Fracture-induced pore fluid pressure weakening and dehydration of serpentinite

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**A B S T R A C T**

We investigate the strength, deformation processes, and pore fluid weakening during localized shear of antigorite serpentinite. Recent work has shown that some phyllosilicates, including antigorite, undergo a reverse transition from ductile to localized deformation at the pressure-temperature conditions of deep slow slip and tremor in subduction zones. Here, we investigate the processes that lead to and occur during localized deformation. Because high pore fluid pressure is hypothesized to control the location and style of fault slip at these conditions, we investigate the role of pore fluids on these deformation processes. We present the results of undrained general shear experiments on antigorite-rich serpentinite deformed to varying strains at 500°C, 1 GPa pressure, and with 0 to 2 wt.% added pore water. At all fluid conditions, the serpentinite exhibits strain hardening during distributed deformation and subsequent strain weakening associated with the formation of a prominent shear fracture zone. The magnitude of strain weakening correlates with increasing pore water content. We evaluate two end-member scenarios for how the effective stress influences strength during localized deformation and find that either an increase in fluid pressure or increase in the parameter \(\alpha\) the effective stress can explain the weakening. At all fluid conditions, we also find evidence for localized dehydration of antigorite within the fracture zones, at pressures and temperatures where antigorite is considered stable. Although the extent of the reaction did not measurably affect fault strength in our experiments, at the time scales of in-situ deformation in the Earth, reaction weakening and associated pore fluid pressurization may occur.

1. Introduction

Some phyllosilicates that are common in subduction zone lithologies have mechanical properties distinct from other silicates. These lithologies undergo ‘reverse’ transitions from ductile (distributed) to localized deformation with increasing temperature (Escartin et al., 2008; Chernak and Hirth, 2011; Brantut et al., 2011; Proctor and Hirth, 2016; Gasc et al., 2017). The temperature at which this transition occurs is consistent with the locations of slow slip phenomena below the subduction seismogenic zone and along the deep San Andreas fault where subduction-related phyllosilicate-rich rocks are thought to exist (Escartin et al., 2008; Proctor and Hirth, 2016). As a result, the unique material properties of these minerals may impart some control on how these plate boundary faults slip.

High pore fluid pressure is also proposed to control the location and style of fault slip at the conditions of deep slow slip and tremor (e.g., Dobson et al., 2002; Kodaira et al., 2004; Thomas et al., 2009). Currently, the mechanical effects of pore fluids are approximated by extrapolating data from low pressure laboratory measurements (≤ 300 MPa) to pressures at the base of the subduction seismogenic zone (≈ 1 GPa) (e.g., Gao and Wang, 2017). The role of pore fluid pressure during frictional deformation is expressed as the Coulomb-Amontons’ friction law: \(\tau = C + \mu(n(a_n - a_f))\), where \(\tau\) is the friction shear strength, \(\mu\) is a friction coefficient, \(a_n\) is normal stress across the fault, and \(a_f\) is pore fluid pressure. Due to the constant \(\alpha\) is a constant, and \(C\) is the fault cohesion, often assumed to be zero. The term ‘\(a_n - a_f\)’ is the ‘effective normal stress’ and the parameter \(\alpha\) determines how efficiently pore fluid pressure reduces the shear strength of the fault (e.g., Boitnort and Scholz, 1990). One significant challenge for estimating the shear strength of faults is that variations in \(P_f\) and \(\alpha\) at depths near and below the seismogenic to aseismic transition are poorly constrained, in part because monitoring fluid pressures greater than ~ 300 MPa in the laboratory is technically challenging (Chernak and Hirth, 2010; Proctor and Hirth, 2015; Okazaki and Hirth, 2016). The parameter \(\alpha\), in particular, has been
proposed to evolve from α = 1 at near-surface conditions to α = 0.1 or less at the base of the seismogenic zone using theoretical arguments and naturally deformed rocks (Hirth and Beeler, 2015). However, there is no experimental validation of this evolution and limited experiments on quartz analog minerals (halite) suggest that α = 1 throughout brittle and semi-brittle deformation (Noda and Takahashi, 2016).

