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Key Points:

- Rotary-shear friction experiments induced mechanical amorphization of quartz and kaolinite gouges at slip velocities of 0.001 and 1 m s⁻¹
- The amount of amorphous phase produced depends on mineralogy of the fault gouge and total frictional work, regardless of slip velocities
- Up to 90% of kaolinite was amorphized, and the implications of this for faulting processes may be important

Supporting Information:

- Supporting Information S1

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Mechanical Amorphization of Synthetic Fault Gouges During Rotary-Shear Friction Experiments at Subseismic to Seismic Slip Velocities

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Abstract Although the effects of mechanical amorphization by fault motion on fault rocks have been investigated both in nature and experiments, the relationship between slip processes and the amount of amorphous materials produced remains unclear. We performed rotary-shear friction experiments on synthetic quartz and kaolinite gouges at room temperature, normal stresses of 1 or 3 MPa, slip velocities of 0.001 or 1 m s⁻¹, and displacements of 1–101 m. X-ray diffraction and microscopic observation data revealed that mechanical amorphization in both materials was accompanied by grain-size reduction, particle rounding, and the formation of ultrafine particles. The amount of amorphous materials produced was strongly dependent on mineralogy and total frictional work regardless of slip velocity. Therefore, mechanical amorphization can occur during both coseismic and subseismic slip. Amorphization of ~7 wt% of quartz gouge required 30.33 MJ kg⁻¹ of frictional work, whereas for kaolinite gouge, only 0.77 MJ kg⁻¹ was required, which is consistent with observed preferential amorphization of clay minerals in faults. For kaolinite, up to 6% of frictional work can be used for mechanical amorphization, indicating its potential importance for faulting energetics. Because some kinds of amorphous phyllosilicates release water at lower temperature than crystalline, mechanical amorphization of fault rocks may influence thermochemical pressurization. Gradual weakening of quartz gouge at 0.001 m s⁻¹ slip velocity suggested that <4 wt% of amorphous silica can weaken a fault by amorphous silica-related lubrication. Mechanical amorphization may accelerate pressure solution healing of faults if dissolution can occur under high porous conditions.

1. Introduction

Frictional slip is known to induce various physicochemical reactions in and around faults (Rowe & Griffith, 2015, and references therein). Amorphization is one of the processes that occur in fault rocks during frictional slip (Verberne et al., 2019). Mechanisms that lead to amorphization of rocks include (1) frictional melting (e.g., Magloughlin, 1992), (2) mechanical deformation (e.g., Yund et al., 1990), (3) devolatilization (removal of volatile substances) (e.g., Brantut et al., 2008), and (4) fluid-rock interactions (e.g., Amagai et al., 2019). Examples of each of these mechanisms are provided below.

Frictional melting of fault rocks leads to the formation of pseudotachylytes during rapid post-slip cooling (Sibson, 1975); their presence is a reliable indicator of past earthquakes (Cowan, 1999). Mechanical deformation of minerals can induce intense comminution and breakdown of crystal structures (i.e., amorphization) (e.g., Yund et al., 1990). Devolatilization and amorphization of minerals can occur at slip-induced high temperatures, for instance by dehydroxylation of kaolinite (“dehydration” according to Brantut et al., 2008) or high-temperature gas reactions followed by thermal decomposition of calcite (Oohashi et al., 2014). Fluid-rock interactions can cause deposition of amorphous silica particles from silica-saturated fluid by flash vaporization at temperatures ≥200°C (Amagai et al., 2019) or bacterial-mediated weathering of materials (e.g., Potysz et al., 2016).

Among the above mechanisms, mechanical amorphization differs in that it does not require high temperatures (several hundred degrees Celsius). Numerous studies have reported mechanical amorphization both in natural fault rocks (e.g., Hirono et al., 2014, 2016; Janssen et al., 2010; Ozawa & Takizawa, 2007; Wu et al., 2020) and in experimentally deformed rocks (e.g., Aretusini et al., 2017, 2019; Hayashi & Tsutsumi, 2010; Hayward et al., 2016; Hirose et al., 2012; Nakamura et al., 2012; Rowe et al., 2019;

Sánchez et al., 2004; Takahashi, 1959; Wada et al., 2016; Yund et al., 1990), but few of these studies have quantified the amount of amorphous material produced during frictional slip (e.g., Aretusini et al., 2017, 2019; Hirono et al., 2016; Yund et al., 1990).

The mechano-thermo-chemical properties of amorphous and crystalline materials differ considerably (e.g., Hirono et al., 2013; Robie et al., 1979; Rowe et al., 2019; Wada et al., 2016). Hirono et al. (2013) suggested that mechanochemical effects, including mechanical amorphization, decrease the activation energy required for dehydroxylation of illite, affect changes of pore pressure due to expulsion of water during frictional slip, and thus have an important influence on fault motion. Rowe et al. (2019) demonstrated through friction experiments on novaculite that the presence of mechanically amorphous silica can weaken frictional strength of fault, also indicating the importance of mechanical amorphization on fault motion. Because the total amount of amorphous material in a fault is likely to affect the magnitude of pore pressure change and amorphization-related fault weakening during frictional slip, investigation of the amount of amorphous material produced by slip processes is important for understanding the evolution of the mechano-thermo-chemical properties of fault rocks and fault motion.

In this study, we investigated the evolution of the amorphous content of synthetic quartz and kaolinite gouges during frictional slip. The samples in which amorphous content was measured were prepared by friction experiments designed to reproduce the mechanical amorphization of fault gouge in natural faults. Our measurements and observations of the experimental products allowed us to infer the relationship between slip processes and the amount of amorphous material produced. We then discuss the implications of our experimental results for mechanical amorphization in natural fault rocks and the qualitative effects of amorphization on fault motion.

2. Method for Quantifying Amorphous Content

Several methods have been proposed to quantify the mineral compositions of rock samples from X-ray diffraction (XRD) profiles. These include the Rietveld refinement method (e.g., Pourghahramani et al., 2008), the reference intensity ratio method (e.g., Hillier, 2000), and a method that combines these two approaches (e.g., Gualtieri, 2000). However, each of these methods measures amorphous content indirectly as the residue after removal of crystalline content from one. Some studies have attempted to directly quantify the amount of glassy material in pseudotachylytes (e.g., Lin, 1994; Tsutsumi, 1999) according to a linear relationship between the amount of glassy material and the integrated area of a broad XRD peak observed at around 20–30°. This method was used by Hirono et al. (2016) to measure mechanically amorphized material. They performed XRD measurements on synthetic mixtures of crystalline quartz and amorphous silica and reported that the integrated area of the broad peak is proportional to the amorphous content. On the basis of that relationship, they calculated the amount of mechanically amorphized materials in natural fault gouges and surrounding rocks exposed along the Arima-Takatsuki Tectonic Line in Southwest Japan. However, the calibration line they determined from crystalline quartz and amorphous silica may not be applicable for amorphous content in fault gouges of other compositions. In this study, we determined individual calibration lines to quantify the amorphous contents of fault gouges composed entirely of either quartz or kaolinite. We used quartz and kaolinite to represent non-clay and clay mineral fault gouges, respectively.

2.1. Material Preparation

For our quartz samples, we used commercially available quartz powder (Wako Pure Chemical Industries, product no. 172-00015) as the crystalline phase and amorphous silica powder (Kanto Chemical, product no. 37562-79) as the amorphous phase. We used crystallized kaolinite powder (Clay Mineral Society, product no. KGa-1b), but because we were unable to find commercially available amorphous kaolinite powder, we milled the crystallized powder in a planetary ball mill apparatus (Pulverisette 6, Fritsch) at a rotation speed of 600 rpm. To prevent heating of the sample, milling was suspended for 5 min between 20-min periods of milling. After milling for 24 h or more, XRD profiles of the kaolinite powder showed no clear crystal peaks and an almost flat area of the broad peak (Figure S1). We therefore considered the kaolinite powder to be completely amorphized after 30 h of milling (hereafter referred to as amorphous kaolinite). We sieved all of the powders to extract particles with grain size of <75 μm and dried them at 50°C for 1 day before mixing them as follows: for each mineral, crystalline and amorphous powders were mixed at weight ratios of 0:10,

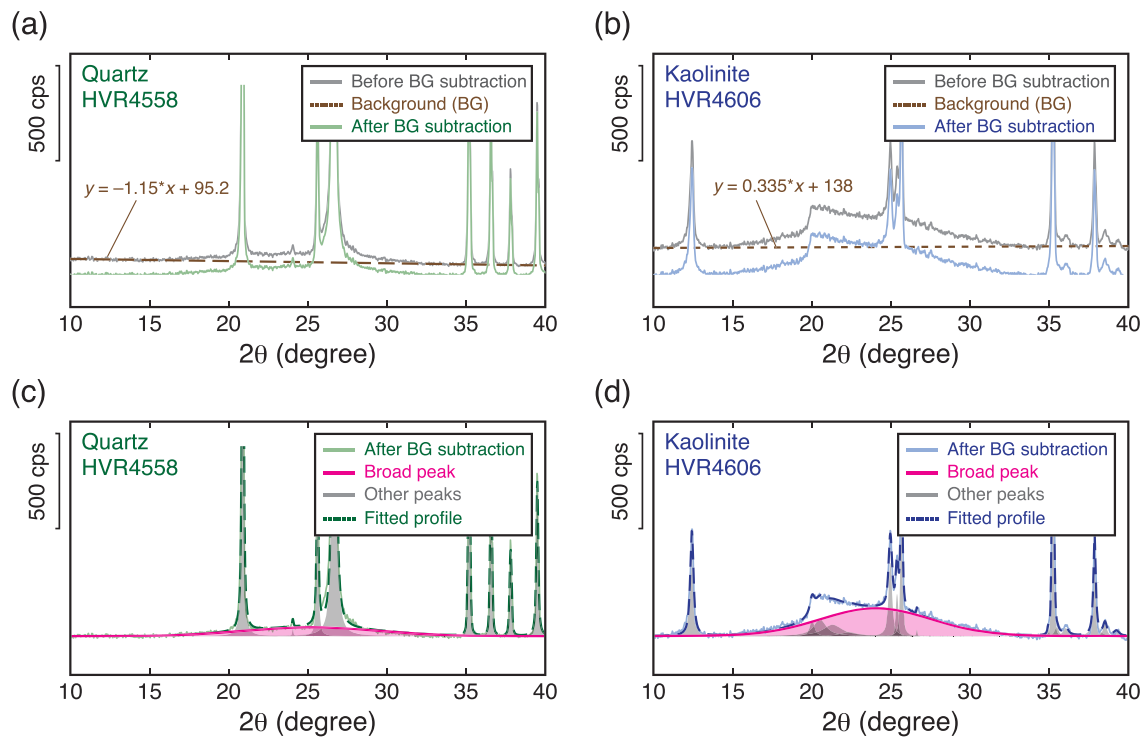


Figure 1. Methodology for calculating the area of the broad peak at around 20–30°, the S value, from XRD profiles. (a, b) Representative XRD profiles (gray lines) of quartz and kaolinite samples, respectively, together with a linear background (BG) baseline (dotted brown line) and profiles after baseline correction (green and blue lines, respectively). (c, d) Estimated profiles for quartz and kaolinite samples (dotted green and blue lines, respectively) that best fit the profiles after baseline correction. Peaks used for the fitting procedure, including the broad peak (pink line), are also shown.

1:9, 2:8,..., and 10:0. To provide an internal standard, we then mixed 20 wt% corundum (Al_2O_3) powder into all of the mixed samples.

2.2. Measurement Procedures

The mixed samples with 20 wt% corundum were mounted on non-diffractive silicon plates. XRD profiles were then obtained with a Spectris PANalytical X'Pert PRO MPD spectrometer installed at the Kochi Core Center, Japan, with monochromatized $\text{CuK}\alpha$ radiation. The detailed settings are described in Text S1. For background correction, an XRD profile of a sample-free silicon plate was subtracted from each profile (Figure S2).

2.3. Analytical Procedures

We calculated the area of the broad peak S , which appears at around 20–30° 2θ , for each XRD profile as follows. We first normalized each profile so that the peak at around 57.5°, which corresponds to the (116) plane of corundum, had an intensity of 1,000 cps. A linear baseline, which was determined from the intensity data in the ranges 10–11° and 33–34° by the least squares method (Figures 1a and 1b), was then subtracted from the normalized profile. Next, we used Peak-Fit 4.12 software (Systat Software Inc.) to fit each peak in the baseline-subtracted normalized profile, including the broad peak, with a Voigt function to obtain the best-fit curve in the 10–40° range (Figures 1c and 1d). The Voigt function is a representative function used for spectral fitting of XRD profiles (Langford, 1978). Because this analytical procedure assumes that the broad peak is present in all XRD profiles, the calculated S values are not zero even in the amorphous-free samples. To make comparable data sets of the S values for the different sample mixtures, we should put our focus on calculating the S value by following the systematic procedure, rather than on getting better fitting curves by changing the fitting procedure depending on profiles. It was thus important to include the same number of peaks to express the overlapping, non-symmetric peaks of each mineral. We therefore consistently used 9 and 19 peaks to fit the profiles of quartz and kaolinite samples, respectively (Figures 1c and 1d), except for completely amorphized samples.

2.4. Calibration Lines for Quartz and Kaolinite

The normalized XRD profiles of both quartz and kaolinite samples (Figures 2a and 2b, respectively) show a broad peak at around 20–30° and a gradual disappearance of sharp crystal peaks with increasing amorphous content (Figure S3). We used the XRD profiles after normalization and background correction with best-fit curves in the range 10–40° (Figures 2c and 2d) to calculate the S value for each XRD profile. We expressed the S value as a function of the weight ratio M_{am} of amorphous content to the entire sample by assuming the linear relation

$$S_i = a_i M_{\text{am},i} + b_i, \quad (1)$$

where a and b are the slope and intercept, respectively, of the calibration line, and subscript i indicates the mineral (quartz or kaolinite). Because we assumed the presence of the broad peak in all profiles as described above, the b values of each calibration lines were not forced to be zero. Instead, the b value is fixed at the S value of the sample with $M_{\text{am}} = 0$ wt%, and the a value is then determined by a least squares method. For both minerals, S and M_{am} showed a strong linear relation with a coefficient of determination R^2 of 0.98 and 0.99 (Figures 2e and 2f), clearly indicating that these calibration lines can be used to determine the M_{am} values from the S values as long as they are determined by following the analytical protocol in section 2.3. We determined $a = 29.67 \text{ cps}^\circ$ and $b = 5.21 \text{ cps}^\circ$ for quartz and $a = 12.80 \text{ cps}^\circ$ and $b = 252.55 \text{ cps}^\circ$ for kaolinite.

