ABSTRACT

Hydrolytic weakening has been suggested as a major process facilitating strain localization, in line with many studies that found a positive correlation between water content and intensity of deformation. We examine the role of water in the unusually thick ultramylonite of the El Pichao shear zone, northwestern Argentina. We used Fourier transform infrared spectroscopy to measure water content in quartz and feldspar, comparing ultramylonitic rocks to mylonites and weakly deformed rocks. Quartz and feldspar in ultramylonites contained half the water of weakly deformed rocks, contrary to findings in previous studies. We propose that the kilometer-thick ultramylonite formed in three stages: (1) localized deformation and recrystallization caused release of intracrystalline water to grain boundaries, which promoted grain-boundary sliding, forming the ultramylonite; (2) high pressure in the shear zone continuously expelled intercrystalline water to the surroundings, drying the boundaries and leading to strain hardening; and (3) water migrated to less deformed rocks causing hydrolytic weakening, repeating the cycle and widening the ultramylonite.

INTRODUCTION

Strain localization creates strongly deformed shear zones. Strain weakening allows shear zones to narrow or to maintain a steady-state width (Platt and Behr, 2011). Alternatively, shear zone strength may increase due to strain hardening, caused by accumulation of dislocations, growth of harder minerals, dehydration of the shear zone, or changes in deformation style (Hull, 1988; Johnson et al., 2011; Oliot et al., 2014). This causes widening of the shear zone (Means, 1984), which may also occur when the host rock weakens due to water influx (e.g., Oliot et al., 2014; Sibson, 1977).

The weakening effect of molecular H₂O and OH species (herein referred to as “water”) on quartz was first proposed by Griggs and Blacic (1964, 1965). When water resides on grain boundaries, it reduces the intercrystalline rock strength, facilitating dissolution–precipitation and accelerating grain boundary migration (GBM) and grain boundary sliding (GBS) (e.g., Chen and Argon, 1979; Kronenberg, 1994; Mancktelow and Pennacchioni, 2004). When it resides in crystals, water can weaken crystals in a number of ways, including by hydrolysis, which decreases the strength of Si-O bonds (hydrolytic weakening; Griggs and Blacic, 1965). This allows easier glide of dislocations (Kohlstedt, 2006), diffusion at lower temperatures (Sibson, 1977), and an increase in the number of cation vacancies (Hobbs, 1981). Molecular water is unlikely to be the main cause of hydrolytic weakening because the equilibrium solubility of water in quartz (H:106 Si ratio <200; Paterson, 1989) is an order of magnitude lower than the amount required for hydrolytic weakening (values of H:106 Si from hundreds to thousands; Kronenberg et al., 1990; Nakashima et al., 1995). Instead it has been suggested that water in dislocations and fluid inclusions may increase water activity and allow higher rates of diffusion through the lattice (Gerretsen et al., 1989; Kronenberg et al., 1990; Paterson, 1989; Post and Tullis, 1998).

Studies on naturally deformed rocks using Fourier transform infrared spectroscopy (FTIR) have found that water content increases with deformation. In a narrow granitic shear zone, Kronenberg et al. (1990) found that water content in quartz increased from <2000 H:106 Si in the protolith to 4000–11000 H:106 Si in the most deformed rocks. This study and others concluded that the high water content caused weakening and strain localization in quartz and also feldspar (see also Han et al., 2013; Kronenberg and Wolf, 1990; Nakashima et al., 1995). However, alteration in feldspar affects the water content (Nakashima et al., 1995) and was not described in these studies.

Fluids in shear zones may also reside on grain boundaries. A free fluid phase may be externally derived or may develop in situ through liberation of fluids from hydrous phases (e.g., Mittempergher et al., 2014) and from quartz and feldspar during recrystallization (Kerrich, 1976). Faleiros et al. (2010) found that quartz recrystallized by subgrain rotation (SGR) or GBM contained fewer fluid inclusions than unrecrystallized grains. Thus, recrystallization and mineral breakdown free up water that may then be extracted from the shear zone (Mancktelow, 2002; Oliot et al., 2014), weakening its margins (Oliot et al., 2014). In this case, the most deformed rocks should contain less water than their protoliths, a possibility at odds with the current literature.

