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 such an event is usually limited to the slow slip regimes. This gap between seismic events and the geological record is due to the lack of evidence for the occurrence of past earthquakes. However, the presence of graphite in fault zones can provide valuable information on earthquake mechanics (Oohashi et al., 2012).

Fault zone graphitization has been proposed for the principal slip zone (PSZ) of the Longmenshan thrust fault that ruptured in a devastating A.D. 2008 Mw 7.9 Wenchuan earthquake in southeast Tibet (Kuo et al., 2014). According to data from the Wenchuan Earthquake Fault Scientific Drilling-1 project borehole 1 (WFSD-1), at 590 m depth, the active fault zone includes an ~54-cm-thick black gouge made of quartz, feldspar, clay minerals, plus graphite and CM, surrounded by an ~2-m-thick fault breccia made of quartz, feldspar, calcite, clay minerals, and CM (mainly poorly crystalline anthracite), but without graphite (Fig. 1). Li et al. (2013), Si et al. (2014), Wang et al. (2014) demonstrated that CM within the Wenchuan fault zone originated from adjacent host rocks (Late Triassic Xujiahe Formation). Kuo et al. (2014) speculated that gouge graphitization occurred within CM-bearing fault gouges during the 2008 Mw 7.9 Wenchuan earthquake. However, it remained unclear if CM graphitization could be associated only with seismic slip. These crucial questions are addressed here, where we also demonstrate that the experimental products obtained at seismic slip rates are almost identical to those found in the PSZ of the Longmenshan fault, making CM graphitization a powerful tool to investigate the seismogenic potential of active faults, especially if cropping out in areas with incomplete historical earthquake catalogues.

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 a mechanical and petrological model of the fault zone that is consistent with the observed graphite and CM distribution.
in two slip velocity–dependent behaviors (Fig. 2; Item DR2 in the GSA Data Repository1). When sheared at seismic slip rates (V = 3 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 = 0.003 m/s), the effective friction coefficient evolved with slip from an initial value of 0.40 up to ~0.55 under 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 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 conditions (s1105; seismic, WD and s1104; room-humidity, RH). 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

1GSA Data Repository item 2017329, Items DR1–DR6 (summary of experiments, methods, and results), is available online at http://www.geosociety.org /datarepository/2017/ or on request from editing@geosociety.org.

Figure 1. Wenchuan Earthquake Fault Scientific Drilling WFSD-1 borehole (southeast Tibet) core with location of studied samples and results of micro-Raman analysis. A: Core images exhibiting major portions of Longmenshan fault along WFSD-1 borehole. Locations of analyzed samples are indicated by red (black gouge) and black (breccia) boxes. B: Defect band (D1) to graphite band (G) (D1/G) peak width ratio with respect to fault breccia. Inset shows representative first-order region of Raman spectrum and defines relevant spectrum decomposition parameters (width, intensity, etc.). The D3 band is attributed to out-of-phase defects. C: Ratio of D1 or G peak width of gouge to average breccia peak width versus G band peak position. Inset shows systematic shift toward higher frequencies of G band observed in black gouge with respect to fault breccia. PSZ—principal slip zone.
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 WSFSD-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 WSFSD-1 borehole suggested that coseismic drainage was critical for later healing 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 pseudotachylytes (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., 2014; Li 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 gouge 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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REFERENCES CITED

Barker, C.E., and Goldstein, R.H., 1990, Fluid-inclusion technique for determining maximum temperature in calcite and its comparison to the vitrinite reflectance geothermometer: Geology, v. 18, p. 1003–1006, doi:10.1130/0091-7613(1990)018<1003:FITFDM>2.3.CO;2.

Beyssac, Q., Goffé, B., Chopin, C., and Rouzaud, J.N., 2002, Raman spectra of carbonaceous materials in a fault zone in the Longmenshan belt, China: Correlations with those of sedimentary and metamorphic rocks: Tectonophysics, v. 369, p. 129–145, doi:10.1016/S0040-1951(02)00324-7.

Li, P., et al., 2013, Characteristics of the fault-related rocks, fault zones and the principal slip zone in the Wenchuan Earthquake Fault Scientific Drilling Hole-1 (WFSD-1): Tectonophysics, v. 584, p. 23–42, doi:10.1016/j.tecto.2012.08.021.