We present the results of deformation experiments designed to investigate deformation processes and pore fluid weakening of serpentinite, a common subduction zone lithology, during high-pressure localized deformation. We measured the strength of antigorite serpentine deformed in general shear with different amounts of pore fluids added. In addition, we measured the dependence of strength on deformation rate to evaluate the effects of pore fluids on deformation mechanisms. The conditions of our experiments target those of localized deformation at temperatures greater than the ‘ductile to brittle’ transition documented by Proctor and Hirth (2016). We measure the structural and chemical evolution of the rock during localization and weakening to evaluate the processes that contribute to fault weakening and slip under conditions of pore fluid pressurization.

2. Methods

2.1. Antigorite sample

We tested a serpentinite from the Nagasaki metamorphic belt in Japan that is ~ 99 vol. % antigorite (Sawai et al., 2013) with minor oxides and sulfides. Wavelength dispersive spectroscopy (WDS) measurements show that the antigorite contains 6.31 wt. % FeO and 1.22 wt. % Al₂O₃. This is the same serpentinite tested by Proctor and Hirth (2016), who conducted experiments at the same pressures, temperatures, and deformation rates, but without added water. We followed the same sample preparation procedures so the results of our experiments are directly comparable to those of Proctor and Hirth (2016). The serpentinite was ground and sieved to a grain size of 35–53 μm, and the magnetic particles in the original serpentinite were removed.

2.2. Deformation experiments

Layers of serpentinite were deformed in a general shear geometry using a Griggs triaxial deformation apparatus with NaCl confining medium. Experiments were conducted at temperatures of 400°C and 500°C, and a confining pressure of 1 GPa. The samples were prepared by placing 0.15 g of serpentinite powder between cylindrical alumina pistons cut 45° to their axes; this produces a 1.2 mm thick layer when compacted to 1 GPa (Proctor and Hirth, 2016) (Fig. 1a and b). The equivalent of 1 or 2 wt. % water was added to the sample capsule in two different ways. Water was either added directly to the serpentine layer (1.5 or 3.0 μl) or 3.2 × 10⁻³ g of brucite nanopowder was added to the serpentine powder during sample assembly. When samples with added brucite are confined and heated, up to 2 wt. % water is released to the system by the following reaction (Fig. 1c).

\[
\text{antigorite(Mg}_2\text{Si}_2\text{O}_5\text{(OH)}_4) + \text{brucite(Mg(OH)}_2) \rightarrow 2 \text{ olivine(Mg}_2\text{Si}_2\text{O}_4) + 3\text{H}_2\text{O}
\]  

(1)

Given the ratio of brucite to antigorite in our sample, all of the brucite and 11% of the antigorite is consumed if this reaction goes to completion. Some reactant may have been produced by simple dehydration of brucite to MgO, although the experiments are conducted within the stability field for brucite for the following reaction to periclase, so we expect this reaction to be minor (Fig. 1c).

\[
\text{brucite(Mg(OH)}_2) \rightarrow \text{MgO} + \text{H}_2\text{O}
\]  

(2)

The conditions of these experiments are within the established stability field of pure antigorite (Fig. 1c). The addition of liquid water in the sample means that H₂O activity is equal to 1, and the dehydration reaction of antigorite to olivine and a talc-like phase or talc is not predicted to occur until ~ 600°C (Perrillat et al., 2005), which is higher than the temperature of these experiments.

The sample and pistons were placed in an annealed cylindrical silver jacket with platinum discs at the ends, which prevents fluid escape. Because water cannot be expelled from or drawn into the sample during deformation, all experiments reported here are ‘undrained’. Samples were first pressurized to 250 MPa confining pressure over 1 h at ambient temperature and then the confining pressure and temperature were simultaneously raised to the experimental conditions over 2 h. The samples were held at these conditions for 12 h, then sheared in constant displacement rate tests at axial displacement rates of 18.0 nm/s (25.5 nm/s parallel to the shear boundary) to axial displacement of 0.59 to 3.0 mm (shear displacements along the sawcut of 0.85 to 4.3 mm). These displacements correspond to engineering shear strains, equal to shear displacement along the surface divided by a layer thickness of 1.2 mm, between γ = 0.69 and 3.56. Two rate-stepping tests were conducted at shear displacement rates from 0.255 to 25.5 nm/s on samples with 1 and 2 wt. % water added.