GEOLoGIC SETTING AND ROCK DESCRIPTION

The PSZ is exposed in Sierra de Quilmes, part of the Sierras Pampeanas in northwestern Argentina (Fig. 1). Regional metamorphism and thrusting on the PSZ occurred during the Famatinian orogeny (490–430 Ma; Büttner et al., 2005; Finch et al., 2015). The 1-km-thick basal ultramylonite of the PSZ contains less deformed lithons of mylonites, protomylonites, and diatexites. The diatexites in these lithons are the protoliths to the ultramylonite (see the GSA Data Repository1 for further details), an interpretation supported by geochemical similarities and characteristic gradational contacts between rock types (see Finch et al., 2015). The protolith consists of phenocrysts of feldspar, quartz, and garnet in a matrix of Qtz + Kfs + Pl + Bt ± Ms ± Chl ± Sil ± Ap (Finch et al., 2015), and shearing led to feldspathic and micaceous layers and quartz ribbons.

Transition from protolith through to ultramylonites is defined by an increase in the proportion of recrystallized matrix and a decrease in size and proportion of quartz ribbons and porphyroclasts (Fig. DR1 in the Data Repository). The matrix of protomylonitic and mylonitic rocks has a mean quartz grain size of 95 ± 20 μm and mica grain size of 170 ± 60 μm, whereas ultramylonites show a mean quartz grain size of 60 ± 10 μm and mean mica grain size of 120 ± 40 μm (Finch et al., 2015). Quartz ribbons decrease in length from ~1.75 mm in protomylonites to 1.5 mm in mylonites and <0.5 mm in ultramylonites.

We investigate the role of water in the 1-km-thick ultramylonite at the base of the 3.5-km-thick El Pichao shear zone (PSZ) in northwestern Argentina (Fig. 1; Finch et al., 2015). Following Sibson (1977), protomylonites consist of 10%–50% recrystallized matrix, mylonites 50%–90%, and ultramylonites >90%. After describing the microstructures of the three rock types, we present the results of an FTIR investigation of the water content in rocks with different strains and, expanding on the model of Oliot et al. (2014), propose a model for the origin of the exceptionally thick ultramylonite.

1GSA Data Repository item 2016195, supplementary methods and results, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org.
in ultramylonites. The minimum diameter of roughly elliptical porphyroclasts also changes from 3.8 ± 2.5 mm in weakly deformed orthogneisses and protomylonites, to 3.3 ± 2 mm in mylonites, to 1.85 ± 1.3 mm in ultramylonites. Deformation occurred at amphibolite facies (Finch et al., 2015), and analysis of the crystallographic preferred orientation (CPO) of quartz indicates that mylonites show stronger CPO than protomylonites and both rock types deformed by grain size–insensitive creep and underwent grain-size reduction through recrystallization (see the Data Repository for details). In contrast, ultramylonites deformed by grain size–sensitive processes, which caused phase mixing and weakened the CPO (Figs. DR1 and DR4).

METHOD
We measured water concentration in quartz and feldspars by FTIR in one double-polished XZ thin section for each sample (for sample thicknesses, see Table DR1 in the Data Repository) using a Varian FTS 7000 FTIR spectrometer with a Varian 600 UMA microscope. Samples were collected from across the width of the ultramylonite and its less deformed lithons. Note that samples from locations now only a few hundred meters apart across strike may have been originally kilometers apart (e.g., Shelley and Bossière, 2002; see the Data Repository for a description of the sampling). Samples were separated into three categories: (1) weakly deformed rocks, (2) mylonites, and (3) ultramylonites. Protomylonites contained only a few percent more recrystallized matrix than diaclastics, so they were grouped together. Spectra were collected from a range of locations within samples, including quartz and feldspar in the matrix, quartz ribbons, and cores and edges of porphyroclasts (Fig. DR2). Between 15 and 92 spectra were collected for each type of location in each sample, depending on the number of optically clear areas.