To calculate M_{am} in each sample, we transform Equation 1 to the form

$$M_{\text{am},ik} = \frac{S_{ik} - b_i}{a_i}, \quad (2)$$

where subscript k is the sample index (i.e., the run number of the friction experiment). By linearizing a non-linear function $M_{\text{am},ik} = M_{\text{am},ik}(S_{ik}, a_i)$, the variance of $M_{\text{am},ik}$ can be expressed as

$$\text{Var}(M_{\text{am},ik}) \cong \left(\frac{\partial M_{\text{am},ik}}{\partial S_{ik}} \right)_E^2 \text{Var}(S_{ik}) + \left(\frac{\partial M_{\text{am},ik}}{\partial a_i} \right)_E^2 \text{Var}(a_i) + \text{Cov}(S_{ik}, a_i), \quad (3)$$

where $\text{Var}(x)$ is the variance of x , subscript E indicates that derivatives are evaluated at a specific point E ($S_{ik} = \langle S_{ik} \rangle, a_i = \langle a_i \rangle$), $\langle x \rangle$ indicates the expectation of x , and $\text{Cov}(S_{ik}, a_i)$ is the covariance term. The two variables in Equation 3 are independent, so the covariance term vanishes. Equation 3 then becomes

$$\text{Var}(M_{\text{am},ik}) \cong \left(\frac{1}{\langle a_i \rangle} \right)^2 \text{Var}(S_{ik}) + \left(-\frac{\langle S_{ik} \rangle - \langle \bar{S}_i \rangle}{\langle a_i \rangle^2} \right)^2 \text{Var}(a_i). \quad (4)$$

$\langle S_{ik} \rangle$ and $\text{Var}(S_{ik})$ are calculated from repeated XRD measurements of each sample. $\langle a_i \rangle$ and $\text{Var}(a_i)$ are calculated from the data plots of the calibration lines. The $\langle a_i \rangle$ values are the same as the slope values shown at the end of the previous paragraph. We calculated $\text{Var}(a_i) = 0.00353 (\text{cps}^\circ)^2$ for quartz and $\text{Var}(a_i) = 0.00138 (\text{cps}^\circ)^2$ for kaolinite.

3. Amorphization of Fault Gouge by Friction Experiments

3.1. Starting Materials

To simulate and compare the behaviors of quartz and kaolinite gouges, we prepared two types of starting materials for our friction experiments: crystalline quartz powder (Wako Pure Chemical Industries, product no. 172-00015) and crystalline kaolinite powder (Clay Mineral Society, product no. KGa-1b). We sieved the powder to extract particles of <75 μm in grain size and dried them at 50°C for 1 day. Both are the same samples adopted as crystalline phase in section 2.1.

3.2. Experimental Procedure

We used a rotary-shear friction apparatus at Yamaguchi University, Japan (HVR apparatus), for our friction experiments (Figure S4a). Synthetic fault gouge was placed between the ends of two solid cylinders of gabbro (diameter $25.01 \pm 0.01 \text{ mm}$) under air condition. The amounts of placed gouge samples were 612 and 585 mg for the quartz and kaolinite gouges, respectively. The surfaces of the gabbro cylinders that were in contact with the gouge were roughened with coarse carborundum powder (#100, 106- to 125- μm grain size) and

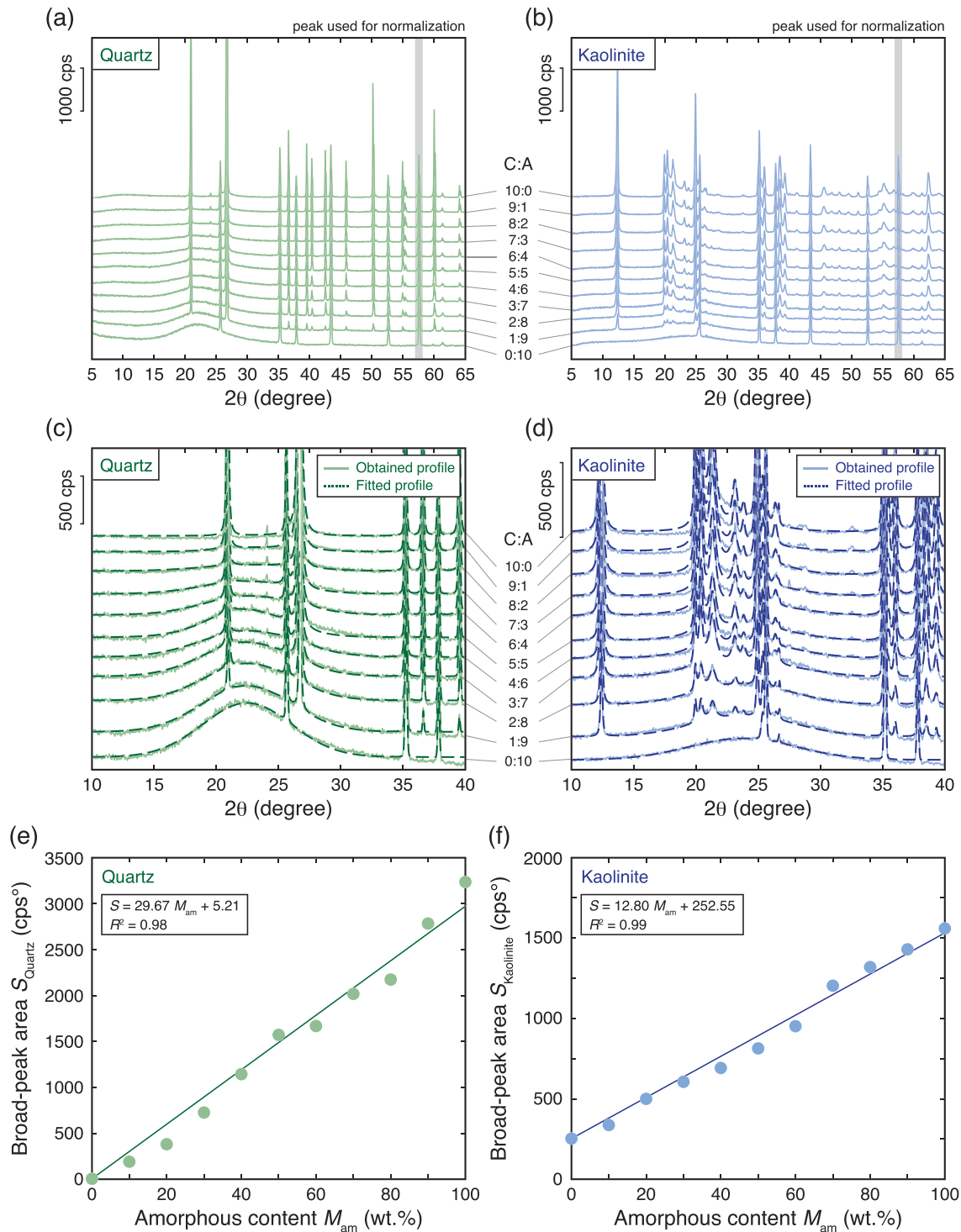


Figure 2. Determination of calibration lines for measurement of amorphous content in quartz and kaolinite samples. (a, b) Normalized XRD profiles of mixtures of crystalline and amorphous powder at different weight ratios for quartz and kaolinite (green and blue lines), respectively. C:A, weight ratio of crystalline to amorphous powder. (c, d) The same XRD profiles for quartz and kaolinite after baseline correction with the best-fit curves shown (dotted green and blue lines, respectively). (e, f) Relationships between the weight ratio M_{am} of amorphous content to the whole samples and the calculated broad peak area S for quartz and kaolinite samples, respectively. The calibration line for each mineral was assumed to be described by Equation 1. All profiles show clear peaks of corundum (internal standard).

Table 1
Summary of Experimental Conditions and Frictional Properties for Quartz Gouges

Run no.	Experimental conditions			Frictional properties				
	V_e (m s ⁻¹)	σ_n (MPa)	D_{final} (m)	τ (MPa)	τ_p (MPa)	τ_{ss} (MPa)	τ_r (MPa)	D_c (m)
HVR4593	0.001	2.93–3.02	0.6	1.74–2.49	–	–	–	–
HVR4595 ^a	0.001	2.92–3.02	2.0	1.76–2.31	–	–	–	–
HVR4596	0.001	2.92–3.03	2.0	1.79–2.30	–	–	–	–
HVR4600	0.001	2.96–3.06	4.0	1.68–2.34	–	–	–	–
HVR4598	0.001	2.92–3.04	10.0	1.37–2.32	–	–	–	–
HVR4558	0.001	2.96–3.07	6.6	1.41–2.38	–	–	–	–
HVR4599	0.001	2.93–3.04	14.8	0.77–2.19	–	–	–	–
HVR4586 ^a	1.0	0.90–1.05	1.1	–	0.91 ± 0.00	0.16 ± 0.03	0.68 ± 0.00	2.94 ± 0.15
HVR4587	1.0	0.90–1.06	0.9	–	0.79 ± 0.00	0.16 ± 0.03	0.64 ± 0.00	3.48 ± 0.20
HVR4588 ^a	1.0	0.92–1.07	5.0	–	1.05 ± 0.00	0.16 ± 0.03	0.41 ± 0.00	3.91 ± 0.26
HVR4589	1.0	0.92–1.06	5.1	–	1.00 ± 0.00	0.16 ± 0.03	0.40 ± 0.01	4.05 ± 0.26
HVR4590	1.0	0.91–1.06	10.2	–	1.03 ± 0.00	0.16 ± 0.03	0.25 ± 0.01	4.41 ± 0.38
HVR4591 ^a	1.0	0.94–1.15	30.1	–	1.00	0.19	0.19	3.77
HVR4550	1.0	0.93–1.16	50.0	–	1.08	0.14	0.14	3.34
HVR4592	1.0	0.91–1.15	75.1	–	0.87	0.15	0.15	4.44
HVR4553	1.0	0.91–1.13	100.2	–	0.90	0.13	0.13	3.98
HVR4613 ^a	1.0	0.93–1.10	101.2	–	0.90	0.21	0.21	4.23

Note. V_e , area-averaged slip velocity; σ_n , normal stress; D_{final} , final equivalent displacement; τ , shear stress; τ_p , peak shear stress; τ_{ss} , steady-state shear stress; τ_r , residual shear stress; D_c , critical slip-weakening distance.

^aSamples used for thin sections.

dried at 80°C for 1 day before the experiments. To prevent gouge leakage during experiments, we sealed the sample powders and gabbro cylinders in a hollow polytetrafluoroethylene (PTFE) sleeve (inner diameter 24.97 ± 0.02 mm, outer diameter 34.97 ± 0.02 mm; Figure S4b). The inner surface of the PTFE sleeve was smoothed with sandpaper (#1000, ~12- μ m grain size) before it was fixed to the stationary gabbro cylinder. After placing the sample assembly in the apparatus, it was rotated 2–3 times under a normal stress of 0.4 MPa to ensure a uniform thickness of gouge. The thickness of gouge at this stage was ~1 mm. After increasing the normal stress σ_n to the target value, it was held constant for 5 min. To simulate the anoxic environment of faults at depth, N₂ gas was flowed into the sample chamber for 5 min before the experiments, and the sample chamber was sealed by a transparent plastic window to prevent air contamination during the experiments. In the experimental configuration we used, slip velocity and slip displacement were not uniform across the circular simulated fault plane. We used the area-averaged slip velocity V_e and displacement D , as defined by Shimamoto and Tsutsumi (1994). We performed rotary-shear friction experiments at room temperature for V_e values (slip velocity hereafter) of 0.001 and 1 m s⁻¹ (i.e., at angular velocities of 1 and 1,145 rpm for 25-mm diameter cylinders) and with final equivalent displacements D_{final} of 1 to 101 m. The normal stresses were set to 3 MPa (1 MPa) for slip velocities 0.001 m s⁻¹ (1 m s⁻¹), because these σ_n values are the empirical upper limits to prevent gouge leakage during experiments using the current HVR apparatus. The experimental conditions for quartz and kaolinite gouges are summarized in Tables 1 and 2, respectively. We observed no gouge leakage during the experiments.

Raw mechanical data were recorded at frequencies of 1 Hz (200 Hz) for slip velocities of 0.001 m s⁻¹ (1 m s⁻¹). For some of the experiments at both slip velocities, we measured temperature at a position 3 mm from the outer margin of the stationary gabbro cylinder, using a K-type thermocouple (Figure S4b). To correct for the background torque between the gabbro cylinders and the PTFE sleeve, data acquired without gouge samples were subtracted from the torque obtained during the experiments (Figure S5). The corrected torque data thus represented the frictional resistance of the gouge layer and were finally converted to shear stress by assuming uniform shear stress τ on the simulated fault.

We performed 26 experimental runs for subsequent XRD measurements and scanning electron microscope (SEM) observations on powder gouge samples (Tables 1 and 2). Because of the geometry of our sample assembly, slip displacement was proportional to the radius of the gabbro cylinders, so the outer edge of the gouge samples underwent the greatest shear deformation. To ensure that our analyses of gouge

Table 2
Summary of Experimental Conditions and Frictional Properties for Kaolinite Gouges

Run no.	Experimental conditions			Frictional properties				
	V_e (m s ⁻¹)	σ_n (MPa)	D_{final} (m)	τ (MPa)	τ_p (MPa)	τ_{ss} (MPa)	τ_r (MPa)	D_c (m)
HVR4602	0.001	2.91–3.09	1.0	1.42–2.59	–	–	–	–
HVR4604	0.001	2.93–3.12	2.0	1.57–2.73	–	–	–	–
HVR4605 ^a	0.001	2.92–3.12	3.1	1.49–2.74	–	–	–	–
HVR4559	0.001	2.93–3.04	4.3	1.67–2.91	–	–	–	–
HVR4601	0.001	2.92–3.09	5.9	1.58–2.80	–	–	–	–
HVR4606	0.001	2.90–3.09	10.0	1.43–2.86	–	–	–	–
HVR4607	0.001	2.91–3.11	17.0	1.43–2.88	–	–	–	–
HVR4566	1.0	0.93–1.09	1.0	–	0.84 ± 0.00	0.18 ± 0.05	0.71 ± 0.00	4.84 ± 0.38
HVR4608 ^a	1.0	0.88–1.07	0.9	–	0.80 ± 0.00	0.18 ± 0.05	0.62 ± 0.00	2.76 ± 0.24
HVR4565	1.0	0.91–1.13	5.0	–	0.95 ± 0.02	0.18 ± 0.05	0.30 ± 0.01	2.58 ± 0.37
HVR4609 ^a	1.0	0.88–1.12	5.0	–	0.85 ± 0.02	0.18 ± 0.05	0.26 ± 0.02	2.38 ± 0.40
HVR4564	1.0	0.92–1.14	10.1	–	0.86	0.21	0.21	2.05
HVR4563	1.0	0.93–1.14	19.9	–	0.93	0.23	0.23	1.89
HVR4610 ^a	1.0	0.95–1.17	30.1	–	0.80	0.13	0.13	2.74
HVR4562	1.0	0.93–1.15	30.1	–	0.94	0.20	0.20	2.42
HVR4561	1.0	0.91–1.15	40.1	–	0.84	0.12	0.12	2.95
HVR4557	1.0	0.91–1.14	59.8	–	0.81	0.17	0.17	2.69
HVR4611 ^a	1.0	0.92–1.14	61.8	–	0.71	0.15	0.15	2.62
HVR4554	1.0	0.93–1.14	50.0	–	0.79	0.23	0.23	2.11

Note. V_e , area-averaged slip velocity; σ_n , normal stress; D_{final} , final equivalent displacement; τ , shear stress; τ_p , peak shear stress; τ_{ss} , steady-state shear stress; τ_r , residual shear stress; D_c , critical slip-weakening distance.