Confining pressure, axial force, and axial force were recorded during the experiments. Axial force measurements were corrected for the strength of the solid confining medium and apparatus assembly using the corrections of Proctor and Hirth (2016). The precision and accuracy of stress are ~1 MPa and 25 MPa, respectively.
Mechanical data are reported as shear stress (τ) along the 45° surface and shear strain (γ). The shear stress is corrected for the decrease in the overlapping area of the sawcut pistons during shear (Fig. 1b). At the end of each experiment, the differential stress was reduced to zero at an axial displacement rate of 18.0 nm/s, and the sample temperature was quenched to 100°C over 10 min. The confining pressure and temperature were then subsequently reduced to ambient conditions over 2 h. The experiments conducted by Proctor and Hirth (2016) were run at identical conditions in the same sample configuration, but without added water; they were prepared at room humidity, and adsorbed water was not removed from antigorite surfaces.

We verified that water was contained in two experiments (#2094 and #2095) for which pore fluid was generated by the reaction between brucite and antigorite (Table 1). To do so, we weighed the sealed samples at the end of the experiments, punctured the jackets, heated the samples to 100°C for 30 min to vaporize pore water, and then weighed them again. In both cases we measured a decrease in mass equivalent to 1 wt. %, which is half the water that would be produced if all brucite had been consumed. Heating to 100°C is sufficient to evaporate free water, but not the water adsorbed to mineral surfaces. Thus, 1 wt. % represents the water in excess of adsorbed water, which is the baseline established by samples sheared in ‘room-dry’ conditions by Proctor and Hirth (2016). For a dominantly antigorite mineralogy with density 2550 kg/m³, 1 wt. % water corresponds to 2.5% porosity. We group experiments where enough brucite was added to produce 2 wt. % water with the experiments for which 2 wt. % liquid water was added, as we find these experiments exhibit similar results.

### 2.3. Structural and chemical measurements

Microstructures and chemical composition were analyzed for 6 samples deformed from γ = 0.69 to 2.69, including one deformed without added water (i.e., room-dry) to γ = 2.54 by Proctor and Hirth (2016) (Table 1). Thin sections were prepared to a 0.3 µm polish with alumina and diamond powders. Back-scattered electron (BSE) images and elemental maps were collected with a JEOL JXA 8530F Hyperprobe field emission microscope at Rice University. Structural measurements were made from BSE images collected at an accelerating voltage of 10 kV and current of 0.05 µA. Elemental maps were created from wavelength dispersive spectroscopy (WDS) measurements of 10 oxides and elements (SiO₂, MgO, FeO, Al₂O₃, MnO, Na₂O, CaO, S, K, and Cl) at an accelerating voltage of 15 kV, current of 0.05 µA, and a dwell time of 30 ms. Elemental maps were created from measurements along a 410 by 310 grid in the X and Y directions, which corresponds to points spacing between 0.22 and 0.40 µm. Transmission electron microscope (TEM) foils were prepared from one sample deformed with liquid water added (#2055) with an FEI Helios 660 focused ion beam scanning electron microscope (SEM). A JEOL 2100F TEM was used for selected area electron diffraction (SAD) and bright field imaging at 200 kV accelerating voltage.

### 3. Results

#### 3.1. Mechanics

During deformation, the serpentine exhibits an initial stage of elastic loading and strain hardening followed by strain weakening, as observed during the experiments on room-dry antigorite (Fig. 2).
The magnitude of the peak and steady state strengths with 1 wt. % added water are similar to those of room-dry antigorite at the highest deformation rate, and strain weakening is minor. Samples with 2 wt. % added water exhibit lower peak strengths and greater strain weakening; relative to room-dry conditions, the magnitude of the peak and steady state strengths are reduced by 14% and 30%, respectively (Table 1). Two samples deformed with 2 wt. % water exhibited an episode of abrupt, though never dynamic, strain weakening. While the sample with 1 wt. % added water has a similar strength to room-dry antigorite at the highest deformation rate, it weakens at the lower rates of the rate-stepping test and approaches the strength of antigorite with 2 wt. % added water (Figs. 2 and 3).

