Fault gouge graphitization as evidence of past seismic slip

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ABSTRACT

One moderate- to large-magnitude earthquake (M > 6) nucleates in Earth’s crust every three days on average, but the geological record of ancient fault slip at meters-per-second seismic velocities (as opposed to subseismic slow-slip creep) remains debated because of the lack of established fault-zone evidence of seismic slip. Here we show that the irreversible temperature-dependent transformation of carbonaceous material (CM), a constituent of many fault gouges, into graphite is a reliable tracer of seismic fault slip. We sheared CM-bearing fault rocks in the laboratory at just above subseismic and at seismic velocities under both water-rich and water-deficient conditions and modeled the temperature evolution with slip. By means of micro-Raman spectroscopy and focused-ion beam transmission electron microscopy, we detected graphite grains similar to those found in the principal slip zone of the A.D. 2008 Wenchuan (Mw 7.9) earthquake (southeast Tibet) only in experiments conducted at seismic velocities. The experimental evidence presented here suggests that high-temperature pulses associated with seismic slip induce graphitization of CM. Importantly, the occurrence of graphitized fault-zone CM may allow us to ascertain the seismogenic potential of faults in areas worldwide with incomplete historical earthquake catalogues.

INTRODUCTION

Fault rocks accommodate most of the slip during earthquakes (Sibson, 2003), but their record of deformation events occurring at typical seismic slip rates of ~1 m/s, as opposed to slow-slip and aseismic creep events, remains uncertain because of the lack of unequivocal characteristics (Cowan, 1999; Rowe and Griffith, 2015). Seismic slip is thought to be accommodated in centimeter- to submillimeter-thick slipping zones, and localized frictional sliding may trigger processes such as flash heating and melting, dehydration and decarbonation reactions, and thermal decomposition of fault rocks (Sibson, 2003; Di Toro et al., 2011). Because of the relatively high seismic slip rates at seismogenic depths, the natural slipping zone should record an abrupt and transient increase in temperature during earthquakes. Importantly, disordered organic compounds or amorphous carbonaceous material (CM) can be progressively and irreversibly transformed into stable graphite through thermally activated graphitization (Buseck and Beyssac, 1994). Therefore, the progressive increase in crystallographic order of CM associated with graphitization is widely utilized as an indicator of the maximum temperatures achieved by sedimentary and metamorphic rocks (Barker and Goldstein, 1990; Beyssac et al., 2002). Because CM is also found in natural fault zones, its graphitization may provide valuable information on earthquake mechanics (Oohashi et al., 2012).

EXPERIMENTAL METHODS

To investigate the graphitization process of the CM-bearing materials, we sheared with the rotary-shear machine SHIVA (Di Toro et al., 2010; Niemeijer et al., 2011) the graphite-free rocks of the fault breccia retrieved from 589.32 m depth. The bulk fault breccia was gently pulverized down to <250 μm in size and poured into a ring-shaped metal sample holder designed for confinement of non-cohesive materials (Smith et al., 2012). The gouges were sheared for 3 m of slip at equivalent slip rates, V, of 0.0003 m/s (simulating just above subseismic, referred as subseismic hereafter) and 3 m/s (seismic) under a normal stress of 8.5 MPa. The experiments were conducted on 5 g of gouges (corresponding to an initial thickness of ~3 mm) at room temperature and humidity and, by the addition of 0.5 g of distilled water, at water-dampened conditions. Deformed samples were collected for microanalytical investigations including micro-Raman spectroscopy, field-emission scanning electron microscopy (FESEM), and focused ion beam–transmission electron microscopy (FIB-TEM) with energy dispersive X-ray spectroscopy (EDS). The natural materials of the active fault zone (black gouge and breccia) were investigated with micro-Raman spectroscopy and compared with the experimental products (Fig. 1).

