, \( A \) is the surface area and \( \sigma_{n,\text{macro}} \) is the macroscopic normal stress. This equation was confirmed to be plausible by the analysis of a single-crystal muscovite surface (Sakuma et al. 2018). The macroscopic frictional coefficient \( \mu_{\text{macro}} = \mu + C/p \) is estimated to be \( \mu_{\text{macro}} = 0.134 \) by using \( \mu = 0.078 \) and \( C = 0.182 \) GPa for averaging six sliding paths in our simulations and the experimental value of \( p = 3.3 \) GPa (Zhang et al. 2013). The macroscopic frictional value (0.134) is smaller than those experimentally measured friction coefficients of pyrophyllite gouge (0.276 for wet and 0.375 for dry) (Moore and Lockner 2004). The reason for this discrepancy should be the presence of large frictional forces in
experiments among various crystallographic planes (Moore and Lockner 2004; Kawai et al. 2015). Pyrophyllite is a hydrophobic mineral and the effect of water would enhance the preferred orientation of gouge particles rather than the lubrication of adsorbed water.

**The friction coefficient of randomly oriented pyrophyllite particles**

Here the friction coefficient of simulated gouge was estimated by using a model, schematically shown in Fig. 8. In the shear zone, pyrophyllite particles should have a distribution in the orientation. The orientation of pyrophyllite particles was defined by a unit vector \( \mathbf{n} \) perpendicular to the basal plane as shown in Fig. 8 (A). The external force \( \mathbf{F}_{\text{ext}} \) can be decomposed to in-plane \( \mathbf{F}_{\text{interlayer}} \) and out-of-plane forces \( \mathbf{F}_{\text{normal}} \) for the top pyrophyllite particle as shown in Fig. 8 (C) and (D). Both forces depend on the angles \( \theta \) and \( \phi \) as follows in cartesian coordinates.

\[
\begin{align*}
\mathbf{F}_{\text{interlayer}} &= |\mathbf{F}_{\text{ext}}|(- \sin^2 \theta \cos \phi \sin \phi, 1 - \sin^2 \theta \sin^2 \phi, - \sin \theta \cos \theta \sin \phi) \\
\mathbf{F}_{\text{normal}} &= |\mathbf{F}_{\text{ext}}|(\sin^2 \theta \cos \phi \sin \phi, \sin^2 \theta \sin^2 \phi, \sin \theta \cos \theta \sin \phi)
\end{align*}
\]

The force \( F_{\text{friction}} \) required to slide the interlayer of pyrophyllite can be estimated by the macroscopic frictional coefficient of 0.134 calculated in this study and by the normal force.
applied to the basal plane. If the confining pressure $P_c$ is applied on the gouge, the normal force $F_{nc}$ from the confining pressure on the basal plane of pyrophyllite is independent of the orientation. The net normal force $F_n$ was calculated as follows.

$$F_n = \begin{cases} F_{nc} - |F_{normal}|, & \text{for } 0 \leq \varphi < \pi \\ F_{nc} + |F_{normal}|, & \text{for } \pi \leq \varphi < 2\pi \end{cases}$$ (8)

Here, the direction toward the basal plane was defined to be positive and the direction changes at below and above $\varphi = 180^\circ$ as observed in Fig. 8 (C) and (D). The interlayer frictional force can be described as follows.

$$F_{friction} = \mu_{macro}F_n$$ (9)

If the interlayer force $F_{interlayer}$ is larger than the frictional force $F_{friction}$, then interlayer sliding occurs. If the frictional force $F_{friction}$ is larger than the frictional force between the edges of pyrophyllite particles, then sliding should occur at the edge-edge interface. The friction coefficient, except for interlayer sliding, can be calculated from Byerlee’s law (Byerlee 1978). We used the friction coefficient of 0.85 for the frictional force $F_{Byerlee}$. The
external forces $F_{\text{ext}}$ for randomly oriented pyrophyllite particles were calculated by following the above criterion and the average friction coefficient $\mu_{\text{gouge}}$ was obtained as follows.

$$\mu_{\text{gouge}} = \frac{1}{N} \sum_{i=1}^{N} \frac{F_{\text{ext}}(i)}{F_n}$$

Here $F_{\text{ext}}(i)$ is the external force of the $i$-th oriented pyrophyllite, $N$ is the number of differently oriented pyrophyllite particles. The sampled normal vectors $\mathbf{n}$ of pyrophyllite are plotted in Fig. 8 (B). The figure indicates that the vectors were randomly distributed in space with $N = 50,000$. Examples of the forces at $\varphi = 90^\circ$ and $270^\circ$ are plotted in Fig. 8 (E) and (F), respectively. The net normal force $F_n$ increased and decreased with increasing $\cos \theta$ at $\varphi = 90^\circ$ and $\varphi = 270^\circ$, respectively. These changes of $F_n$ were because of the presence of $F_{\text{normal}}$ generated by the external force $F_{\text{ext}}$. The friction coefficient of $i$-th particle $\mu_{\text{gouge}}(i)$ was determined using lower force between $|F_{\text{ext}}|$ and $F_{\text{Byerlee}}$. The macroscopic coefficient of pyrophyllite gouge calculated by this simple model was $\mu_{\text{gouge}} = 0.203 \pm 0.001$, which is slightly smaller than 0.276 of preferentially oriented pyrophyllite gouge in wet triaxial experiments (Moore and Lockner 2004) and clearly smaller than Byerlee’s law.
The difference between the estimated and experimental friction coefficients may imply a difference in the degree of preferred orientation and the presence of other deformation mechanisms which are ignored in this study. From these results, macroscopic friction is strongly related to atomic-scale friction in the interlayer and therefore the crystallographic structure has a large effect on the frictional properties of gouge layers.