The rate-stepping tests show that strength decreases with decreasing deformation rate (i.e., velocity strengthening behavior) with both 1 and 2 wt. % added water; following a step in deformation rate, the strength evolves to a new steady-state strength over a shear displacement of 0.1 mm ($\gamma = 0.25$) (Fig. 2). A modest strain weakening event occurred at the end of the rate-stepping test for the sample with 2 wt. % added water; the reason for this event and whether it is related to rate-stepping are not clear. We fit both power-law and frictional constitutive equations to the data acquired through rate-stepping tests to evaluate the deformation mechanisms (Fig. 3). The power-law relation tested is given by $n = d \log \tau / d \log \dot{\epsilon}$, where shear stress, $\tau$, is converted to the equivalent shear stress $\tau_e = \sqrt{3} \tau$ and strain rate $\dot{\epsilon}$ is converted to equivalent strain rate $\dot{\epsilon}_e = \dot{\epsilon} / \sqrt{3}$ for comparison of our tests with constitutive relations derived from axisymmetric compression experiments (e.g., Paterson and Olgaard, 2000).

The friction coefficient, $\mu$, was calculated as the ratio of shear stress, $\tau$, to normal stress, $\sigma_n$, parallel to the 45° serpentinite layer. Because the friction coefficient is defined as $\mu = \tau / (\sigma_n - P_f)$, and $P_f$ is not known in these experiments, the measured values of $\mu$ are apparent friction coefficients. The rate dependence of frictional strength is quantified by the relation $a - b = d \mu / d \ln(V)$, where $\mu_a$ is the steady-state friction coefficient, $V$ is shear displacement velocity, and $a - b$ is the standard rate-and-state friction parameter (e.g., Dieterich, 1978; Ruina, 1983). An apparent value of $a - b$ was determined from each rate-step by measuring the change in apparent steady-state friction coefficient for that step. When we compare our results to those of Proctor and Hirth (2016), it is clear that the measured rate dependence does not vary systematically with water content (Fig. 3). Furthermore, the power-law exponent is too large ($n = 12$ to 34) to reflect diffusion limited dislocation creep (Hilairet et al., 2007; Amiguet et al., 2012; Proctor and Hirth, 2016) (Fig. 3b). However, the frictional rate dependence is within the range of values reported for serpentinite at lower pressures and similar slip rates ($a - b = 0.014$ to 0.038) (Reinen et al., 1994; Takahashi et al., 2011).
intragranular microcracks and transgranular ‘R1’ and ‘P’ fractures.

By shear strains of $\gamma = 0.95$, deformation is localized in zones of fractured serpentinite oriented $\sim 30^\circ$ to $\alpha_1$ and $\sim 15^\circ$ to the shear boundary in an ‘R1’ orientation (Fig. 4 b–d). Although multiple fracture zones are present in all of the samples, each contains one prominent fracture zone that is thicker than the others (average thickness of $\sim 0.05\text{m}$), which we infer accommodates the greatest displacement. A second set of transgranular fractures occurs sub-parallel to the shear boundary and $\sim 45^\circ$ to $\alpha_1$ in a ‘Y’ orientation. Microcracks along the basal planes of antigorite grains are also aligned in a ‘Y’ orientation, and kinked grains occur adjacent to the prominent fracture zone (Figs. 5 and 6). As is the case when deformation is distributed, microcracks and transgranular fractures are the clearest evidence for porosity. Within the fracture zones, transgranular fractures are particularly abundant and well-connected (Fig. 5). The structures that develop in the samples of Proctor and Hirth (2016) deformed under room-dry conditions are similar to those that develop with added pore fluids (Fig. 4d).

### 3.3. Chemistry

Back-scattered electron imaging shows that there are zones of brighter material within the most prominent fracture zone of each sample that stands out from the surrounding matrix, indicating material with higher atomic density than antigorite (Figs. 4 b–d, 5, and 6). The zones of dense material are observed in every sample we imaged with a prominent fracture zone, independent of whether the experiments were conducted with added water, water released by the dehydration of brucite, or under room-dry conditions (Fig. 6). The brighter zones are up to $\sim 1\text{m}$ thick and frequently occur in two orientations: at a high angle, approaching normal, to $\alpha_1$ and sub-parallel to the boundaries of the main fracture zone at $\sim 30^\circ$ to $\alpha_1$ (Fig. 6). The zones have an anastomosing character, and in some cases they appear to be offset along small microcracks (Fig. 6). This material is not observed outside the fracture zone or in the sample that does not develop a fracture zone (Fig. 4a). Of the samples that we imaged, the dense material is most abundant at the highest strain ($\# 2055$, Fig. 4c); this rate-stepping experiment was also held longer at run temperature owing to the duration of the lowest strain rate interval (Table 1).