^aSamples used for thin sections.

particles were representative of the displacement imposed during the experiments, we sampled gouge from the annular region of the simulated circular fault plane between radii of 6.0 and 12.5 mm. After most of the experiments at 1 m s⁻¹ had been performed, we recognized consolidation of the gouge in this region; therefore, to focus on the deformed gouge, we restricted our collection to this region of consolidation. However, because the gouge was extracted manually, these samples likely contained some less-deformed or undeformed gouge. After extraction, we disaggregated these samples with an agate mortar and pestle.

We also carried out additional 10 experimental runs for microstructural observations (Tables 1 and 2). We impregnated the sample assembly after experiments under vacuum with epoxy resin and then cut through the assembly perpendicular to the gouge layer 3 mm from the edge of cylinder (Figure S4b). For each experiment, we made two thin sections: one with cover glass for optical microscope observations and another without cover glass for SEM backscattered electron (BSE) observations.

3.3. Mechanical Data

Examination of the evolution of mechanical data and temperature as a function of slip (Figure 3) shows that the perturbations of normal stress during the experiments were ±4% for a slip velocity of 0.001 m s⁻¹ and ±10–15% for 1 m s⁻¹, regardless of mineral type (Figure 3 and Tables 1 and 2). For the experiments on quartz gouge at 0.001 m s⁻¹ slip velocity, shear stress remained almost constant at around 1.8–2.1 MPa at displacements up to ~5 m, corresponding to a friction coefficient of 0.6–0.7 (Figure 3a). However, at displacements greater than 5 m, the shear stress decreased gradually to 1.2 MPa, corresponding to a friction coefficient of 0.4 (Figure 3a). Shear stress for quartz at 1 m s⁻¹ slip velocity showed a dramatic decrease with displacement from its initial peak and reached steady state at a displacement of ~20 m (Figure 3b). The steady-state shear stress was 0.1–0.2 MPa, corresponding to a friction coefficient of 0.1–0.2 (Figure 3b).

Shear stress for kaolinite at 0.001 m s⁻¹ slip velocity was lower than that for quartz at the initiation of slip (1.6–1.7 MPa) and increased gradually to a steady state at 2.4–2.7 MPa, corresponding to a friction coefficient of 0.8–0.9 (Figure 3c). Thereafter, shear stress remained almost constant until displacement reached ~10 m, after which it decreased slightly to ~2.0 MPa, but with considerable perturbation (Figure 3c). The shear stress for kaolinite at 0.001 m s⁻¹ was higher than that for quartz at the same displacement, except at the initiation of slip. Shear stress for kaolinite at 1 m s⁻¹ slip velocity also showed a dramatic decrease and reached steady

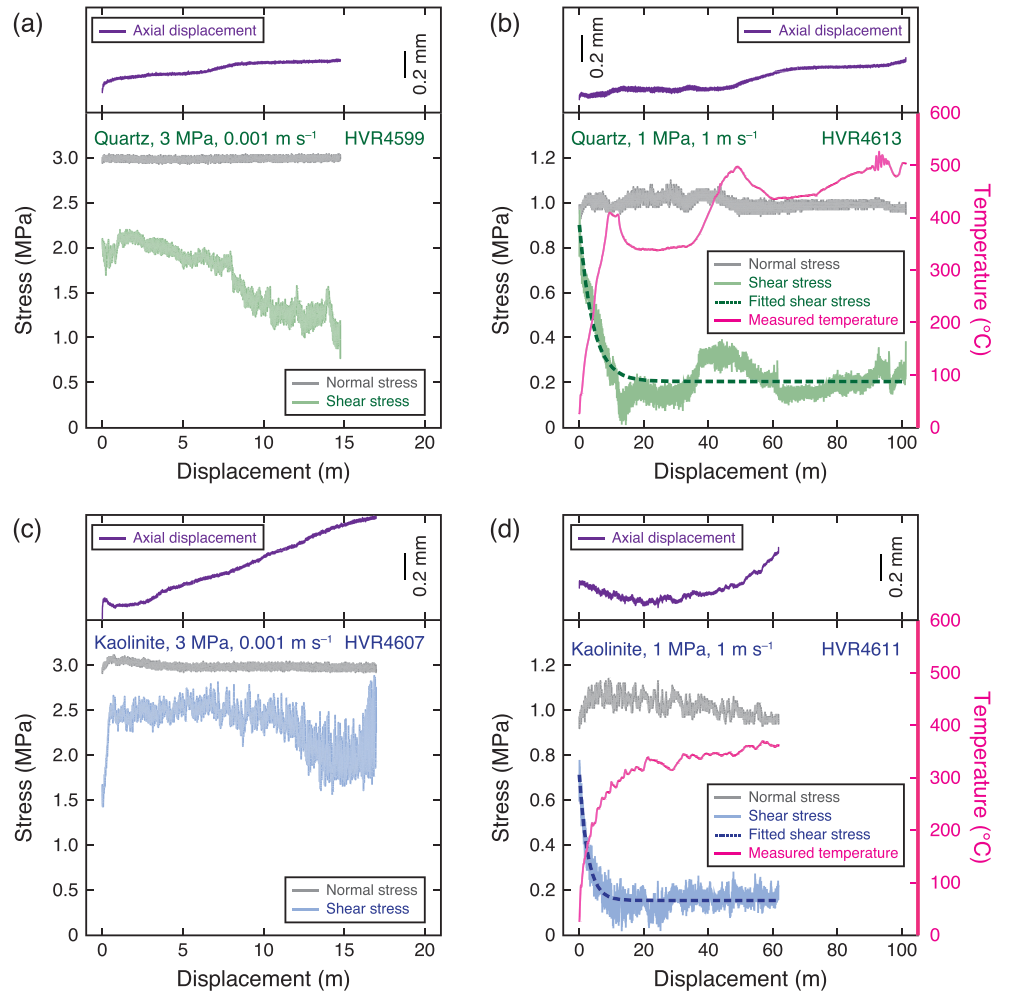


Figure 3. Representative examples of the evolution of mechanical data and temperature with slip during friction experiments for quartz gouge (a) at slip velocity of 0.001 m s^{-1} and normal stress of 3 MPa and (b) at slip velocity of 1 m s^{-1} and normal stress of 1 MPa and (c, d) for kaolinite gouge under the same experimental conditions.

state at a displacement of $\sim 10 \text{ m}$ (Figure 3d). The steady-state shear stress for kaolinite at 1 m s^{-1} slip velocity was $0.1\text{--}0.2 \text{ MPa}$, corresponding to a friction coefficient of $0.1\text{--}0.2$ (Figure 3d). The steady-state shear stresses of quartz and kaolinite for a slip velocity of 1 m s^{-1} were similar, but the displacement required to achieve steady state was smaller for kaolinite gouge than for quartz gouge.

Dramatic decreases of shear stress such as those we observed with increasing displacement at 1 m s^{-1} slip velocity have been observed during previous laboratory friction experiments in which slip velocity was faster than $0.01\text{--}0.1 \text{ m s}^{-1}$ (e.g., Di Toro et al., 2011). This slip-weakening behavior has been well described with the exponential function (e.g., Hirose & Shimamoto, 2005):

$$\tau = \tau_{ss} + (\tau_p - \tau_{ss}) \exp(-D/D_c), \quad (5)$$

where τ is shear stress as a function of displacement D , τ_{ss} is steady-state shear stress, τ_p is peak shear stress, and D_c is critical slip-weakening distance. D_c is the displacement at which $(\tau_p - \tau_{ss})$ decreases to $1/e$ of its initial value. For each of our experiments at 1 m s^{-1} slip velocity, we applied Equation 5 to determine the frictional properties τ_{ss} , τ_p , and D_c that best fit the experimental data (Figures 3b and 3d). For our experiments at 0.001 m s^{-1} slip velocity, we did not perform this fitting procedure because the initiation of weakening was too difficult to determine. Shear stress during some experiments at 1 m s^{-1} did not achieve a steady state, so for these experiments, we assumed τ_{ss} to be the mean value of τ_{ss} and its error for the experiments that did achieve steady-state conditions ($0.16 \pm 0.03 \text{ MPa}$ for quartz and $0.18 \pm 0.05 \text{ MPa}$

for kaolinite). The evolution of normal and shear stresses with displacement in all of our experiments, together with best-fit curves, are shown in Figures S6–S9; all of the derived frictional properties for each experiment are provided in Tables 1 and 2. The τ_p and τ_{ss} values we derived for the quartz and kaolinite gouges were similar, whereas the D_c values for kaolinite were smaller than those for quartz.

The measured temperature of quartz gouge during an experiment at 1 m s^{-1} increased rapidly to $\sim 400^\circ\text{C}$ at a displacement of $\sim 10 \text{ m}$ and then increased gradually to a maximum of 525°C (Figure 3b). Similarly, the measured temperature of kaolinite gouge during the experiment at 1 m s^{-1} increased rapidly to $\sim 350^\circ\text{C}$ at a displacement of $\sim 20 \text{ m}$ and then increased gradually to a maximum temperature of 369°C (Figure 3d). On the other hand, the maximum temperatures during the experiments at 0.001 m s^{-1} were only 37 and 41°C for quartz and kaolinite gouges, respectively (Figure S10), and are thus negligibly small compared to those during the experiments at 1 m s^{-1} . These are consistent with the results of Mizoguchi and Hirose (2016), who performed friction experiments on diorite at 0.001 m s^{-1} slip velocity under 3 MPa normal stress using HVR apparatus and reported that the maximum temperature reached was only $34.6 \pm 3.7^\circ\text{C}$.

During some of the experiments, the axial displacement dramatically changes (Figures 3 and S6–9). Because we observed no gouge leakage during any of the experiments, we can attribute the change in the axial displacement to (1) thermal expansion, (2) shear-induced compaction, and (3) vaporization of the pre-existing water absorbed on the surfaces of mineral grains, of fault gouges. For experiments at 0.001 m s^{-1} slip velocity, both types of fault gouges showed large compaction with increasing displacement, which may be attributable to shear-induced compaction. For experiments at 1 m s^{-1} using quartz, the axial displacement keeps almost its original value. In contrast, in the case of kaolinite gouge, gradual increase and subsequent decrease in gouge thickness occurred, which may be explained by thermal expansion and/or vaporization of absorbed water (e.g., Chen et al., 2013, 2017) and subsequent shear-induced compaction, respectively.

Using the obtained shear stress data and the calculated frictional properties, we determined three other frictional parameters: frictional work per unit area $W_{f,a}$, seismic fracture energy per unit area $G_{c,a}$, and average frictional power per unit area $P_{f,a}$ for the entire circular fault surface. These parameters are defined as

$$W_{f,a} = \int \tau dD, G_{c,a} = \int (\tau - \tau_r) dD, P_{f,a} = W_{f,a} \frac{V_e}{D_{\text{final}}}, \quad (6)$$

where τ_r is residual shear stress, which is the shear stress at $D = D_{\text{final}}$ (Figure S11). For experiments at 1 m s^{-1} that achieved a steady-state condition, we assumed $\tau_r = \tau_{ss}$. For experiments at 1 m s^{-1} that did not achieve a steady-state condition, we calculated τ_r based on the best-fit curves described by Equation 5. For experiments at 0.001 m s^{-1} , $G_{c,a}$ was not calculated because of the lack of fitting curves for the experimental data. We then calculated the frictional work per area, the seismic fracture energy per area, and the average frictional power per area in the annular region on the fault plane between radii of 6.0 and 12.5 mm as

$$W_{f,6.0-12.5} = pW_{f,a}, G_{c,6.0-12.5} = pG_{c,a}, P_{f,6.0-12.5} = pP_{f,a}, \quad (7)$$

where $W_{f,6.0-12.5}$, $G_{c,6.0-12.5}$, and $P_{f,6.0-12.5}$ are the frictional work, seismic fracture energy, and frictional power in the annular region described above and p is the ratio of the equivalent slip velocity to V_e in that annular region, such that

$$p = \frac{1}{12.5} \frac{(12.5)^2 + 12.5 \times 6.0 + (6.0)^2}{6.0 + 12.5} = 1.15567. \quad (8)$$

We then converted the frictional parameters calculated with Equation 7 to the frictional work per amount of sample W_f , the seismic fracture energy per amount of sample G_c , and the average frictional power per amount of sample P_f . These parameters were defined as

$$W_f = W_{f,6.0-12.5} \frac{q}{m_{\text{col}}}, G_c = G_{c,6.0-12.5} \frac{q}{m_{\text{col}}}, P_f = P_{f,6.0-12.5} \frac{q}{m_{\text{col}}}, \quad (9)$$

where m_{col} is the mass of gouge sample collected after each experiment and q is the area of the annular region of the fault plane defined as

Table 3

Summary of Masses of Collected Gouge Samples, Frictional Parameters, Resultant XRD Parameters, and Amorphous Content for Quartz Gouges

Run no.	m_{col} (10^{-6} kg)	W_f (MJ kg $^{-1}$)	G_c (MJ kg $^{-1}$)	P_f (MW kg $^{-1}$)	S^a (cps $^\circ$)	M_{PTFE}^a (wt%)	M_{am}^b (wt%)
Initial	—	—	—	—	6 ± 2	—	0.0 ± 0.1
HVR4593	410	1.41	—	2.72×10^{-3}	15 ± 0	—	0.3 ± 0.0
HVR4596	425	4.15	—	2.49×10^{-3}	54 ± 9	—	1.7 ± 0.3
HVR4600	297	11.67	—	3.70×10^{-3}	84 ± 2	—	2.6 ± 0.1
HVR4598	400	20.08	—	2.48×10^{-3}	104 ± 4	—	3.3 ± 0.2
HVR4558	204	29.60	—	5.32×10^{-3}	504 ± 15	—	16.8 ± 0.6
HVR4599	354	30.33	—	2.53×10^{-3}	225 ± 2	—	7.4 ± 0.1
HVR4587	444	0.66	0.07 ± 0.00	0.64	4 ± 0	—	0.0 ± 0.0
HVR4589 ^c	379	3.00	1.12 ± 0.02	0.58	48 ± 3	1.3 ± 0.0	1.5 ± 0.1
HVR4590 ^c	426	4.70	2.35 ± 0.11	0.46	70 ± 1	1.8 ± 0.1	2.5 ± 0.1
HVR4550 ^c	375	9.57	2.90	0.19	83 ± 4	2.6 ± 0.1	2.8 ± 0.1
HVR4592 ^c	349	13.39	2.96	0.18	92 ± 7	1.7 ± 0.1	2.6 ± 0.2
HVR4553 ^c	326	15.07	2.85	0.15	118 ± 8	2.7 ± 0.1	3.3 ± 0.2

Note. m_{col} , mass of gouge sample collected after each experiment; W_f , frictional work per amount of sample; G_c , seismic fracture energy per amount of sample; P_f , average frictional power per amount of sample; S , area of the broad peak at around 20–30 $^\circ$; M_{PTFE} , weight ratio of PTFE content to the entire sample; M_{am} , the weight ratio of amorphous content to the entire samples.