Kuo, L.W., Li, H., Smith, S., Di Toro, G., Suppe, J., Song, S.R., Nielsen, S., Sheu, H.S., and Ji, S., 2014, Gouge graphitization and dynamic fault weakening during the 2008 Mw 7.9 Wenchuan earthquake: Geology, v. 42, p. 47–50, doi:10.1130/G34862.1.

PROC. GEOL. UNION, ROME 2016: Union Geophysical Monograph 170, p. 153–166, doi:10.1029/170GM16.

Ross, J.V., and Bustin, R.M., 1990, The role of strain energy in creep graphitization of anhydrite: Nature, v. 343, p. 58–60, doi:10.1038/343058a0.

Ross, J.V., and Griffith, W.A., 2015, Do faults preserve a record of seismic slip? A second opinion: Journal of Structural Geology, v. 78, p. 1–26, doi:10.1016/j.jsg.2015.06.006.

Rumble, D., 2014, Hydrothermal graphitic carbon: Elements, v. 10, p. 427–433, doi:10.2113/gselements.10.6.427.

Rutter, E.H., Hackston, A.J., Yeatman, E., Brodie, K.H., Mecklenburg, J., and May, S.E., 2013, Reduction of friction on geological faults by weak-phase smearing: Journal of Structural Geology, v. 51, p. 52–60, doi:10.1016/j.jsg.2013.03.008.

Si, J., Li, H., Kuo, L.W., Pei, J., Song, S.R., and Wang, H., 2014, Clay mineral anomalies in the Yingxiu-Beichuan fault zone from the WFSD-1 drilling core and its implication for the faulting mechanism during the 2008 Wenchuan earthquake (Mw 7.9): Geology, v. 41, p. 171–178, doi:10.1130/G33588.1.

Sibson, R.H., 2003, Thickness of the seismic slip zone: Bulletin of the Seismological Society of America, v. 93, p. 1169–1178, doi:10.1785/0120020061.

Sibson, R.H., and Toy, V.G., 2006, The habitat of fault-generated pseudotachylyte: Present vs. absence of friction-melt, in Abercrombie, R., et al., eds., Earthquakes: Radiated Energy and the Physics of Faulting: American Geophysical Union Geophysical Monograph 170, p. 153–166, doi:10.1029/170GM16.

Smith, S.A.F., Di Toro, G., Kim, S., Ree, J.-H., Nielsen, S., Billi, A., and Spiess, R., 2012, Coseismic recrystallization during shallow earthquake slip: Geology, v. 41, p. 63–66, doi:10.1130/G33588.1.

Thomas, P., Delbe, K., Himmel, D., Mansot, J.L., Cadore, F., and Guerin, K., 2006, Tribological properties of low-temperature graphite fluorides: Influence of the structure on the lubricating performances: Journal of Physics and Chemistry of Solids, v. 67, p. 1095–1099, doi:10.1016/j.jpcs.2006.01.084.

Wang, H., Li, H., Janssen, C., and He, X., 2016, Seismic energy partitioning during the 2008 Wenchuan earthquake from WFSD-1 core sample: Abstract S33C–2850 presented at the 2016 Fall Meeting, American Geophysical Union, San Francisco, California, 12–16 December.

Yao, L., Ma, S., Shimamoto, T., Yao, L., Chen, J., Yang, X., He, H., Dang, J., Hou, L., and Togo, T., 2014, Internal structures and high-velocity frictional properties of Longmenshan fault zone at Shexinxiu activated during the 2008 Wenchuan earthquake: Earthquake Science, v. 27, p. 499–528, doi:10.1785/0120150096-6.

Xue, L., et al., 2013, Continuous permeability measurements record healing inside the Wenchuan earthquake fault zone: Science, v. 340, p. 1555–1559, doi:10.1126/science.1237237.

Yao, L., Ma, S., Platt, J.D., Niemeier, A.R., and Shimamoto, T., 2015, The crucial role of temperature in high-velocity weakening of faults: Experiments on gouge using host blocks with different thermal conductivities: Geology, v. 44, p. 63–66, doi:10.1130/G37310.1.

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