OH species give rise to sharp absorptions at 3650 and 3200 cm⁻¹ due to hydrogen point defects, and a broad absorbance peak from 2800 to 3800 cm⁻¹ due to fluid inclusions (Kats, 1962; Kronenberg, 1994). The latter broad peak is associated with hydrolytic weakening, and the height of the peak increases with greater water content (Kekulawala et al., 1978). The concentration of OH and H₂O in quartz was calculated as the integral area under the peak using the calibration of Gleason and DeSisto (2008) and Kronenberg and Wolf (1990) (see the Data Repository).

FTIR RESULTS
The data show that mean water content is lowest in ultramylonites and highest in mylonites and weakly deformed rocks in all grain types, and all values have large standard deviations (Table 1; Fig. 2; e.g., Gleason and DeSisto, 2008; Han et al., 2013) that reflect the many sites water can reside (Post and Tullis, 1998). A modified version of the Analysis of Variance test (ANOVA) and post-hoc tests were used to test if the mean values for each group of results were significantly different. ANOVA tests whether the variance is a result of natural scatter (null hypothesis) or a result of the data forming statistically different groups. We found that water content in matrix and ribbon quartz in ultramylonites is significantly lower than in weakly deformed rocks and mylonites (see the Data Repository). Feldspar in matrix and edges of porphyroclasts in ultramylonites and mylonites contain significantly less water than in weakly deformed rocks, with no statistical difference between mylonites and ultramylonites. Porphyroclast cores in ultramylonites also contain significantly less water than those in weakly deformed and mylonitic rocks, whereas the latter two are statistically indistinguishable. We found a small to moderate positive correlation (correlation coefficient $R = 0.3343$; see the Data Repository) between porphyroclast size and water content in porphyroclast cores in mylonites, and a moderate correlation in ultramylonites ($R = 0.44$).

DISCUSSION
Low Water Content in Ultramylonites
The decrease in water content in quartz and feldspar as strain increases in the PSZ (Fig. 2; Figs. DR5 and DR6) is the opposite of what the literature reports. While our findings could indicate that the ultramylonites developed from water-poor protoliths, they are more suggestive of a process of water loss during deformation (Faleiros et al., 2010; Kerrich, 1976). As discussed earlier, ultramylonites have the same composition and were likely derived from diaclastics (Finch et al., 2015). Furthermore, ultramylonites from across the shear zone were originally far apart, and local differences in composition and water content may have been homogenized through shearing. Finally, if the
between water content in porphyroclast cores. However, we found a positive correlation in ultramylonites developed in typical diatexites, such as those preserved in lithons.

The finding that feldspar porphyroclast cores in ultramylonites have lower water contents than their less deformed lithons (Figs. DR5 and DR6) could support the hypothesis that ultramylonites had drier protoliths than less deformed rocks. However, we found a positive correlation between water content in porphyroclast cores and their size in ultramylonites and mylonites, and an absence of such a correlation in weakly deformed rocks (Table DR3). This suggests that water has been lost by strongly deformed porphyroclasts, which could be due to water loss during multiple episodes of fracturing and healing, such as might be expected during clast rotation and erosion. This may be similar to the fracturing and degassing of volcanic glasses out of equilibrium with the surroundings (Cabrera et al., 2011; Tuffen et al., 2003). Additionally, Figure DR5 shows that weakly deformed rocks have higher water content in porphyroclast rims than cores. While it is possible that these rims are magmatic and have retained their original water content, it is more likely that they represent late hydration as a result of water influx originating from the dehydrating ultramylonites.

In summary, while we cannot rule out that ultramylonite protoliths were originally water poor, we argue that deformation is responsible for the systematic decrease in water content with increased strain.