^aError is the standard deviation (1σ) of repeated XRD measurements ($n = 5$). ^bError is the standard deviation (1σ), which is calculated as the square root of variance of M_{am} (see Equation 4 for detail). ^cOnly the consolidated part of the gouge was collected. Data correction methods for frictional parameters and M_{am} are described in sections 3.3 and 4.2, respectively.

$$q = \pi \{ (12.5)^2 - (6.0)^2 \} = 90.25 \pi \text{ [mm}^2\text{]}. \quad (10)$$

For most of the experiments at a slip velocity of 1 m s^{-1} , after which we attempted to sample only the consolidated part of the gouge samples from the annular region of the fault plane, we calculated W_f , G_c , and P_f based on the initial mass m_{init} of gouge samples in the annular region of the fault plane

$$W_f = W_{f, 6.0-12.5} \frac{q}{m_{\text{init}}}, G_c = G_{c, 6.0-12.5} \frac{q}{m_{\text{init}}}, P_f = P_{f, 6.0-12.5} \frac{q}{m_{\text{init}}}. \quad (11)$$

We obtained m_{init} values of 471 and 450 mg for the quartz and kaolinite gouges, respectively. The values of W_f , G_c , P_f , and m_{col} for all experiments are provided in Tables 3 and 4.

3.4. Microstructural Observations of Thin Sections

We performed optical microscope and SEM BSE observations on the prepared thin sections to investigate the development of the deformation microstructures. For SEM BSE observations, thin sections were coated with a thin platinum film by using a magnetron sputtering apparatus (JFC-1600, JEOL) at Osaka University, Japan. The Pt-coated thin sections were examined with a field emission SEM (SU6600, HITACHI) at Osaka University at magnifications of 300 $\times$. Detailed settings for the SEM BSE observations are described in Text S2.

Figure 4 shows the optical micrographs under plane-polarized light and SEM BSE images of thin sections after the friction experiments. For the quartz gouge sheared at 0.001 m s^{-1} , the optical micrograph showed no significant variation in particle shapes within the gouge zone (Figure 4a). However, SEM BSE images clearly indicated that there was a region on the stationary side of the gouge zone where drastic size reduction and rounding of grains occurred (Figure 4b). A slightly brighter zone $\sim 120 \mu\text{m}$ thick in this region indicated that the bulk density of this zone was higher compared to that of surrounding regions, possibly as a result of the shear localization and subsequent compaction during experiments. We thus infer that this zone is a localized slip zone (LSZ) in this sample. Quartz gouge sheared at 1 m s^{-1} showed different deformation microstructures for different final displacements (Figures 4e, 4f, 4i, 4j, 4m, 4n, 4q, and 4r). At the initial stage of slip ($D_{\text{final}} = 1 \text{ m}$), size reduction and rounding of quartz grains occurred on the stationary side of the gouge zone under optical microscope observations (Figure 4e). This zone was composed of a fine-grained matrix of well-rounded quartz grains compared to a surrounding granular zone (Figure 4f). Because these features indicate that the shear deformation was localized in this zone, we inferred this zone as an LSZ in this sample. At the early and intermediate stages of slip ($D_{\text{final}} = 5$ and 30 m), there were size reductions and rounding of

Table 4

Summary of Masses of Collected Gouge Samples, Frictional Parameters, Resultant XRD Parameters, and Amorphous Content for Kaolinite Gouges

Run no.	m_{col} (10^{-6} kg)	W_f (MJ kg $^{-1}$)	G_c (MJ kg $^{-1}$)	P_f (MW kg $^{-1}$)	S^a (cps $^\circ$)	M_{PTFE}^a (wt%)	M_{am}^b (wt%)
Initial	–	–	–	–	242 ± 6	–	0.0 ± 0.6
HVR4602	409	2.27	–	2.80×10^{-3}	365 ± 4	–	9.6 ± 0.4
HVR4604	386	5.65	–	3.32×10^{-3}	391 ± 3	–	11.6 ± 0.3
HVR4559	235	20.44	–	5.52×10^{-3}	950 ± 3	–	55.3 ± 0.3
HVR4601	240	27.10	–	5.56×10^{-3}	1,044 ± 4	–	62.6 ± 0.4
HVR4606	354	30.46	–	3.66×10^{-3}	1,293 ± 12	–	82.1 ± 1.0
HVR4607	249	69.51	–	4.90×10^{-3}	1,388 ± 1	–	89.5 ± 0.3
HVR4566 ^c	400	0.77	0.06 ± 0.00	0.68	343 ± 13	–	7.1 ± 1.0
HVR4565 ^c	383	2.52	1.11 ± 0.05	0.50	363 ± 4	–	8.1 ± 0.3
HVR4564 ^c	347	3.34	1.30	0.33	500 ± 9	–	15.7 ± 0.6
HVR4563 ^c	408	5.81	1.28	0.29	670 ± 2	4.3 ± 0.2	35.5 ± 0.2
HVR4561 ^c	341	6.69	2.07	0.17	691 ± 3	3.1 ± 0.0	29.9 ± 0.3
HVR4562 ^c	499	7.63	1.75	0.25	562 ± 2	5.7 ± 0.0	35.5 ± 0.2
HVR4557 ^c	297	11.46	1.69	0.19	610 ± 1	12.8 ± 0.2	31.0 ± 0.3
HVR4554 ^c	222	12.44	1.14	0.25	856 ± 4	3.1 ± 0.1	26.3 ± 0.3

Note. m_{col} , mass of gouge sample collected after each experiment; W_f , frictional work per amount of sample; G_c , seismic fracture energy per amount of sample; P_f , average frictional power per amount of sample; S , area of the broad peak at around 20–30 $^\circ$; M_{PTFE} , weight ratio of PTFE content to the entire sample; M_{am} , the weight ratio of amorphous content to the entire samples.

^aError is the standard deviation (1σ) of repeated XRD measurements ($n = 5$). ^bError is the standard deviation (1σ), which is calculated as the square root of variance of M_{am} (see Equation 4 for detail). ^cOnly the consolidated part of the gouge was collected. Data correction methods for frictional parameters and M_{am} are described in sections 3.3 and 4.2, respectively.

quartz grains within the entire gouge zones under optical microscope (Figures 4i and 4m) and under SEM BSE observations (Figures 4j and 4n), suggesting the absence of LSZ in these samples. At the final stage of slip ($D_{\text{final}} = 101$ m), there was a region on the stationary side of the gouge that was composed mostly of a fine-grained matrix with a small amount of well-rounded quartz grains under optical microscope observation (Figure 4q). Under SEM BSE observations, we confirmed that this region was composed of a brighter matrix with well-rounded quartz grains compared to surrounding granular regions, indicating that this zone can be classified as an LSZ ~ 100 μm thick (Figure 4r). Differences in the color of the inside and outside parts of the LSZ under optical microscope observations may be attributable to contamination by PTFE toward the end of this experiment (Figure 4q). This possibility is discussed in section 4.2. We observed no clear deformation structures such as R_1 -shear in quartz gouges, except for HVR4591 ($V_e = 1$ m s $^{-1}$ and $D_{\text{final}} = 30$ m) where the development of some cracks almost parallel to the shear direction was confirmed (Figure 4n).

The kaolinite gouge sheared at 0.001 m s $^{-1}$ clearly showed a preferred orientation of the kaolinite on both the moving and stationary sides of the gouge zone under optical microscope observations (Figure 4c). We also observed a clear existence of R_1 -shear on the stationary side of the gouge zone. SEM BSE observations also revealed the existence of R_1 -shears and shear-parallel cracks not only on the stationary side but also almost at the center of the gouge zone (Figure 4d). These suggest that the deformation was not localized but likely to be homogeneously distributed within the entire gouge zone. When sheared at 1 m s $^{-1}$, all of the gouges showed a preferred orientation of the kaolinite on the stationary sides of the gouge zone under optical microscope, whereas R_1 -shear was absent (Figures 4g, 4k, 4o, and 4s). Under SEM BSE observations, these preferred-orientation regions were composed of a fine-grained matrix and separated by a clear crack parallel to the shear direction, which was likely to form an LSZ and a slip surface by shear localization during experiments. SEM BSE images also showed different deformation microstructures for different final displacements (Figures 4h, 4l, 4p, and 4t), as was the case for the quartz gouge. At the initial and early stages of slip ($D_{\text{final}} = 1$ and 5 m), these regions showed a homogeneous, brighter matrix compared to surrounding heterogeneous regions (Figures 4h and 4l), indicating that these zones are likely to form LSZ ~ 30 and ~ 60 μm thick, respectively. At the intermediate and final stages of slip ($D_{\text{final}} = 30$ and 60 m), some shear-parallel cracks developed within a fine-grained zone, which was likely to form LSZ ~ 150 and ~ 120 μm thick on the stationary side of the gouge zone, respectively (Figures 4p and 4t). The thickness of the LSZ increased with increasing final displacement.

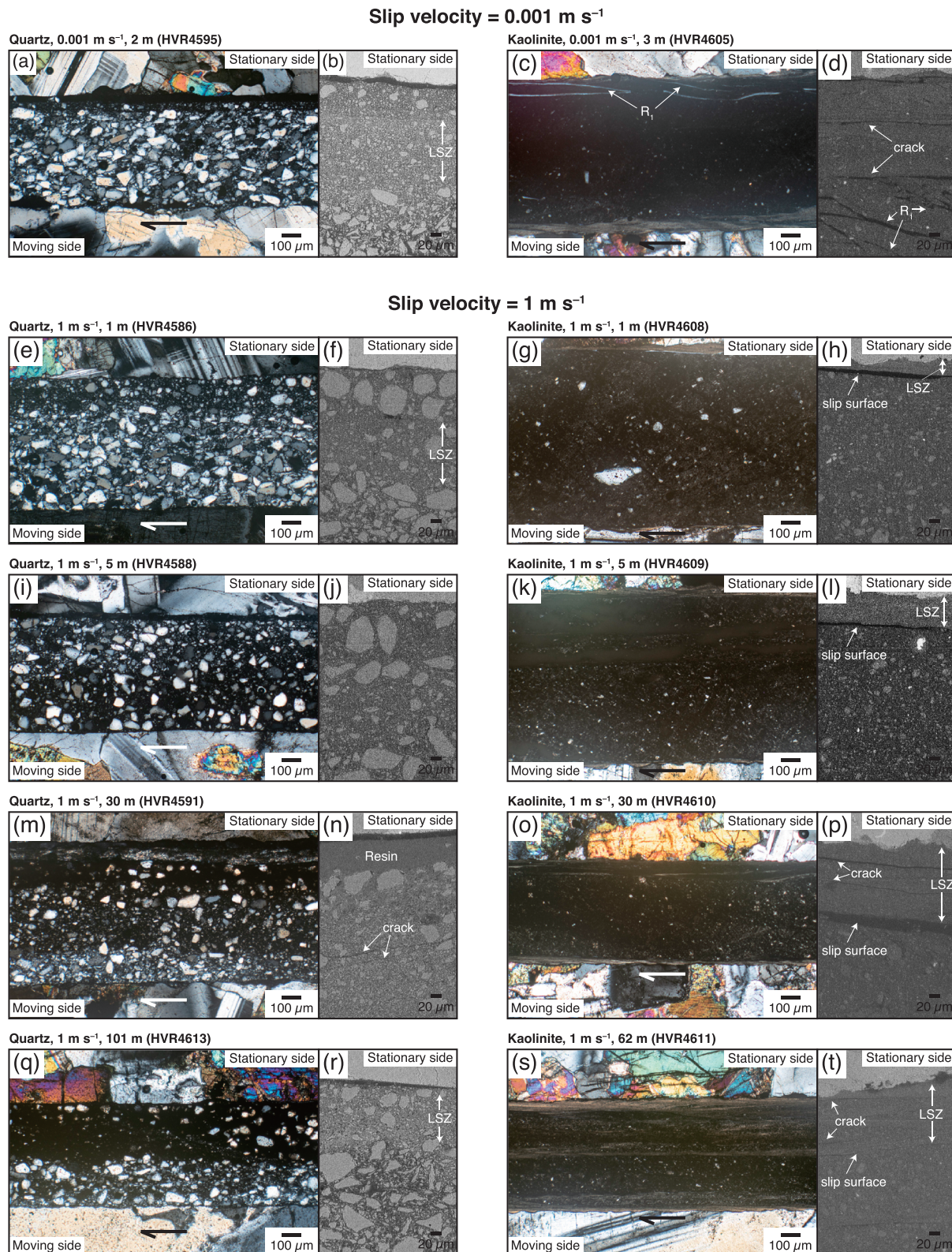


Figure 4. Results of microstructural observations of thin sections after friction experiments. (a, b) Quartz gouge sheared at 0.001 m s^{-1} for 2 m, (c, d) kaolinite gouge sheared at 0.001 m s^{-1} for 3 m, quartz gouge sheared at 1 m s^{-1} for (e, f) 1 m, (i, j) 5 m, (m, n) 30 m, and (q, r) 101 m, respectively, and kaolinite gouge sheared at 1 m s^{-1} for (g, h) 1 m, (k, l) 5 m, (o, p) 30 m, and (s, t) 62 m, respectively. For each experimental run, left and right columns are the results of optical microscope and SEM backscattered electron observations, respectively. LSZ, localized slip zone; R₁, R₁-shear.

