Supporting Online Material for

Ultralow Friction of Carbonate Faults Caused by Thermal Decomposition

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Materials and Methods

Specimen configuration and equivalent slip-rate
Each experiment was conducted on a pair of solid cylindrical specimens of Carrara marble (pure calcite rock from Italy) (Fig. S1). The diameter and length of the specimen are 21.8 to 24.8 mm and about 20 mm, respectively. We used solid- rather than hollow-cylindrical specimens because the latter cannot support high normal stress. To prevent thermal fracturing of the specimens due to rapid and inhomogeneous frictional heating on sliding, we mounted an aluminium sleeve (\( \sim 1.3 \) mm thick) around each specimen with a diameter of 21.8 mm and a narrow gap was left between the two aluminium sleeves to avoid metal-to-metal frictional contact, except one pair of the larger specimens (24.8 mm in diameter) for which no aluminium sleeve was used. All of our friction tests were conducted on bare surface of solid rock cylinder without pre-inserting any gouge between the specimens.

Since there is a slip-rate gradient across the fault plane due to the configuration of the cylindrical specimens (increasing slip rate from the center to the periphery of the specimen), we use ‘equivalent slip rate’ \((S_1, S_2)\) here. Assuming no velocity dependence of the shear stress, the total frictional work on a fault per unit time, \( W \), is defined by

\[
W = \tau VA = \frac{4}{3} \pi^2 R \tau (r_2^2 - r_1^2)
\]

where \( \tau \) is shear stress, \( V \) is equivalent slip rate, \( A \) is fault area, \( R \) is rotation rate, \( r_1 \) and \( r_2 \) are the inner and the outer radii of a hollow cylindrical specimen, respectively. Since the fault area, \( A \), is \( \pi (r_2^2 - r_1^2) \), the equivalent slip rate is given by
For our solid cylindrical specimens, where \( r_1 = 0 \), the above equation is written as below:

\[
V = \frac{4\pi R(r_1^2 + r_2^2)}{3(r_1 + r_2)}.
\]

where \( r \) is the radius of the solid cylindrical specimen.

**CO₂ concentration measurement**

We measured the emission of CO₂ released from deforming specimens using two solid electrolyte-type CO₂ sensors (TGS4161 with an accuracy of about 20 %; Figaro Co. Ltd., Osaka, Japan). Commercially available sensors of this type have a filter protecting the sensor. As this filter retards the response of the sensor, we used two sensors, one with and one without a filter. Sensor 1 (without a filter) was set very close to fault (about 30 mm away) to detect the onset of decomposition. It takes for this sensor about 0.9-1.0 s to yield an initial DC output and about 10 s to give outputs corresponding to the 90 % of CO₂ concentration when the sensor is instantly exposed to an atmosphere with a different CO₂ concentration. Sensor 2 with a filter has the initial response time of about 2 s and 90 % response time of around 90 s. This sensor was used to determine the total amount of CO₂ emission by putting it on a corner of the specimen chamber, sealed with tapes as much as possible, and by monitoring CO₂ concentration until the output becomes stable after the completion of experiment. The location of the sensors is shown in Fig. S2. The sensor output was directly recorded in mV for sensor 1 to shorten its response time, whereas the sensor output was transformed with an IC circuit to convert the output to CO₂ concentration in ppm for sensor 2. Neither of these sensors can yield real-time changes in CO₂ concentration accurately since it takes the sensors tens of seconds or longer to give output corresponding to the concentration.

**Temperature measurement**

We used a radiation thermometer (Minolta, TR-630A) to measure temperature along the sliding surface. The thermometer detects radiation energy emitted from a body
and the radiation enters through optical lenses into the thermometer and then is transformed into current. The thermometer equipped with a close-up lens can detect radiation energy from a small area (0.4 mm in diameter) at the measuring distance of about 20 cm that represents an average bulk temperature over the small area, but cannot give us any information on the local temperature over smaller areas. The ‘minimum’ detectable temperature is about 550 °C.

*Experiment on pre-heated specimens and treatment of specimens*

We statically heated three cylindrical specimens of Carrara marble in the oven and all the specimens were taken out of the oven at the same time and cooled in room-air. Then, we measured the weight of the specimens to check if the heating time (one and a half hours at 900 to 904 °C) was enough for the complete decomposition of the specimens and found that the weight after heating was the same as the expected weight of a fully decomposed specimen. Two of them were jacketed with aluminium sleeves and the other specimen was kept in a plastic zipper bag for the later XRD analysis. Two jacketed specimens were loaded into the friction testing apparatus and we conducted the run, HVR739. All these procedures under room-humidity condition before starting the run took less than 20 minutes. XRD analysis on the pre-heated specimen was conducted several hours later, and the X-ray diffraction spectrum for the pre-heated specimen shows strong peaks of lime and very weak, almost unnoticeable, peaks of hydrated lime without calcite peak (Fig. 2D). No peak of calcite excludes the possibility of the re-carbonation of lime which requires sequential reactions including hydration of lime followed by slow re-carbonation reaction of hydrated lime into calcite by absorbing CO₂ from air (S3). The very weak peaks of hydrated lime in the pre-decomposed specimen (Fig. 2D) raises the possibility that at least a very small amount of lime may have been hydrated when the specimen had been exposed to room humidity less than 20 minutes before the run. The hydration of lime during static heating (and friction tests at high slip rates) is unlikely, since the decomposition temperature of hydrated lime (470-640 °C, S4) is lower than that of calcite.