Chemical maps show that the regions of higher atomic density also have lower intracrystalline water contents than the surrounding antigorite, which we interpret to mean that these zones form by a dehydration reaction of antigorite. Intracrystalline water content is estimated by summing the wt. % of oxides and elements from the WDS analyses, and then subtracting this anhydrous total from 100 wt. %. Whereas antigorite contains 13 wt. % structural water, the water content in the fracture zone varies spatially from 5 to 13 wt. %, and the lowest water content occurs in the narrow zones with the highest atomic density (Fig. 6). The analyzed composition of material in the fracture zones also provides evidence for reaction. The chemical composition of grains in the low strain sample and grains outside of the fracture zones in higher strain samples can both be fit with stoichiometric coefficients for antigorite ($\text{[(Mg,Fe,Ni,Mn)$_2$,Si$_{12},O_{23}(OH)_4\text{]}}$). In contrast, the chemical composition within fracture zones is variable and the material with higher atomic density and lower water content cannot be fit with the stoichiometric coefficients of antigorite or even the expected breakdown products of antigorite (Ulmer and Trommsdorff, 1995; Perrillat et al., 2005).

To evaluate the degree to which water loss from the antigorite structure correlates with a redistribution of elements, we map the mole fraction of each oxide, calculated as the moles of that oxide per unit mass divided by the total moles of oxides and elements per unit mass. If a reaction is a simple loss of water, the mole fraction of each oxide would be spatially homogeneous. However, we observe evidence of chemical redistribution (Fig. 6). Overall, the distribution of chemical species is heterogeneous at the 1 to 10 μm scale. Most commonly, the dehydrated material has higher concentrations of MgO and FeO and lower concentrations of SiO$_2$ relative to the surrounding antigorite. These patterns are apparent in samples sheared with and without added pore water, and for both methods of pore water production (Fig. 6).

TEM images show that the zones of atomically dense material contain aggregates that are elliptical (axes 50–100 nm) in cross-section and composed of nanocrystalline (grain diameter < 100 nm) particles (Fig. 7 a–c). Each aggregate contains multiple phases of nanocrystalline material. The selected area electron diffraction (SAED) pattern of the nanocrystalline material is consistent with the expected pattern for olivine, talc-like phase, antigorite, with the olivine signal being the strongest (Fig. 7d). Brightfield images of nanocrystalline grains also show evidence of grains with lattice spacing consistent with the talc-like phase (Fig. 7b). TEM images and diffraction patterns do not show clear evidence of amorphous material and we do not see the bubbles or vesicles that develop within partially amorphous material of other lithologies deformed under similar conditions (Pec et al., 2012).

On the basis of the BSE images, WDS maps, and TEM images and diffraction patterns, we interpret that antigorite undergoes a dehydration reaction within narrow (~1 μm) zones that are themselves restricted to fracture zones. These zones are composed of nanocrystalline reactants. Observations of heterogeneous water content and chemical segregation at the 1–100 μm scale indicate that the composition of the nanocrystalline material is not spatially uniform (Fig. 6).

Examination of a sample in which water was generated by the dehydration reaction between brucite and antigorite shows that some brucite still exists and is distributed throughout the layer. Evidence for brucite includes regions that are less dense than antigorite, that chemical maps and anhydrous totals shown are ~70 wt. % MgO and 30 wt. % water. We see no evidence for anhydrous MgO which would indicate that reaction (2) occurred. This observation indicates that the reaction was not complete, consistent with mass balance calculations of pore water at the end of the experiments.