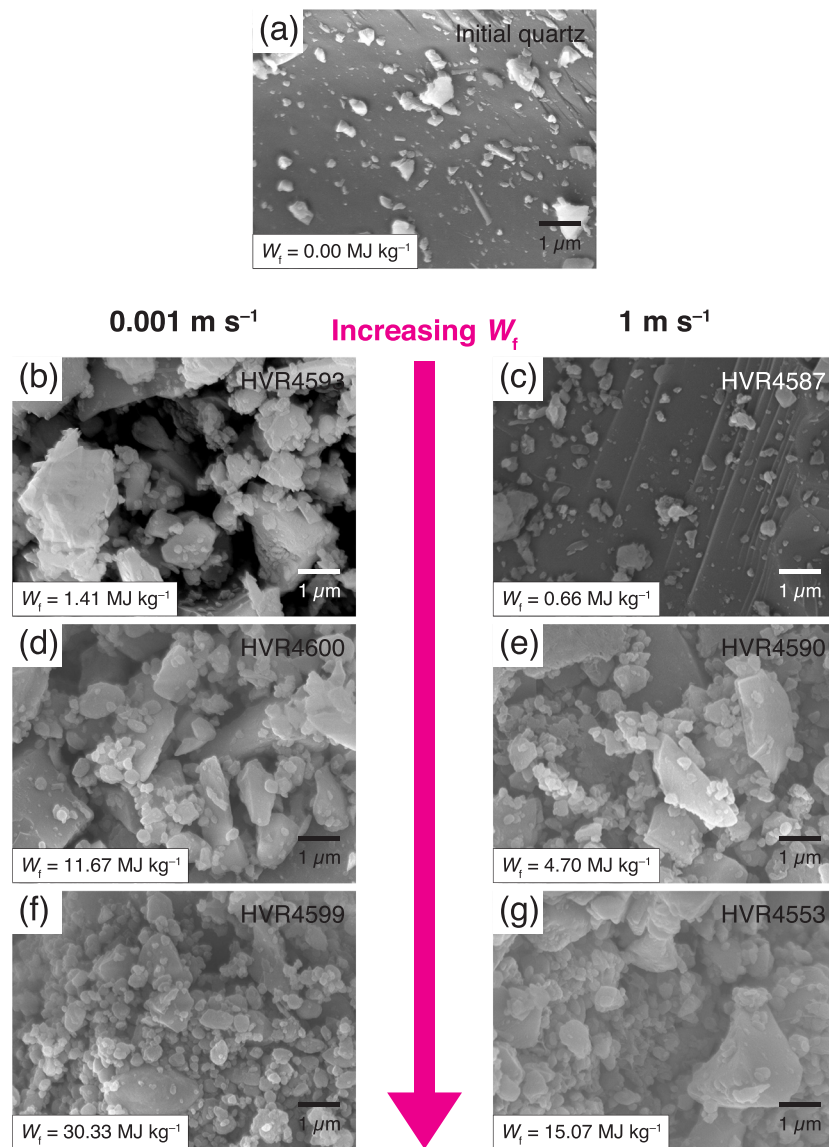


Figure 5. Representative SEM images of unsheared and sheared quartz gouge powder with W_f values annotated. (a) Unsheared quartz, (b, d, f) samples sheared at $0.001 m s^{-1}$ slip velocity, and (c, e, g) samples sheared at $1 m s^{-1}$ slip velocity.

3.5. SEM Observations on Powder Gouge Samples

We performed SEM observations on unsheared and sheared quartz and kaolinite powder samples. Small amounts of dried sample were mounted on carbon tape and coated with a thin platinum film by using a magnetron sputtering apparatus (JFC-1600, JEOL) at Kochi Core Center, Japan. The Pt-coated powders were examined with a field emission SEM (JSM-6500-F, JEOL) at Kochi Core Center at magnification of 12,000 $\times$. Detailed settings for the SEM observations are described in Text S2.

Representative SEM images of quartz and kaolinite gouges are shown in Figures 5 and 6, respectively. The unsheared quartz grains had smooth surfaces with a few particles of submicrometer size (Figure 5a). After friction experiments at both slip velocities, they showed drastic reductions in grain size with the appearance of numerous well-rounded ultrafine particles (diameters from several ten to several hundred nanometers; Figures 5b–5g). Some aggregation of these ultrafine particles was also evident. The unsheared kaolinite grains showed well-ordered sheet-stacking structures with thicknesses of several to several tens of

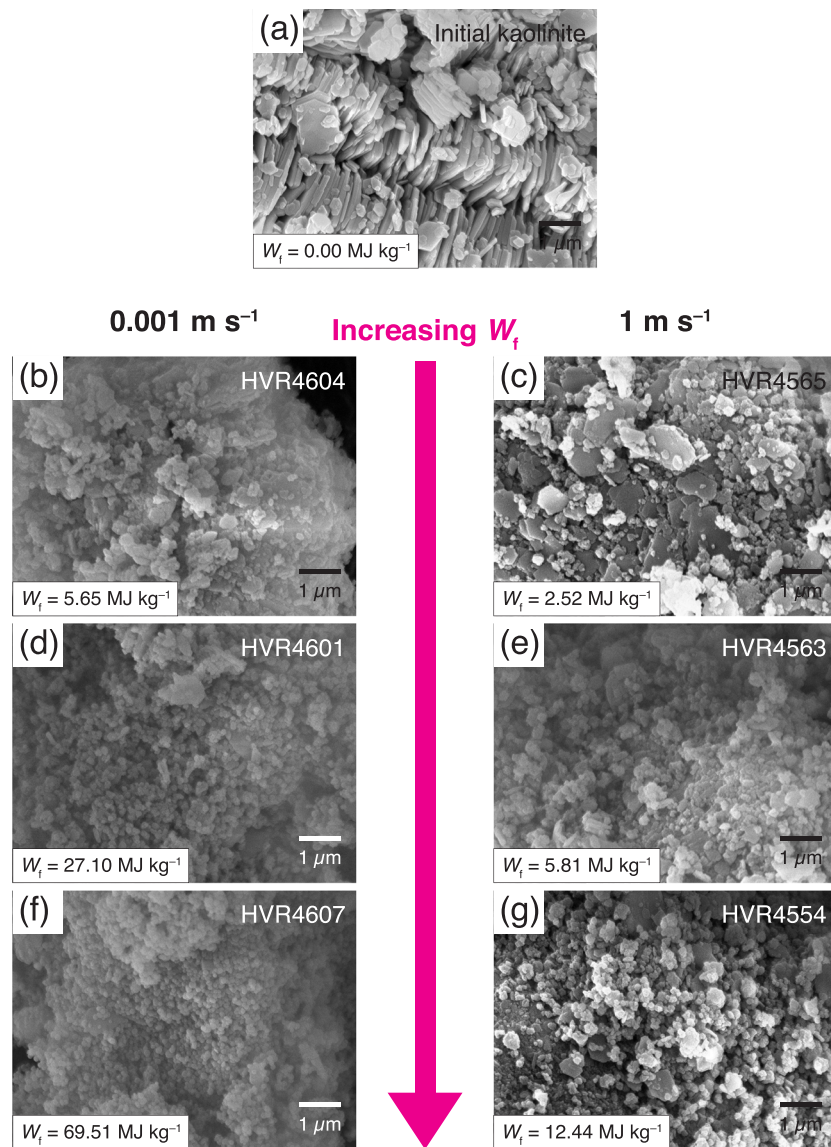


Figure 6. Representative SEM images of unsheared and sheared kaolinite gouge powder with W_f values annotated. (a) Unsheared kaolinite, (b, d, f) samples sheared at 0.001 m s^{-1} slip velocity, and (c, e, g) samples sheared at 1 m s^{-1} slip velocity.

nanometers (Figure 6a). After friction experiments at both slip velocities, the sheet-stacking structures were largely destroyed and there were numerous ultrafine particles (Figures 6b–6g). As W_f increased, the surfaces of the larger kaolinite particles were increasingly covered by these ultrafine particles. For both quartz and kaolinite gouges, the amount of ultrafine particles appeared to increase with increasing W_f . SEM images at magnifications $1,000\times$ and $12,000\times$ for all samples after shearing are provided in Figures S12–S15.

4. Amorphous Content Determined From XRD Measurements

4.1. XRD Profiles of Unsheared and Sheared Samples

We performed XRD measurements on unsheared and sheared quartz and kaolinite gouges to investigate the changes in amorphous content during our friction experiments. To calculate measurement errors, we obtained five XRD profiles for each sample. XRD measurements and calculations of the S values for each profile were done by following the analytical protocol described in sections 2.2 and 2.3.

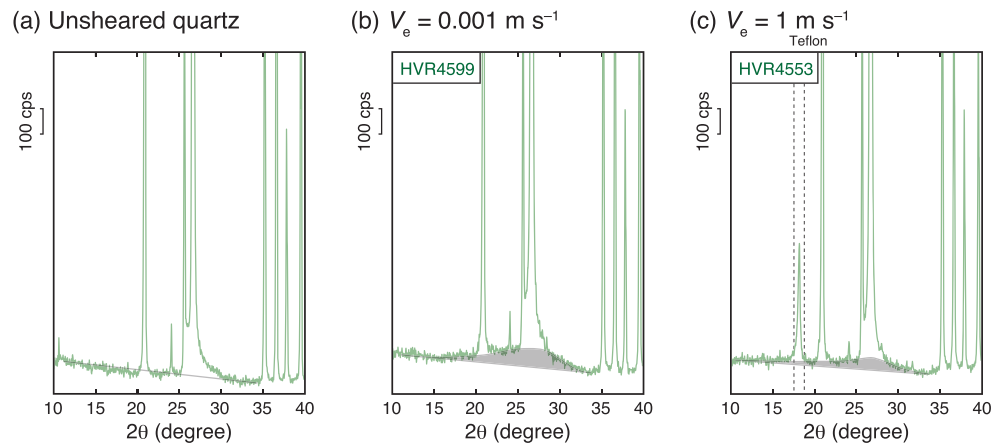


Figure 7. Representative XRD profiles of unsheared and sheared quartz gouge powder for 2θ range $10\text{--}40^\circ$. (a) Unsheared quartz, (b) slip velocity 0.001 m s^{-1} , and (c) slip velocity 1 m s^{-1} . Gray-shaded area indicates the broad peak derived from amorphous phase. All profiles show clear peaks of corundum (internal standard).

Normalized XRD profiles of quartz and kaolinite gouges after friction experiments with the largest W_f values at slip velocities of 0.001 and 1 m s^{-1} are shown in Figures 7 and 8, respectively, together with XRD profiles for unsheared gouges. All of the representative XRD profiles of quartz and kaolinite gouges after friction experiments are also shown in Figures S16 and S17, respectively. For both gouges, the development of broad peak at around $20\text{--}30^\circ$ was clearly observed after friction experiments at both slip velocities (Figures 7 and 8). For the quartz gouge, the XRD profiles after the experiments at 0.001 m s^{-1} slip velocity showed systematic decrease in the intensity of crystal peaks and the development of the broad peak at around $20\text{--}30^\circ$ with increasing W_f (Figure S16a). In the case of experiments at 1 m s^{-1} , gradual development of the broad peak and clear decrease in the intensity of crystal peaks were confirmed with increasing W_f (Figure S16b). These facts clearly indicate that distortion of crystalline structures (amorphization) of quartz gouge is evident after some of the experiments. The XRD profiles of quartz after some of the experiments at 1 m s^{-1} also showed small but distinct peaks at around 18° (Figures 7c, S16b, and S16d) that correspond to the (100) plane of PTFE (e.g., Li et al., 1998). After application of background corrections and normalization treatment, the obtained profiles were fitted with the best-fit curves described by following the protocol of section 2.3 (Figures S16c and S16d).

For kaolinite, the XRD profiles of gouge sheared at both slip velocities showed systematic decreases in the intensity of crystal peaks and development of the broad peak at around $20\text{--}30^\circ$ with increasing W_f

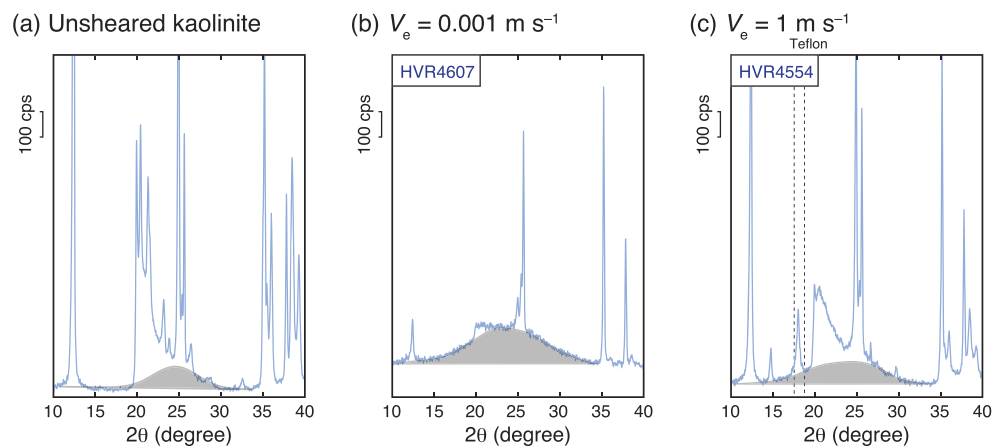


Figure 8. Representative XRD profiles of unsheared and sheared kaolinite gouge powder for 2θ range $10\text{--}40^\circ$. (a) Unsheared kaolinite, (b) slip velocity 0.001 m s^{-1} , and (c) slip velocity 1 m s^{-1} . Gray-shaded area indicates the broad peak derived from amorphous phase. All profiles show clear peaks of corundum (internal standard).

(Figures S17a and S17b), suggesting the occurrence of amorphization of kaolinite gouges. Some of the experiments at 1 m s^{-1} showed a clear XRD peak representative of PTFE at around 18° (Figures 8c, S17b, and S17d). Normalized background-corrected XRD profiles at both slip velocities were also reproduced by the best-fit curves (Figures S17c and S17d).

4.2. Amount of Amorphous Material in Fault Gouge

The XRD profiles clearly indicated contamination of gouge from the PTFE sleeve in some of the experiments at 1 m s^{-1} slip velocity (Figures 7 and 8). Honda et al. (2013) reported contamination by PTFE fragments in similar friction experiments on shale gouge at 1.31 m s^{-1} slip velocity. The presence of PTFE in our samples after shearing needs to be taken into account when determining the amount of amorphous material in our samples.