RESULTS

The mechanical data, consistent with previous studies (Oohashi et al., 2011; Rutter et al., 2013; Kuo et al., 2014; Kouketsu et al., 2017), resulted...
in two slip velocity–dependent behaviors (Fig. 2; Item DR2 in the GSA Data Repository1). When sheared at seismic slip rates \((V = 3\ \text{m/s})\), the experimental gouges showed pronounced weakening, with the apparent friction coefficient (defined as the ratio of shear stress to normal stress) decaying, in the room-humidity experiments, from a peak value of 0.50 to a minimum value of 0.20, and in the water-dampened experiments, from 0.18 to 0.02 (the latter had a quite complicated evolution of the friction coefficient, with minimum friction followed by re-strengthening up to 0.2 after 0.5 m and 0.25 after 2.3 m of slip). In contrast, when the gouges were sheared at subseismic slip rates \((V = 0.0003\ \text{m/s})\), the effective friction coefficient evolved with slip from an initial value of 0.40 up to ~0.55 under room-humidity conditions, and from 0.26 to 0.37 under water-dampened conditions. The temperature evolution with slip was modeled with COMSOL Multiphysics software (https://www.comsol.com) using the measured frictional power dissipation (product of shear stress with slip rate) and the thermal properties of the WFSD fault gouge (Item DR3; Li et al., 2015). The initial temperature for the modeling was set to 25°C. In the slipping zone of the gouge layer sheared under room-humidity conditions at 3 m/s (experiment s1108; seismic, RH in Fig. 2), the modeled temperature rose from 25°C to ~200°C after 0.5 m of slip, and further increased up to ~300°C by the end of the experiment. Instead, under water-dampened conditions (s1105; seismic, WD in Fig. 2), the temperature increased up to ~50°C after 0.5 m of slip and progressively to ~280°C until the sample was decelerated and the experiment completed. The modeled temperature in the gouges sheared at subseismic slip rates \((V = 0.0003\ \text{m/s})\) was ~26°C independent of the presence of liquid water (Fig. 2).

In Raman spectroscopy, the peak parameters of the D1 (defect) band and the G (graphite) band are commonly used as a gauge to quantify the degree of the graphitization process (Beyssac et al., 2002, 2003) (Fig. 1B, inset; Item DR4). Here the ratio of D1 to G peak width was compared with the ratio of D1 to G peak intensity. The ratio of D1 to G peak width of either starting material (i.e., gouges) or fault breccia, normalized with the average peak width of the fault breccia, was compared to peak position (i.e., Raman shift). We analyzed five fault breccia samples, seven black gouge samples (including the PSZ of the 2008 Wenchuan earthquake), one starting material (fault breccia), and four experimental products, the latter obtained under a range of deformation conditions (Items DR5 and DR6).

The black gouge samples, compared to the fault breccia, have a lower D1/G peak intensity ratio and higher D1/G peak width ratio (Fig. 1B). Although fault breccia and black gouge have similar D1 band position, the G band position of the black gouge has higher frequency (Fig. 1C). In addition, the G peak width ratio of the black gouge was smaller than that of the fault breccia.

Independent of the imposed slip rates and the presence of liquid water, the sheared gouges have a lower D1/G peak intensity ratio and higher D1/G peak width ratio with respect to the starting materials (Fig. 3A). Both starting materials and deformed gouges have a similar D1 band position and peak width ratio (Fig. 3B). Variations occur in the G band position and peak width ratio, comparing sheared samples with starting material (Fig. 3B). In the sheared materials, the G band position is shifted to higher wavelength numbers independent of slip rates.

Strain localization in the gouge layers occurred during rock deformation experiments at both subseismic and seismic rates in both wet and room-humidity conditions, developing an experimental PSZ (Figs. 4A and 4B). Volumes of the slipping zones that underwent the highest degree of strain localization were investigated with FIB-TEM-EDS and selected area electron diffraction. Starting materials and gouges sheared at subseismic slip rates had amorphous carbon (i.e., no graphite) and similar disordered regions of ~1–200 nm in size (Fig. 4C). On the contrary, gouges sheared at seismic slip rates had perfectly stacking layers (lattice spacing of d002 ~3.55Å) in...
defect-free carbon-built grains with ordered structures, suggesting that amorphous carbon was transformed into graphitic carbon (Fig. 4D; Item DR1).

**DISCUSSION AND CONCLUSION**

Amorphous CM usually contains two types of electronic configuration of carbon atoms: sp³ or diamond-like, and sp² or graphite-like. The conversion of sp³-bond carbon into sp²-bond carbon results in graphitization of CM and in the transformation of the sp²-bond carbon into graphite (Ferrari and Robertson, 2000). It is well established that the D1/G peak intensity ratio is inversely proportional to the average size of the sp² clusters from conversion of sp³ bonds (Fig. 3A; Ferrari and Robertson, 2000). In addition, the G band shifts toward higher frequencies in the gouges sheared at both subseismic and seismic slip rates (Fig. 3B). Therefore, the Raman spectra on experimental products show that the transformation of sp²-bond carbon into sp²-bond carbon in the amorphous carbon network was driven by bulk shear strain, suggesting rehybridization of interacting dangling bonds of carbon during both subseismic and seismic slip (Pastewka et al., 2011).