### 4. Discussion

#### 4.1. Fracture induced dehydration reaction

The dehydration reaction that produces the nanocrystalline material is enhanced by fracturing, because it does not occur outside fracture zones (Figs. 4 and 5). Previous studies on antigorite also show evidence for a dehydration reaction within the antigorite stability field during localized deformation (Takahashi et al., 2011; Ferrand et al., 2017; Gasc et al., 2017). Takahashi et al. (2011) documented micro-scale forsterite grains interpreted to form by dehydration of antigorite, and Ferrand et al. (2017) and Gasc et al. (2017) identified a talc-like phase using synchrotron x-ray diffraction, but they did not have constraints on the spatial distribution of the phase or the process by which it formed. Although Proctor and Hirth (2016) did not observe evidence of
dehydration, this is likely because the reaction is localized to fracture zones and only apparent in high resolution BSE and TEM images, which were not part of their analyses. To constrain the cause of antigorite breakdown within its expected stability field, we outline coupled deformation and chemical processes known to be active at the conditions of these experiments and evaluate whether they might lead to fracture-induced dehydration of antigorite. We discuss processes that could drive the reaction at the fracture-scale by a local change in temperature or pressure, and those that change the stability field boundary.

Because the reactant is spatially correlated with fracture surfaces, we first evaluate whether shear heating along fractures is sufficient to locally increase temperature and cause dehydration of serpentine (e.g., Kelemen and Hirth, 2007; Kohli et al., 2011). During shear heating, mechanical energy is dissipated as heat at frictional contacts; at high enough slip rates, the heat generated is sufficient to cause a phase change (Kohli et al., 2011). As an end-member constraint, we calculate

Fig. 6. Backscattered electron images from within serpentinite fracture zones (top), WDS maps for the anhydrous total wt.% of the 10 oxides and elements measured (2nd row), and maps of the mole fraction of SiO₂, MgO, and FeO. Mole fraction is defined as total moles of each oxide per unit mass divided by the total moles of all oxides and elements per unit mass. Maps are shown for serpentine sheared (a) with added water (# 2055, $\gamma = 2.69$, dashed white box in Fig. 4c.), (b) with water produced from brucite (# 2094, $\gamma = 1.46$), and (c) without added water (# 1937, $\gamma = 2.54$, dashed box in Fig. 4d). Red arrows show dehydration products (bright material) sub-perpendicular to $\sigma_1$, green arrows show dehydration products offset by microfractures, and the white arrow shows a kinked grain. Sense of shear is sinistral in all images and scale bars are 10 $\mu$m.
the temperature rise due to flash heating (rather than shear within a distributed zone) to provide an upper bound on the temperature rise (Rice, 2006). The velocity, \( V \), required to raise the temperature by \( \Delta T \), is given by \( V = (\kappa \alpha_0 D)/(\rho c \Delta T/\tau_c)^2 \), where \( \tau_c \) and \( D \) are the contact shear stress and diameter, respectively, \( \alpha_0 \) is thermal diffusivity, and \( \rho c \) is the specific heat capacity (Rice, 2006). This is a minimum velocity, as the formulation assumes that the relevant slip distance that promotes ‘flash weakening’ is on the order of the size of a frictional contact asperity. We use the same values for the thermal parameters (\( \alpha_0 = 0.90 \text{ mm}^2/\text{s} \) and \( \rho c = 2700 \text{ kJ/K/m}^3 \) (Osako et al., 2010)) and contact shear stress (\( \tau_c = 3 \text{ GPa} \)) as Kohli et al. (2011) and (Proctor et al., 2014) who studied dynamic weakening in antigorite. We assume the diameter of the slipping contact is the same as microfractures in the fracture zone (\( \sim 1-10 \mu \text{m} \)) and that the temperature rise required to promote dehydration to occur is 50 to 100°C. The corresponding range of slip velocities that could produce this range of \( \Delta T \) for this range of contact sizes is \( V = 0.5 - 20 \text{ mm/s} \). These velocities are 2–4 orders of magnitude larger than the velocity across the serpentine layer. Although this condition may occasionally be met at contacts, it is unlikely to be met often enough to produce the number of reaction zones that we observe.