To further investigate PTFE contamination during our experiments, we examined the distribution of representative kaolinite and PTFE elements (Si, O, Al, Cl, and F) in samples by energy-dispersive X-ray spectroscopy (EDS) using a JED-2300F (JEOL Ltd.) apparatus at Kochi Core Center (Figure S18). These analyses showed that the representative constitutive elements of kaolinite (Si, O, and Al) were abundant where kaolinite particles were present. Other minor element such as F (which is in PTFE but not in kaolinite) in amorphous kaolinite samples was comparable to that of Cl (background reference). In contrast, the amount of F in our kaolinite gouge after the friction experiments at 1 m s^{-1} slip velocity (HVR4557) was markedly greater than that of Cl. These results suggest that PTFE contamination was homogeneously distributed on the surface of mineral grains after our experiments. In contrast, fragments of PTFE sleeve, which were observed by Honda et al. (2013), were absent in gouge samples under SEM observations (Figures S12–S15), indicating that PTFE contamination by mechanical scratching of a PTFE sleeve was not evident. Maximum temperature reached during some of experiments at 1 m s^{-1} slip velocity far exceeded the melting point of PTFE (327°C) (Figures 3b and 3d), and it is thus likely that the PTFE contamination occurred via melting and subsequent dispersing through the gouge zone during experiments. This statement is strongly supported by the optical observations of PTFE sleeves after some of experiments; a clear black ring on the inner surface of a PTFE sleeve, which indicates the melting of PTFE, is present after experiments only if PTFE contamination was confirmed by XRD measurements (Figure S19). XRD profiles after some experiments showed a clear peak at about 18° which corresponds to crystalline structures of PTFE (Figures 7, 8, S16, and S17). In contrast, we observed no shoulder peak at around 16° which corresponds to amorphous structures of PTFE (Gong et al., 1990). These suggest that the contaminated PTFE was fully crystalline. In summary, we concluded that PTFE contamination was likely to occur via melting, dispersing on the surface of mineral grains, and fully crystallized to be detected as a sharp peak at 18° (crystalline PTFE) without a shoulder peak at 16° (amorphous PTFE) in XRD profiles.

To determine the amount of PTFE contamination, we performed XRD measurements on the pure PTFE samples with 20 wt% corundum (Figure S20a). Because we observed a small shoulder peak at around 16° , which corresponds to amorphous structures of PTFE (Gong et al., 1990), we first quantify the amount of amorphous phase in the initial PTFE. Hu (1982) suggested that crystallinity of PTFE C_{PTFE} can be calculated using

$$C_{\text{PTFE}} = \frac{\Delta H_m}{\Delta H_m^0}, \quad (12)$$

where ΔH_m and ΔH_m^0 are the latent heats of the measured PTFE and the theoretical PTFE, respectively. ΔH_m^0 is 14.6 cal g^{-1} (Hu, 1982), and ΔH_m of the initial PTFE is reported to be 32.70 J g^{-1} (Honda et al., 2013). The weight ratio of PTFE content to the entire sample M_{PTFE} can be then expressed as

$$M_{\text{PTFE}} = \frac{I_{\text{sample}}^{18}}{I_{\text{PTFE}}^{18}/C_{\text{PTFE}}}, \quad (13)$$

where I_{sample}^{18} and I_{PTFE}^{18} are the peak intensities of the measured samples at about 18° and the peak intensity of the initial PTFE at about 18° , respectively. The background of the XRD profile of PTFE sleeve was

subtracted by the method described in section 2.3 (Figure S20b). Calculated M_{PTFE} values for each experiment are provided in Tables 3 and 4. For both quartz and kaolinite, no PTFE contamination was evident after any of the experiments at 0.001 m s^{-1} slip velocity, possibly because the temperature reached during the experiments was far insufficient to cause melting of PTFE (Figure S10).

In experiments at 1 m s^{-1} , M_{PTFE} in the quartz and kaolinite gouges started to increase at $D_{\text{final}} = 5$ and 20 m , respectively, corresponding to $W_f = 3.73$ and 6.42 MJ kg^{-1} , respectively (Tables 1–4). The maximum M_{PTFE} in kaolinite gouge (12.8 wt%) was greater than that in quartz gouge (2.7 wt%) (Tables 3 and 4). These values are comparable to those reported by Honda et al. (2013), which were up to 16.3 wt%. Honda et al. (2013) also performed friction experiments at 1.31 m s^{-1} on shale gouge with initial M_{PTFE} values of 0, 10, 20, and 30 wt% and demonstrated that PTFE contamination causes significant decrease in peak shear stress if M_{PTFE} is greater than 10 wt%, whereas no marked effect on steady-state shear stress was observed. Because the M_{PTFE} values of most of our experiments are less than 10 wt%, the effect of PTFE contamination on the measured shear stress can be negligible in most cases. Even in the case of the M_{PTFE} value of 12.8 wt% (HVR4557), the measured peak shear stress of 0.81 MPa was comparable to those of other experiments with zero or much less M_{PTFE} values (Table 4). This can be explained by the fact that PTFE contamination in kaolinite gouge occurred at displacement greater than 20 m (Table 4), and at this stage, the shear stress has already passed its peak value and reached to steady state. We could thus conclude that the effect of PTFE contamination on the measured shear stress is negligible.

Other possible effects of PTFE contamination can be on the calculated S values and on frictional parameters. For correction on the S values, we determined the integrated area of an XRD profile of a PTFE sample in the range $20\text{--}30^\circ 2\theta$ ($S_{\text{PTFE}} = -944 \text{ cps}^\circ$, Figure S20c). Because the XRD profiles of crystalline and amorphous PTFE differ in the intensities at around $16\text{--}18^\circ$ (Gong et al., 1990), we can consider the S_{PTFE} value as constant regardless of crystallinity of PTFE. We then calculated the corrected broad peak area S_{corr} as

$$S_{\text{corr}} = \frac{S - M_{\text{PTFE}} S_{\text{PTFE}}}{1 - M_{\text{PTFE}}}. \quad (14)$$

We used Equations 2, 4, 13, and 14 to calculate the weight ratio M_{am} of amorphous content to the entire samples and their errors before and after friction experiments. For most of the experiments at 1 m s^{-1} slip velocity, where only the consolidated part of gouge samples was recovered, we corrected the M_{am} values by the relationship

$$M_{\text{am, corr}} = M_{\text{am}} \frac{m_{\text{col}}}{m_{\text{init}}}, \quad (15)$$

where $M_{\text{am, corr}}$ is the weight ratio of corrected amorphous content to the entire sample. Finally, all the calculated M_{am} values were corrected such that the mean M_{am} values of unsheared samples are identical to zero. For correction on the frictional parameters, we calculated the energy taken up by melting of PTFE sleeve with latent heat of 32.70 J g^{-1} (Honda et al., 2013). The calculated ratios of the energy of PTFE melting to each frictional parameter did not exceed 0.1%, indicating that melting of PTFE has negligible effects on the frictional parameters.

We next considered the relationship of the calculated M_{am} values for the quartz and kaolinite gouges (Tables 3 and 4) to final displacement (Figure 9). Because our experiments at both slip velocities were performed under different normal stress conditions, we can only compare the M_{am} values between different minerals at the same slip velocity. M_{am} for quartz after experiments at 0.001 m s^{-1} showed gradual slight increases with increasing D_{final} (Figure 9a), except for D_{final} of 6.6 m (HVR4558), which showed an M_{am} value clearly higher than the others. M_{am} for kaolinite after experiments at 0.001 m s^{-1} increased systematically with increasing D_{final} (Figure 9c). M_{am} values after the experiments on quartz gouge at 1 m s^{-1} were only slightly higher than those of the unsheared samples (Figure 9b). After the experiments at 1 m s^{-1} using kaolinite, M_{am} showed marked increases with increasing D_{final} and then became almost constant at $D_{\text{final}} \geq 20 \text{ m}$ (Figure 9d). The M_{am} values of both the quartz and kaolinite gouges after experiments that achieved steady-state shear stress were higher than those that did not. At both slip velocities, the M_{am} values of kaolinite were higher than those of quartz at the same final displacement.

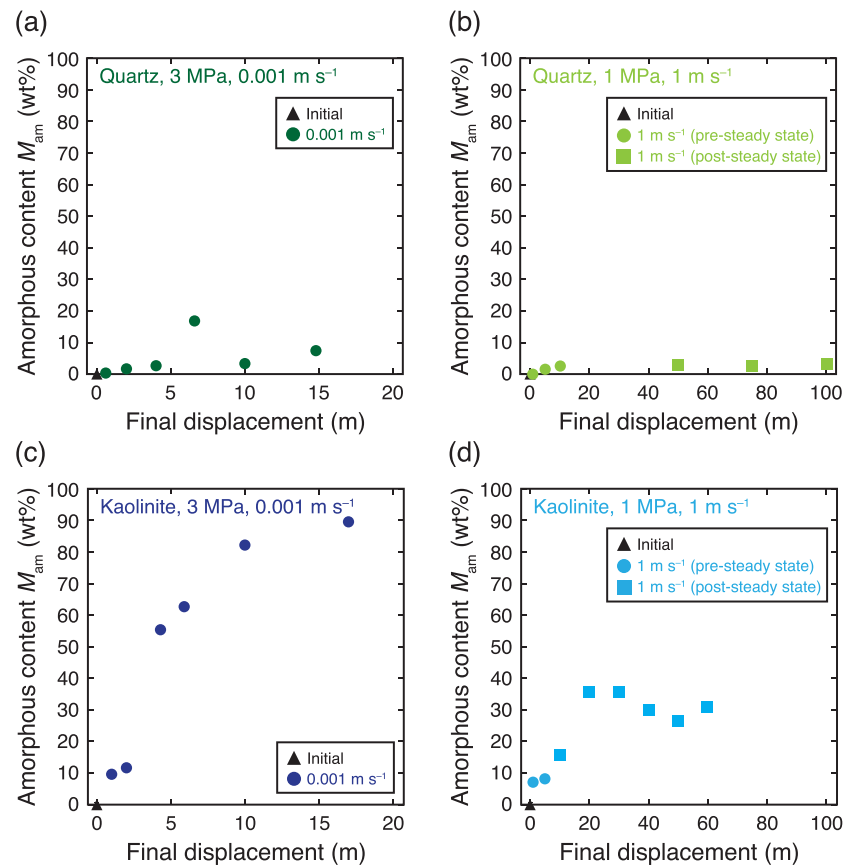


Figure 9. Relationship between the weight ratio M_{am} of amorphous content to the entire sample and final slip displacement D_{final} for friction experiments. Quartz gouge (a) at slip velocity of 0.001 m s^{-1} and normal stress of 3 MPa and (b) at slip velocity of 1 m s^{-1} and normal stress of 1 MPa. Kaolinite gouge (c) at slip velocity of 0.001 m s^{-1} and normal stress of 3 MPa and (d) at slip velocity of 1 m s^{-1} and normal stress of 1 MPa. For experiments at 1 m s^{-1} , data points for when steady-state shear stress was achieved or not achieved are differentiated by symbol type (squares and circles, respectively). Because errors for M_{am} were small, the error bars are obscured by the circles and squares.

5. Discussion

5.1. Process Leading to Amorphization

Our microstructural observations and the results of our XRD measurements on samples after friction experiments clearly show that some parts of the synthetic fault gouge were amorphized during our experiments (Figures 9 and 10); amorphization was accompanied by grain-size reduction, particle rounding, and formation of ultrafine particles (Figures 4–6). As mentioned in section 1 of this paper, mechanisms responsible for amorphization of fault gouge include frictional melting, mechanical deformation, devolatilization, and fluid-rock interaction.

Because our SEM observations both on thin sections and gouge powders did not provide any microstructural evidence for partial melting of the fault gouge (Figures 4–6), such as injection veins, vesicles, and embayment structures, we exclude any contribution of frictional melting to the observed amorphization. Under dry conditions, dehydroxylation of kaolinite samples such as those used in this study has been shown to start at 483°C , to peak at 575°C , and to finish at 618°C at a heating rate of $10^\circ\text{C min}^{-1}$ (Guggenheim & van Groos, 2001), and higher heating rates increase the temperature required for the dehydroxylation reaction (Masumoto et al., 2018). In the case for mechanochemically activated kaolinite, corresponding to kaolinite gouges after experiments in this study, the reaction temperature for dehydroxylation can decrease, as in the case for illite (Hirono et al., 2013). For example, Vizcayno et al. (2010) demonstrated through milling experiments and thermal analysis that the ground kaolinite samples dehydroxylate at lower temperature with

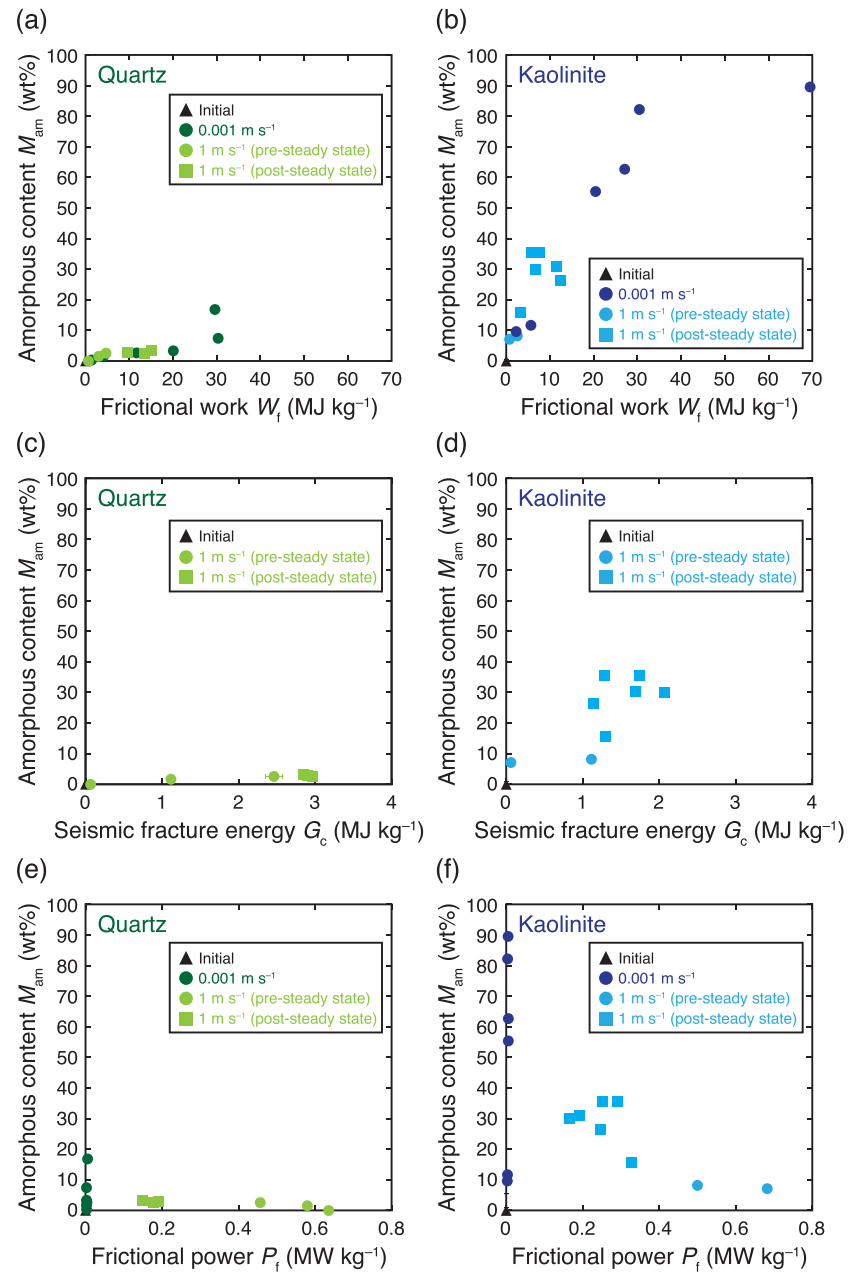


Figure 10. Relationships of the weight ratio M_{am} of amorphous content to the entire sample with frictional parameters for slip velocities of 0.001 and 1 m s^{-1} . M_{am} for quartz and kaolinite gouge after friction experiments are plotted against (a, b) frictional work per amount of sample W_f , (c, d) seismic fracture energy per amount of sample G_c , and (e, f) average frictional power per amount of sample P_f . For experiments at 1 m s^{-1} , data points for when steady-state shear stress was achieved or not achieved are differentiated by symbol type (squares and circles, respectively). Because errors for M_{am} were small, the error bars are obscured by the circles and squares.