Heating has been suggested to order phases of sp² and result in the formation of graphite from clusters of carbon atoms (Thomas et al., 2006), determining a smaller G band peak width (Beyssac et al., 2002). In the experiments performed on gouges at seismic slip rates and room-humidity conditions, high temperatures (up to 300 °C) were achieved during frictional sliding, and the small width ratio of G bands (red triangles in Fig. 3B; Fig. 4D) suggests the crystallization of carbon into graphite. By contrast, in the water-dampened experiments performed on gouges at seismic slip rates, water vaporization possibly buffered the temperature increase (limited to <200 °C) and impeded the formation of graphite (blue triangles in Fig. 3B; Chen et al., 2017). Moreover, in the experiments performed at subseismic slip rates and independent of the water content, the temperature remained at ~26 °C (Fig. 2). In the latter sheared gouges, the similar width ratio of both D1 and G compared to the starting materials suggest the presence of a random-order sp²-bond domain (Figs. 3B and 4C; Item DR1) and, therefore, the absence of graphitization processes.

Our rock friction experiments demonstrate that CM graphitization is characterized by (1) decreasing D1/G peak intensity ratio, (2) shift of G peak position toward higher frequencies, and (3) smaller peak width ratio than the starting materials. The changes in the Raman spectra result from the formation of sp² clusters in the CM due to strain (Ross and Bustin, 1990) rather than strain rate. Instead, the decrease in G band peak width ratio, which indicates increased crystallinity of the CM, is attributed to frictional heating. As a consequence, the microstructural and/or mineralogical evolution of CM (amorphous at subseismic slip rates and reordering and graphitization at seismic slip rates) may allow us to individuate active seismogenic faults. However, the absence of evidence of graphitization processes in CM-bearing gouges (see wet experiments at seismic rates) is not indicative of aseismic behavior of the faults.

Because our experiments at seismic slip rates, and in the absence of liquid water, showed enhanced graphitization of CM (Fig. 3), we may interpret the analyses on WFSD-1 fault rocks as follows. The anti-correlation between peak width ratio and peak intensity ratio suggests that the transformation of sp³-bond carbon into sp²-bond carbon occurs within the black gouge (Fig. 1B), and a shift to high frequency of the G band from breccia to gouge is presumably due to strain (Fig. 1C). In particular, the narrower G peak width of black gouge suggests that CM contains abundant well-ordered sp² domains, implying that the black gouge was exposed to an increase in temperature under water-deficient conditions (Kuo et al., 2014). Permeability measurements of the WFSD-1 borehole suggested that coseismic drainage was critical for later heating the fault damage associated with seismic rupture propagation (Xue et al., 2013). It seems likely that, during seismic slip, pore fluids were expelled from the slipping zone, and seismic slip resulted in locally dry conditions allowing gouge graphitization. This hypothesis is consistent with the finding of pseudotachylites (solidified friction melts typically associated with seismic slip under water-deficient conditions; Sibson and Toy, 2006) in the PSZ of the 2008 Mw 7.9 Wenchuan earthquake retrieved at ~1000
m depth from the WFSD-1 borehole (Wang et al., 2016). In addition, because water circulation was vigorous within the fault zone following the main shock (Xue et al., 2013), other chemical interactions with carbon and hydrothermal fluid at various ambient conditions must be taken into consideration (Oohashi et al., 2012; Rumble, 2014).

Importantly, the fault-zone wall rocks have lower thermal conductivity (~1 W m⁻¹ K⁻¹) compared to the sample metal holder (~40 W m⁻¹ K⁻¹; Item DR3). In nature, compared to the experiments, this should result in a higher temperature rise and longer duration of higher temperatures, favoring graphitization kinetics during seismic slip (Yao et al., 2015). However, the higher G peak width ratio of the natural gouges with respect to the gouge deformed at room-humidity conditions implies that the natural gouges were exposed to lower frictional power dissipation with respect to the experimental gouges. Coseismic fluid drainage (and water vaporization) efficiently dissipated the frictional heat generated during seismic slip, buffering the temperature increase, and therefore resulting in less temperature-induced graphitization (Fig. 1C). The micro-Raman measurements presented here are in accordance with those from the WFSD-1 borehole (Kuo et al., 2014; Si et al., 2015) and support the interpretation that the Longmenshan fault was extremely weak during seismic slip.

Our results find application in determining seismic fault movement in general. Due to the resistance of graphitized products to alteration and weathering, the state of graphitization of CM (if graphite is related to faulting and not due to precipitation from percolating fluids, etc.) could be a suitable indicator of historical or ancient earthquakes in faults. Only low-grade amorphous CM was found in the surface rupture of the Longmenshan fault (Kouketsu et al., 2017), suggesting that graphitization requires a certain amount of energy (shear stress, strain, and temperature) to be triggered (Kuo et al., 2014). As a consequence, the presence of graphite at depth (>500 m) within active fault zones might be a robust indicator of seismic hazard in areas worldwide with incomplete historical earthquake catalogues.

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