Acknowledgements

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References


Science Letters, 345–348, 142–150.


modular and open-source software project for quantum simulations of materials.


solution confined between mica surfaces studied by shear resonance measurement.

Physical Review Letters, 96, 046104.


List of figure captions

Fig. 1 (A) Side view of two pyrophyllite layers in the supercell. A sliding plane was placed between the layers. The thin black line indicates the supercell. (B) Top view of the six sliding directions from 1 to 6 between the pyrophyllite layers. Tetrahedral SiO$_4$ sheets on the interface of the top layer are only shown here. The end of each arrow indicates the crystallographic equivalent position from the initial position by sliding.

Fig. 2 Structures of SiO$_4$ tetrahedral sheets at the interface of the sliding plane along path 1 at (A) $x = 0$, (B) $x = 10/19L$, and (C) $x = L$. Triangles indicate the SiO$_4$ tetrahedra in the top pyrophyllite layer and are used as a guide in order to determine the displacement. (D) Definition of the $z$ axis perpendicular to the basal plane. (E) The interlayer energies calculated at various $x$ and $z$ positions. Lines are fitting curves to the calculated values.

Fig. 3 Potential energy changes along six sliding paths as a function of normal stresses from 0 to 10.7 GPa. Solid lines are fitted curves and can be described by a linear combination of sine and cosine functions.
Fig. 4 A comparison of stable and metastable structures obtained from this study. The overlap of interfacial tetrahedral sheets (top) and tetrahedral-octahedral sheets (bottom) are shown for the structures along path 1 at three minimum potential energies.

Fig. 5 Comparison of three stacking structures predicted by our simulations and the observations of natural pyrophyllite by using HRTEM (Kogure et al. 2006) with permission from the American Mineralogical Society. A solid line was added on the HRTEM image as a visual guide for the eye. The asterisks indicate a rare stacking structure found by the HRTEM.

Fig. 6 Shear stress calculated by the displacement derivative of potential energy along six sliding paths. Negative shear stresses were not used for deriving average shear stress by assuming the dissipation of phonon energy.

Fig. 7 Shear stress $\tau$ as a function of normal stress $\sigma_n$ at the real contact area. Lines near the symbols indicate the best-fit linear equations to the calculated values. For comparison, the results of muscovite (Sakuma et al. 2018) are plotted as solid lines.
Fig. 8 (A) Definition of the unit vector $\mathbf{n}$ perpendicular to the basal plane of a pyrophyllite particle. The angles $\theta$ and $\phi$ are defined as shown in the figure. The direction of shear is parallel to the $y_1$ axis. (B) Sampled $\mathbf{n}$ for calculating the frictional force of randomized oriented pyrophyllite particles. One dot corresponds to one $\mathbf{n}$ vector. The number of sampling $N$ was 50,000. Examples of the external interlayer force $F_{\text{interlayer}}$ to slide along the basal plane generated by the external force $F_{\text{ext}}$ at (C) $\phi = 90^\circ$ and (D) $\phi = 270^\circ$. Calculated forces and friction coefficients of gouge at (E) $\phi = 90^\circ$ and (F) $\phi = 270^\circ$. Here all forces on the basal plane of pyrophyllite applied by confining pressure were normalized by external normal force $F_{\text{nc}}$.

Table 1. Calculated and experimental lattice constants of pyrophyllite.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Lattice constants</th>
<th>Calculated lattice constants by PBE + D2</th>
<th>Experimental results (Lee and Guggenheim 1981)</th>
</tr>
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<tbody>
<tr>
<td>Pyrophyllite</td>
<td>$a$</td>
<td>5.175 Å (+0.3%)</td>
<td>5.160</td>
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<tr>
<td></td>
<td>$b$</td>
<td>8.989 Å (+0.3%)</td>
<td>8.966</td>
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<tr>
<td></td>
<td>$c$</td>
<td>9.356 Å (+0.1%)</td>
<td>9.347</td>
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<td></td>
<td>$\alpha$</td>
<td>90.97º (-0.2%)</td>
<td>91.180</td>
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<td>100.460</td>
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<tr>
<td></td>
<td>$\gamma$</td>
<td>89.83º (+0.2%)</td>
<td>86.640</td>
</tr>
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Figure 1
Figure 2

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