increasing milling time. In particular, dehydroxylation starts at $\sim 400^\circ\text{C}$, peaks at $\sim 500^\circ\text{C}$, and finishes at $\sim 600^\circ\text{C}$ in kaolinite samples after milled for 60 min, whose peak intensity of a (001) plane in XRD profiles is less than 20% of that of intact samples (roughly corresponding to $M_{am} \geq 80 \text{ wt\%}$). On the other hand, the M_{am} values of kaolinite after our 1 m s^{-1} experiments using kaolinite are less than 36 wt%, indicating that the onset of dehydroxylation requires the temperature to reach at least 400°C . Maximum temperature reached during our experiments at slip velocity 1 m s^{-1} was 369°C on the stationary side of the rotary-shear apparatus we used (Figure 3d). Given that most of the frictional heat generated during slip likely

occurs in LSZ and that LSZ in our experiments formed on the stationary side (Figures 4), the M_{am} values and the temperatures that we measured strongly suggest that dehydroxylation of kaolinite probably did not occur during our experiments. Furthermore, the vesiculated structures of mineral grains, which can be formed by releasing fluid via chemical reactions (e.g., Collettini et al., 2013), were absent under the SEM observations on powder kaolinite gouges (Figures 6 and S15). Thus, we believe that devolatilization did not contribute to amorphization of the gouge in our experiments. Under water-saturated conditions, aqueous solutions containing dissolved quartz can deposit amorphous silica in the form of spherical nano- to micrometer-scale particles (Amagai et al., 2019). However, because our friction experiments were performed under dry conditions, amorphization cannot be attributed to fluid-rock interactions.

On the basis of the above exclusions, we concluded that mechanical deformation was the dominant cause of amorphization of the fault gouge during our friction experiments. This conclusion is supported by our SEM observations on both thin sections and powder gouge samples, which showed grain-size reduction, particle rounding, and formation of ultrafine particles in LSZ as a result of our experiments (Figures 4–6), all of which have been observed in previous studies that have reported mechanical amorphization during fault slip (e.g., Aretusini et al., 2019; Hirono et al., 2016; Yund et al., 1990).

5.2. Frictional Parameters Related to Mechanical Amorphization

We now consider the relationships between the post-shearing M_{am} values and frictional work, seismic fracture energy, and frictional power (Figure 10).

M_{am} of quartz gouge increased slightly with increasing frictional work (Figure 10a). M_{am} of kaolinite gouge also increased systematically with increasing frictional work, but was larger than that of quartz for the same value of frictional work (Figures 10a and 10b). These increases in M_{am} are consistent with the formation of ultrafine particles that we observed under SEM observations of powder gouge samples (Figures 5 and 6). Ultrafine particles such as these have been reported to be partly or fully amorphized (e.g., Hirono et al., 2016; Pec et al., 2012), which supports our view that the ultrafine particles we observed were similarly a result of amorphization. Importantly, for both minerals, the M_{am} data follow the same trend, regardless of slip velocity (Figures 10a and 10b). This is discussed further in section 5.4.

M_{am} of quartz gouge showed little change in relation to seismic fracture energy (Figure 10c). In contrast, M_{am} of kaolinite gouge increased dramatically across a range of seismic fracture energy from 1 to 2 MJ kg^{−1} (Figure 10d). Given that the seismic fracture energy is defined as the integral of shear stress change over slip, it should change little after steady-state shear stress has been achieved. We attribute the variations in seismic fracture energy in our experiments in which kaolinite gouge achieved a steady-state condition to differences in the residual shear stress (Table 2).

We now consider further the dependency of M_{am} on seismic fracture energy that we observed in kaolinite gouge. If seismic fracture energy is the only energy source for mechanical amorphization of fault gouge, M_{am} should increase with slip until steady-state shear stress is reached and should remain constant thereafter. However, in the kaolinite gouge of our experiments that reached steady state, M_{am} increased markedly with increasing final displacement (Figure 9d), which indicates that mechanical amorphization of kaolinite progressed even after the steady-state condition was achieved. We thus argue that M_{am} is clearly dependent on seismic fracture energy. Fracture energy is generally determined from seismological source parameters (e.g., Abercrombie & Rice, 2005) or from the results of kinematic inversion (e.g., Ide & Takeo, 1997); it is thus not directly comparable to the internal energy stored in a gouge layer.

In both minerals, the experiments at 0.001 m s^{−1} gave much smaller values of frictional power than those at 1 m s^{−1}. At 1 m s^{−1}, there was a clear inverse relationship between frictional power and M_{am} (Figures 10e and 10f). These trends are consistent with results presented by Aretusini et al. (2017, 2019). Because of the 3 orders of magnitude difference between slip velocities of 0.001 and 1 m s^{−1}, it is reasonable that all values of M_{am} in the experiments at 0.001 m s^{−1} correspond to near-zero values of frictional power (Figures 10e and 10f). In the experiments at 1 m s^{−1}, shear stress decreased with increasing displacement (Figures 3b and 3d), which led to the systematic decrease of frictional power with increasing final displacement. Given that greater final displacements resulted in higher M_{am} values (Figure 9), it is also reasonable that M_{am} and frictional power at the slip velocity of 1 m s^{−1} showed anti-correlation (Figures 10e and 10f).

There appears to be a complex, non-monotonic dependency in the relationship of M_{am} to frictional power (Figures 10e and 10f). It is important to consider whether this dependency is a universal relationship of the form $M_{am} = F(P_f)$. Immediately after the initiation of frictional slip, before dynamic weakening becomes significant, frictional power should be roughly proportional to slip velocity because the peak friction coefficient is not very sensitive to slip velocity. On the other hand, during this initial stage of slip, M_{am} may be little different from its initial value. Therefore, the M_{am} versus P_f data points for experiments at various slip velocities V_e and small final displacements should align subhorizontally at the initial value of M_{am} , differing considerably from the relationships shown in Figures 10e and 10f. We therefore argue that the observed non-monotonic dependency does not have profound physical meaning other than that explained in the preceding paragraph.

On the basis of the matters discussed above, we conclude that frictional work is the dominant frictional parameter that controls mechanical amorphization of both quartz and kaolinite gouges.

5.3. Mechanical Amorphization Within LSZ

Our microstructural observations on thin sections revealed the development of LSZ during some of the friction experiments (Figure 4). Because most of the frictional work during the experiments is likely to be done within LSZ, we now consider whether the increases in M_{am} can be attributed entirely to mechanical amorphization of mineral particles within the LSZ. Although simultaneous XRD measurements and thin section observations cannot be done on a particular sample, the high reproducibility of our friction experiments at 1 m s^{-1} slip velocity (Figures S7 and S9) suggests that it is reasonable to compare the post-shear analytical results of different experimental runs performed with the same values of normal stress, slip velocity, and final displacement. We now focus on the experiments at V_e of 1 m s^{-1} and σ_n of 1 MPa with D_{final} of approximately 100 m for quartz gouge and at V_e of 1 m s^{-1} and σ_n of 1 MPa with D_{final} of 1, 5, 30, and ~ 60 m for kaolinite gouge, respectively (quartz: HVR4553 and HVR4613; kaolinite with $D_{final} = 1$ m: HVR4566 and HVR4608; kaolinite with $D_{final} = 5$ m: HVR4565 and HVR4609; kaolinite with $D_{final} = 30$ m: HVR4562 and HVR4610; kaolinite with $D_{final} = \sim 60$ m: HVR4557 and HVR4611). The mass of gouge samples within the LSZ in the annular region of the fault plane can be expressed as

$$m_{LSZ} = m_{init} \frac{w_{LSZ} \rho_{LSZ}}{w_{tot} \rho_{init}}, \quad (16)$$

where w_{LSZ} is the thickness of the LSZ, w_{tot} is the thickness of the entire gouge zone, ρ_{LSZ} is the bulk density of the LSZ, and ρ_{init} is the bulk density of the initial fault gouge. If all of the amorphous phase was produced within the LSZ, the ratio of amorphous content within LSZ to the amount of gouge sample within LSZ can be expressed as

$$M_{am,LSZ} = M_{am} \frac{m_{init}}{m_{LSZ}} = M_{am} \frac{w_{tot} \rho_{init}}{w_{LSZ} \rho_{LSZ}}. \quad (17)$$

We roughly measured each of the above thicknesses on the results of thin section observations (Figure 4): w_{LSZ} of 100, 30, 60, 150, and 120 μm and w_{tot} of 550, 930, 880, 540, and 590 μm for quartz ($D_{final} = \sim 100$ m), kaolinite ($D_{final} = 1$ m), kaolinite ($D_{final} = 5$ m), kaolinite ($D_{final} = 30$ m), and kaolinite ($D_{final} = \sim 60$ m), respectively. Although the ρ_{LSZ} value is unknown, the bulk density of LSZ was higher than the surrounding non- or less-deformed zone as indicated by SEM BSE observations (Figure 4). We thus assume that as an end member, the porosity in the LSZ is zero and the ρ_{LSZ} values are identical to the powder densities of quartz ($2,650 \text{ kg m}^{-3}$) and kaolinite ($2,630 \text{ kg m}^{-3}$) (Brigaud & Vasseur, 1989); this assumption gives the lower limit of the $M_{am,LSZ}$ value. The ρ_{init} values are calculated from the ρ_{LSZ} values and initial gouge thickness (1 mm) to be 1,247 and $1,192 \text{ kg m}^{-3}$ for quartz and kaolinite gouges, respectively. The calculated values of $M_{am,LSZ}$ and their standard deviations are 8.5 ± 0.5 for quartz ($D_{final} = \sim 100$ m), 99.8 ± 14.1 wt% for kaolinite ($D_{final} = 1$ m), 53.8 ± 2.0 wt% for kaolinite ($D_{final} = 5$ m), 57.9 ± 0.3 for kaolinite ($D_{final} = \sim 30$ m), and 69.1 ± 0.7 for kaolinite ($D_{final} = \sim 60$ m). The $M_{am,LSZ}$ values after experiments using both quartz and kaolinite gouges do not exceed 100 wt% and are thus realistic, indicating that LSZ is capable of hosting the entire process of mechanical amorphization. However, this calculation implicitly assumed the homogeneous thickness of LSZ for the entire

gouge zone, and the results can change when considering the spatial variation of LSZ thickness. In addition, we would like to note that these $M_{\text{am,LSZ}}$ values are minimum estimates and should increase when the porosity of LSZ is not zero.

5.4. Dependence of Mechanical Amorphization on Slip Velocity and Mineralogy

As previously mentioned in section 5.2, the trends of the relationships between M_{am} and frictional work in both minerals were not dependent on slip velocity (Figures 10a and 10b). Importantly, M_{am} of the kaolinite gouge showed a strong correlation with frictional work (Figure 10b), which strongly suggests that the mechanically produced amorphous content of kaolinite gouges depends explicitly on frictional work, but only implicitly on slip velocity and final displacement. Aretusini et al. (2017) reported that the content of amorphous phase in smectite-bearing gouges was higher after experiments at slip velocities of 10^{-4} to 10^{-3} m s $^{-1}$ than after those at 1 m s $^{-1}$. Because all of their experiments were performed with the same final displacement of 3 m and higher slip velocities cause dynamic decreases in shear stress, higher frictional work occurred at lower, rather than higher, slip velocities in their experiments (e.g., the amounts of frictional work per unit area of their experiments using 60 wt% Ca-montmorillonite samples were 10.8–11.6 and 4.3–5.1 MJ m $^{-2}$ at slip velocities of 0.001 and 1.5 m s $^{-1}$, respectively, as shown in their Supplementary Table 1). Thus, their results indicate that higher frictional work results in the generation of larger amount of amorphous materials within the fault gouges; this accords well with our results (Figures 10a and 10b).

In our kaolinite gouge, M_{am} increased greatly (up to ~90 wt%) with increasing frictional work (Figure 10b), whereas M_{am} of the quartz gouge increased by only ~17 wt% (Figure 10a). About 7 wt% of the quartz and kaolinite gouges was amorphized at frictional work of 30.33 and 0.77 MJ kg $^{-1}$, respectively (Tables 3 and 4), clearly showing that less work is required to amorphize kaolinite. This result is consistent with the results of previous studies that demonstrated preferential mechanical amorphization of clay minerals over quartz in clay-bearing fault gouges during friction experiments (Aretusini et al., 2017, 2019). For instance, rotary-shear friction experiments by Aretusini et al. (2019) on samples composed of a mixture of smectite and opal-CT showed that the amorphous material produced was mechanically amorphized smectite. Our results show that less frictional work is needed to distort the crystal structure of kaolinite than is the case for quartz, thus providing a clear explanation for the preferential amorphization of clay minerals during fault slip. The reason for the weakness of crystal structures of kaolinite and other clay minerals compared to that of quartz against frictional shear is unclear from our current experimental results. This should be addressed in a future study to understand the mechanical amorphization process in natural faults consisting of various minerals.