Concerning the question whether the possible presence of very small, if any, amount of hydrated lime has a significant effect on the strength of the fault zones consisting of lime grains, we note the weakening in the slide-hold-slide tests under room-humidity condition. In the second slide after a hold (no slide) time of up to several tens of minutes (during which the hydration of lime formed in the first slide may have occurred), the weakening was almost the same as that in the friction tests conducted at the same normal
stress and slip rate but with Ar flowing (or dry) condition. Thus, these experimental results indicate that the mechanical effect of the possible dehydration of hydrated lime is not significant.

For our early specimens carelessly left under room humidity after runs, we certainly confirmed the presence of hydrated lime (e.g. HVR464 in Fig. 2D). However, no hydrated lime was detected in specimens which were carefully stored in a desiccator with silica gel after runs (e.g. HVR520 in Fig. 2D). Thus, hydrated lime is unlikely to have formed along faults during friction experiments.

Material on slip localization surface: SEM and TEM observation

After the experiments, we observed shiny slip surfaces (or slickensides) along which slip was localized. We conducted X-ray diffraction (XRD) analysis on the material collected from the slip localization surface. New diffraction peaks of lime (and/or hydrated lime) and the significant reduction of the diffraction intensity of calcite were detected compared to undeformed specimen, indicating thermal decomposition of calcite into lime (Fig. 2D). In the analysis, no evidence of amorphous material was identified. For more detailed observation on the material collected from the slip localization surface, we have conducted field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) (Fig. S3). The TEM sample was collected from the slip surface and was dispersed in ethanol, and then a drop of ethanol was placed on a Cu grid and was covered with a formvar film. Grain aggregates of about 100 to few hundred nanometers occur and each aggregate consists of ultrafine lime grains of several to a few tens of nanometers in diameter (Fig. 2B, 2C). Those grains are so fine that it is not clear if fault slip took place along a planar surface or within a slip zone of finite width. The use of the term, “slip surface”, does not imply that slip takes place along purely planar surface since calcite gouge zone is deformed.

A selected area electron diffraction (SAED) pattern taken from the material on the slip surface shows that the material is not glass but crystalline lime (Fig. S3). The lime grains formed by thermal decomposition of calcite are unlikely to be molten since its melting temperature is too high (~2,572 °C). Furthermore, temperature on the slip surface usually decreases consistently with decreasing friction during the weakening. Thus, the weakening is more likely associated with thermal decomposition of calcite rather than melting.
Calculation of bulk temperature rise in the very early stage of HVR601

The bulk temperature rise on the sliding surface (S5) is:

$$\Delta T = 2\tau V \sqrt{t} / (c_p \rho \sqrt{\pi \kappa})$$

where $\tau$ is shear stress, $V$ is slip rate, $t$ is time, $c_p$ is specific heat, $\rho$ is density and $\kappa$ is thermal diffusivity. For the rock properties chosen for calcite marble and the sliding condition in HVR601 ($\tau = 4.7$ MPa, $V = 0.72$ m s$^{-1}$, $c_p = 835$ J kg$^{-1}$ K$^{-1}$, $\rho = 2710$ kg m$^{-3}$, $\kappa = 0.81 \times 10^{-6}$ m$^2$ s$^{-1}$), the estimated bulk temperature is as high as 850 °C in 0.2 s (before the onset of weakening). Furthermore, the flash temperature at the asperity contacts should be much higher than the bulk temperature (S6), which may indicate that thermal decomposition occurred almost immediately after the onset of slip in HVR601 (Fig. 3A, 3B) and is consistent with the observed CO$_2$ emission.

Fig. S1. Specimen configuration used in this study. Each experiment was conducted on a pair of solid cylindrical specimen of Carrara marble (pure calcite rock from Italy). We used solid- rather than hollow-cylindrical specimens because the latter cannot support high normal stress. To prevent thermal fracturing of the specimens due to rapid and inhomogeneous frictional heating on sliding, we mounted an aluminium sleeve (~1.3 mm thick) around each specimen with a diameter of 21.8 mm and a narrow gap was left between the two aluminium sleeves to avoid metal-to-metal frictional contact, except one pair of the larger specimens (24.8 mm in diameter) for which no aluminium sleeve was used. All of our friction tests were conducted on bare surface of solid rock cylinder without pre-inserting any gouge between the specimens.
Fig. S2. CO₂ sensors set for monitoring of CO₂ emission during experiment. Sensor 1 without a filter was set very close to fault (about 30 mm away) to detect the onset of decomposition. Sensor 2 with a filter was used to determine the total amount of CO₂ emission by putting it on a corner of the specimen chamber.
**Fig. S3.** SEM photomicrographs (A, B), TEM photomicrograph (C) and selected area electron diffraction (SAED) image (D) taken from the material on the slip surface (or slip localization surface). Slickenside surface with tracks is shown in the dashed red box in A. The material taken from the sliding surface consists of grain aggregates of about 100 to a few hundred nanometres in size (B). Each aggregate is composed of ultra-fine (several to a few tens of nanometres in diameter) grains (C). The red line traces are drawn to show the individual grain size. The SAED pattern indicates that the ultra-fine grains are randomly-oriented crystalline lime (D).
Fig. S4. Monitoring of CO$_2$ emission during the experiment conducted at the normal stress of 9.8 MPa and the slip rate of 0.17 m s$^{-1}$. The inset is the enlargement of the early stage of the experiment. The gray vertical bars indicate the first major emission timing of CO$_2$, considered the response time of Sensor 1, which seems to be simultaneous with the onset of weakening after the transient weakening and strengthening at the very early stage (<7s).

References