**Hydrolytic Weakening in Natural Shear Zones**

The contrast between our results and the high water content in sheared rocks found in other studies may be due to (1) limited water loss during deformation or (2) water infiltration after deformation with efficient diffusion into highly strained zones (Gleason and DeSisto, 2008). Kronenberg et al. (1990) demonstrated that water in the rocks they studied resided in fluid inclusions in microfractures that formed before ductile shearing and suggested that hydrolytic weakening caused strain localization. The lack of extensive recrystallization in their rocks suggests that much of the original water may have remained trapped in the grains.

The same cannot be concluded for studies where rocks are substantially recrystallized (e.g., Gleason and DeSisto, 2008; Han et al., 2013; Nakashima et al., 1995). Positive correlation between water content and deformation in these studies may be due to post-tectonic diffusion of water (Gleason and DeSisto, 2008), perhaps introduced by fault surfaces (e.g., McCaig, 1997). In ultramylonites in the PSZ, water content is highest in the matrix possibly due to late greenschist facies rehydration, evidenced by weak chloritization.

High water content in some shear zones may occur if water remains trapped. The fate of water is controlled by pressure gradients. Shear zones that initiate or rotate into the field of instantaneous shortening thicken due to stretching perpendicular to the shear zone boundaries, reducing mean stress within the shear zone and attracting water into it (Mancktelow, 2002). Only shear zones that rotate to the instantaneous extension direction and undergo stretching and thinning experience higher mean stress than the surroundings, leading to water expulsion (Mancktelow, 2002) and shear zone hardening.

**Water Extraction and Widening of Shear Zones**

Fusseis et al. (2009) suggested in their “dynamic granular fluid pump” model that migration of water through shear zones may be facilitated by GBS, which leads to opening and closure of cavities that pump fluids through the rock. Oliot et al. (2014) combined this model with the pressure gradient model of Mancktelow (2002) to explain widening of a shear zone. They determined that weak rocks in the center of the shear zone experienced grain-size decrease and then began deforming by fluid-assisted granular flow. This gave rise to a pressure gradient that expelled fluids causing hydraulic microfracturing, metasomatism, weakening of the host rock, and shear zone widening (Oliot et al., 2010, 2014). We propose a variation on this model.

Deformation in the PSZ likely localized into a narrow, propitious site (Fig. 3A) through grain size–insensitive mechanisms. This process generated heat, reduced grain size, and caused liberation of water to grain boundaries (Fig. 3A; Faleiros et al., 2010; Kerrich, 1976). High pressure and shear heating expelled water, which weakened the surroundings, widening the shear zone. As deformation progressed and grain size decreased, fluids on grain boundaries in the shear zone promoted grain size–sensitive creep, including GBS (Fig. 3A), and allowed fluid-assisted granular flow (Oliot et al., 2014). These processes caused phase mixing and decreased connectivity of weak phases, homogenizing the rock and giving rise to the ultramylonite. While the rate of water expulsion from the shear zone was roughly balanced with the rate of intracrystalline water liberation by recrystallization, a weak rheology was maintained in the shear zone (Fig. 3A). We suggest that as the rate of intracrystalline water liberation slowed due to continued water loss, the ultramylonite hardened due to inhibition of grain boundary sliding, eventually becoming stronger than the weakened shear zone margins (Fig. 3B). This refocused deformation to the margins and caused repetition of the cycle, gradually building up the 1-km-thick layer of ultramylonite.

**CONCLUSIONS**

Rocks in the ultramylonitic base of the PSZ contain less water than their weakly deformed protoliths, consistent with studies that have found that recrystallization liberates intracrystalline water but is inconsistent with most other studies of natural shear zones. We suggest that some of these shear zones may have undergone limited recrystallization, minimizing water loss, while others may have been hydrated due to post-tectonic fluid infiltration. We expand on the model of Oliot et al. (2014) and propose that the water expulsion cycle—characterized by recrystallization and water liberation within the shear zone, water migration causing weakening of the shear...
zone margins, hardening of the ultramylonite through water loss, and movement of the locus of maximum strain outwards—is responsible for building up this anomalously thick ultramylonite.

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