5.5. Energy Used for Mechanical Amorphization

Although previous studies have attempted to evaluate energy budgets during laboratory friction experiments (e.g., Aubry et al., 2018; Brantut et al., 2008; Sawai et al., 2012; Togo & Shimamoto, 2012), the energy required for mechanical amorphization of fault gouges remains unclear because those studies lacked quantitative data on the amorphous content of the gouges they tested. We quantify the amount of energy used for mechanical amorphization, based on our quantification of the amorphous content of our quartz and kaolinite gouges before and after our friction experiments (see section 4.2).

In our experiments using quartz, the maximum temperature did not exceed 800 K (Figure 3b). The enthalpy change from crystalline quartz to silica glass was in the range 3.7–5.7 kJ mol $^{-1}$ (Robie et al., 1979), which corresponds to 61–95 J g $^{-1}$ with the molecular weight of SiO $_2$ to be 60.085 g mol $^{-1}$. Given that silica glass is perfectly amorphized quartz and thus has a higher value of Gibbs free energy than our post-shear quartz, these ranges of enthalpy change can be regarded as an upper limit when considering mechanical amorphization of quartz.

Thermal analysis of ground kaolinite powders by Vizcayno et al. (2010) showed that mechanically amorphized kaolinite shows the endothermic peak of dehydroxylation, which indicates that thermally dehydroxylated kaolinite (metakaolin) has higher Gibbs free energy than does mechanically amorphized kaolinite. Based on the heat of formation of kaolinite (−964,940 cal mol $^{-1}$) and metakaolin (−767,500 cal mol $^{-1}$) reported by Schieltz and Soliman (1964) and their molecular weights of 258.160 and 222.130 g mol $^{-1}$, respectively, the enthalpy change from crystalline kaolinite to metakaolin at 298 K is 1,182 J g $^{-1}$. As was the case for quartz, using these values yields the maximum amount of energy used for mechanical amorphization of kaolinite.

By using the above ranges of enthalpy required to amorphize quartz and kaolinite, we can calculate the upper limits of the ratio of energy used for mechanical amorphization to frictional work during our friction experiments. The ratios so calculated for quartz gouge did not exceed 0.06%, indicating that the amount of energy required for mechanical amorphization of quartz gouge is negligible, which is consistent with the results of Brantut et al. (2008). The comparable ratios calculated for kaolinite gouge were up to 6.05%; although this is the upper limit of the energy ratio, it suggests that the mechanical amorphization of kaolinite may be potentially important for understanding the energetics of faulting in rocks that are rich in kaolinite. We would like to emphasize that this estimation gives the maximum estimate of energy used for amorphization of kaolinite, and further investigation on this point is required by determining the exact value of enthalpy change from crystalline to mechanically amorphized kaolinite.

5.6. Implications for Mechanical Amorphization in Natural Faults

Although our experiments were performed under dry conditions, natural fault gouges are usually found in a water-saturated environment. Because of the high solubility of the amorphous phase (e.g., Palandri & Kharaka, 2004), some of it may be dissolved in pore fluid during and after slip. Furthermore, thermal pressurization (an increase in pore fluid pressure because of thermal expansion of pre-existing pore fluid) can decrease effective normal stress (Lachenbruch, 1980), thus reducing the amount of frictional work (and therefore the amount of amorphization), even at the normal stresses and slip velocities of our experiments. In contrast, the deposition of amorphous ultrafine particles from silica-saturated pore fluid can increase the apparent amount of amorphization (Amagai et al., 2019). Both of these opposing mechanisms should be considered when extrapolating our experimental results to attempt to understand mechanical amorphization processes in natural faults.

The relationship of M_{am} to S clearly differs for our quartz and kaolinite samples (Figures 2e and 2f). Mechanically amorphized material in natural fault gouges can originate from a variety of minerals (e.g., Hirono et al., 2014, 2016; Janssen et al., 2010; Ozawa & Takizawa, 2007). It is therefore important to establish which mineral is the main constituent of amorphized material after fault slip if a suitable calibration line for quantifying that amorphous content is to be obtained.

Our results clearly show that M_{am} increased during frictional slip at both seismic (1 m s^{-1}) and subseismic (0.001 m s^{-1}) slip velocities (Figures 10a and 10b). These results agree with previous studies that have shown that amorphous phase in fault gouge can be produced at low slip velocities on the order of 10^{-8} to 10^{-3} m s^{-1} (Aretusini et al., 2017, 2019; Hayward et al., 2016; Hirose et al., 2012; Pec et al., 2012). Our results, together with those of previous experiments, indicate that mechanical amorphization likely occurs during coseismic events, but can also occur during fault motion with much lower slip velocity such as fault creep and slow slip events. Consequently, elevated amorphous content within fault gouge cannot be regarded as a definitive record of a coseismic event.

5.7. Implications for Fault Motion

We here discuss three processes that can affect fault motion in association with mechanical amorphization: (1) thermochemical pressurization, (2) fault lubrication due to the formation of amorphous silica, and (3) fault healing by pressure solution.

Thermochemical pressurization increases pore fluid pressure and thus decreases effective normal stress by releasing fluid during devolatilization reactions, for example, by dehydration and dehydroxylation of phyllosilicates (e.g., Brantut et al., 2010, 2011) or by thermal decomposition of carbonates (e.g., De Paola et al., 2011; Platt et al., 2015; Sulem & Famin, 2009) in response to frictional heat. The kinetic parameters of these reactions can be strongly controlled by the crystallinity of minerals. For instance, friction experiments on illite by Hirono et al. (2013) have demonstrated that mechanochemical effects (including mechanical amorphization) can induce a dramatic decrease in the activation energy of the dehydroxylation reaction, from 142.3 to 97.0 kJ mol^{-1} , allowing release of interlayer water at the relatively low temperatures of 200 – 300°C . Similarly, Vizcayno et al. (2010) demonstrated that ground kaolinite samples dehydroxylate at lower temperature with increasing milling time (i.e., with increasing amorphous content). These studies indicate that mechanical amorphization can affect the kinetic parameters of devolatilization of some phyllosilicates, including kaolinite, and decrease the temperature required to start fluid release.

Our results clearly demonstrate that, even under much lower normal stress (up to 3 MPa) than those at seismogenic depths (several tens to several hundreds of MPa), ~90 wt% of kaolinite was amorphized during slip (Figure 10). This result indicates that mechanical amorphization of kaolinite in faults during frictional slip may occur over a wide range of depths. We therefore suggest that when modeling increases in pore fluid pressure due to thermochemical pressurization in kaolinite-bearing faults, mechanical amorphization should be considered to have an influence on the kinetic parameters. Furthermore, mechanical amorphization itself may cause dynamic changes in the density and volume of solid and fluid phases and thus affect pore fluid pressure.

We next discuss the possible mechanism which leads to a gradual decrease in shear stress at displacements greater than 7 m during our experiment on quartz gouge at slip velocity 0.001 m s^{-1} ($M_{\text{am}} = 3.3 \text{ wt\%}$; Figure 3a). The formation of a thin layer of hydrated amorphous silica (usually referred to as “silica gel”) in quartz-rich fault rocks has been reported as a mechanism that can decrease the friction coefficient in faults (e.g., Di Toro et al., 2004; Goldsby & Tullis, 2002; Hayashi & Tsutsumi, 2010; Nakamura et al., 2012). Although our experiments were performed under N_2 gas condition, we placed the gouge samples into the sample assemble under air condition, and some available moisture should be present within the gouge zone. Thus, we cannot exclude the occurrence of hydration of amorphous silica as a possible mechanism for the observed gradual weakening. Furthermore, recent friction experiments performed by Rowe et al. (2019) have suggested that the friction coefficient of novaculite can be lowered by the formation of amorphous silica powder without hydration (“intraparticle plasticity” according to Rowe et al., 2019). These amorphous silica-related lubrication in LSZ may explain the observed decrease in shear stress during our experiments. On the other hand, Kanagawa et al. (2020) recently suggested that not hydration of amorphous silica (formation of silica gel) but frictional heating can be responsible for the decrease in the friction coefficient during their rotary-shear friction experiments using quartz-bearing agate gouges. This mechanism is, however, unlikely to explain a gradual weakening of our quartz gouges as we observed no significant temperature increase during the experiments at 0.001 m s^{-1} using quartz (Figure S10). Although frictional melting of quartz particles at an asperity contact can also cause fault lubrication, we observed no clear evidence of frictional melting as discussed in section 5.1. Flash heating has been suggested as a general fault weakening mechanism during frictional shear (e.g., Rice, 2006). For example, Hirose and Shimamoto (2005) suggested through their rotary-shear friction experiments on gabbro cylinders at 0.85 m s^{-1} that flash heating can reduce its friction coefficient from the peak value of ~0.8 to the steady-state value of ~0.4 without the occurrence of frictional melting. Importantly, the observed weakening due to flash heating during their experiments was initiated at the beginning of slip, which has been also reported in many studies performing similar friction experiments (e.g., Chen et al., 2017; Faulkner et al., 2011; Yao et al., 2016). On the other hand, the gradual weakening observed during our experiments required a sufficient amount of slip (~5 m) to initiate (Figure 3a), which is not consistent with the expected evolution of shear stress by flash heating. We thus conclude that frictional heating and flash heating were unlikely to be responsible for the observed weakening at 0.001 m s^{-1} using quartz in our experiments. In fact, some studies reporting the occurrence of amorphous silica-related lubrication, such as Goldsby and Tullis (2002) and Rowe et al. (2019), demonstrated that amorphous silica-related lubrication probably requires a sufficient amount of slip to form a weak layer, which is consistent with the characteristics of our experimental results (Figure 3a). On the basis of these facts and discussion, we consider amorphous silica-related lubrication as a possible weakening mechanism for some of the friction experiments at 0.001 m s^{-1} slip velocity using quartz. Among seven of our experiments on quartz at slip velocity 0.001 m s^{-1} , only HVR4598 and HVR4599 showed such a gradual decrease in shear stress (Figure S6). M_{am} for HVR4598 (3.3 wt%) was similar to that for HVR4600 (2.6 wt%), which showed no decrease in shear stress (Tables 1 and 3). These findings indicate that less than 4 wt% of amorphous silica in bulk samples may be sufficient to cause amorphous silica-related lubrication in LSZ, although the amount of amorphous silica may not be the only dominant parameter of this lubrication process.

Time-dependent strengthening of faults during interseismic periods (fault healing) is also of great importance in understanding fault motion. Pressure solution under hydrothermal conditions is one of the mechanisms that influence fault healing rate (e.g., Niemeijer et al., 2002; Spiers et al., 1989). In general, pressure solution involves three processes: dissolution, diffusion, and precipitation (e.g., Spiers et al., 1989). On the basis of creep experiments on granular quartz samples, Niemeijer et al. (2002) suggested that dissolution at grain contacts is the rate-limiting process of pressure solution if porosity is greater than ~15%, although

the rate-limiting process at lower porosities possibly changes. Given that the porosity of fault gouges deformed in a brittle manner likely increases if the surrounding rocks are sufficiently consolidated, dissolution is more likely to dominate pressure solution than either diffusion or precipitation. Because the activation energy for dissolution of amorphous material is lower than that for crystalline material (e.g., Palandri & Kharaka, 2004), it is conceivable that more extensive healing occurs in faults in which amorphous material predominates over crystalline material. However, if either diffusion or precipitation is the rate-limiting process for pressure solution, the existence of amorphous material in fault gouges may have little or no effect on fault healing.

6. Conclusions

We investigated the relationship between fault slip processes and the rate of generation of amorphous content of synthetic quartz and kaolinite fault gouges during frictional slip. We first determined calibration lines to use in association with XRD profiles to quantify the amorphous content of the gouges after a series of rotary-shear friction experiments at room temperature, with normal stresses of 1 or 3 MPa, equivalent slip velocities of 0.001 or 1 m s⁻¹, and final equivalent displacements of 1–101 m, under N₂ gas condition. The results led us to the following conclusions.

1. Mechanical amorphization of both quartz and kaolinite gouges was evident after some friction experiments and was accompanied by grain-size reduction, rounding of mineral grains, and formation of ultra-fine particles.
2. Total frictional work was the frictional parameter that dominated the rate of formation of mechanically amorphized materials in both fault gouges. Dependencies of the mechanically amorphized content of the gouges on seismic fracture energy and frictional power are nominal and have no physical meaning. The relationship between amorphous content and frictional work depends on the mineralogy of fault gouges, not on slip velocity.
3. About 7 wt% of the quartz gouge was amorphized for frictional work of 30.33 MJ kg⁻¹, whereas only 0.77 MJ kg⁻¹ was required to amorphize the same amount of kaolinite. These results clearly explain preferential amorphization of clay minerals in fault gouge. About 90 wt% of the kaolinite gouge was amorphized for frictional work of 69.51 MJ kg⁻¹.
4. When sheared at 1 m s⁻¹, the LSZs of both quartz and kaolinite gouges are capable of hosting the entire process of mechanical amorphization under the following assumptions: (i) the thickness of the LSZ is homogeneous in the entire gouge zone, and (ii) the porosity of the LSZ is zero.
5. The amount of energy used for mechanical amorphization relative to total frictional work did not exceed 0.06% for quartz gouge. In contrast, the upper limit of the ratio was 6.05% for kaolinite gouge, indicating that mechanical amorphization of kaolinite may be potentially important for understanding the energetics of faulting in rocks that are rich in kaolinite.
6. The two implications of our research for natural faults are that meaningful quantification of amorphous content in natural fault gouges requires identification of the mineralogic origin of the amorphous phase and that the presence of mechanically amorphized material in faults cannot be regarded as definitive evidence of coseismic events.
7. The three implications of our research for the processes that affect fault motion are as follows. First, given that mechanical amorphization of kaolinite can occur at much lower normal stresses (e.g., 3 MPa) than those of seismogenic zones, mechanical amorphization may need to be considered as an influence on the kinetics of devolatilization, thermochemical pressurization, and thus the fault motion of kaolinite-bearing faults. Second, amorphous silica-related fault lubrication can occur with only small amounts of amorphous silica (<4 wt%), but there may be other parameters that influence the lubrication process. Third, if dissolution at grain contacts is the rate-limiting process of pressure solution, a predominance of amorphous material over crystalline material in faults may accelerate fault healing.

Conflict of Interest

All authors declare that they have no competing interests.

Data Availability Statement

The data for this study are available online (<https://doi.org/10.6084/m9.figshare.12121554>). The data on energy budget during friction experiments in this study are available in Brigaud and Vasseur (1989), Robie et al. (1979), and Schieltz and Soliman (1964).

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