Another means by which fracturing may promote dehydration is by locally decreasing the normal stress along grain faces during fracture-induced dilation. Dilation associated with microfracturing produces high normal stresses at some grain faces and leaves others unsupported, such that normal stress is equal to the pore fluid pressure. Thus, dehydration reactions may progress along the low normal stress surfaces, even if the macroscopic boundary stresses place antigorite within its stability field. Intergranular fractures parallel to antigorite basal planes are shown to result in small pore dilation (Escartin et al., 1997), but transgranular fractures like those within the fracture zones are more dilatant (French and Zhu, 2017). Under dry conditions, unsupported grain faces would have normal stress of 0 MPa and under fluid saturated conditions, the normal stress would be equal to the pore fluid pressure (see Section 4.2). Our results suggest that these normal stresses are sufficiently low to push dry serpentine outside the antigorite stability field. However, under fluid saturated conditions, this process can only explain dehydration if the fluid pressure in the cracks is extremely low, which is possible if newly formed fracture porosity dilates and remains unconnected to the surrounding pore fluids. We would expect that normal stresses are lowest along planes parallel to \( \sigma_1 \) but the reactant tends to form at high angles to \( \sigma_1 \) (Figs. 5 and 6). Nevertheless, low normal stresses along fracture faces due to low pore fluid pressures may promote dehydration. This type of effect was interpreted to occur during deformation experiments conducted on mixtures of quartz and calcite. In this case, evidence for the decarbonation reaction to wollastonite and \( \text{CO}_2 \) was observed along pore boundaries at conditions where the macroscopic stresses were within the quartz + calcite stability field, but the pore fluid pressure was within the wollastonite + \( \text{CO}_2 \) stability field (Milsch et al., 2003).

Finally, fracturing may alter the thermodynamic equilibrium conditions of dehydration reactions through its effects on the rock microstructure. Specifically, grain size reduction within the fracture zones can increase the free energy of the reactants and lower the equilibrium pressure and temperature. Furthermore, because both the dehydration of antigorite and the growth of reaction products (i.e. olivine and the talc-like phase) are diffusion controlled processes with nucleation occurring along angular grain boundaries (Perrillat et al., 2005; Sawai et al., 2013), grain size reduction may also decrease diffusion distances and enhance the reaction kinetics (e.g., Sawai et al., 2013). Although the reaction is localized in fracture zones, we do not observe antigorite with the extremely fine grain sizes expected to promote this kind of shift in phase boundary. Low-temperature plasticity of the reactants can also increase free energy and shift the equilibrium temperature by increasing the local strain energy. We see evidence for kinking and Gasc et al. (2017) showed high defect densities in antigorite fractured at 500°C, which are both evidence of low temperature plasticity (Etheridge et al., 1974; Kronenberg et al., 1990). In general, the effect of dislocation-induced strain on reaction kinetics has been shown to be relatively minor unless dislocation densities are extremely high (Wintsch and Dunning, 1985).

The transition from ductile to localized deformation that was documented by Proctor and Hirth (2016) clearly precedes and then promotes dehydration. On the basis of these analyses, we favor the case that dehydration is promoted by a combination of effects that increase temperature, reduce pressure, and possibly shift the phase boundary. Although we observe evidence of a dehydration reaction in the fractures zones, this reaction is not responsible for strain weakening because room-dry samples also show evidence of dehydration but do not strain weaken.

### 4.2. Pore fluid weakening

The rate dependence of antigorite strength, combined with our microstructural analyses, indicate that dehydration is frictional and not accommodated by fully crystal plastic or diffusional mechanisms (Reinen et al., 1994; Takahashi et al., 2011; Amiguet et al., 2012; Proctor and Hirth, 2016) (Figs. 2 and 3); this interpretation is also consistent with the pressure dependence of antigorite strength at these conditions (Proctor and Hirth, 2016). At the same time, the presence of kinked grains indicates the activation of some crystal plasticity, as reported in previous studies on antigorite deformed at similar conditions (Chernak and Hirth, 2010; Auzende et al., 2015; Amiguet et al., 2014).
Local plasticity is consistent with macroscopic frictional deformation behavior, as plasticity is thought to promote the positive frictional rate dependence in antigorite and some other silicates (e.g., Reinen et al., 1994; Boettcher et al., 2007; King and Marone, 2012; French et al., 2015). Our observations also suggest that the addition of water does not change the dominant deformation mechanism of serpentinite, because the rate dependence of the strength is similar in room-dry and water-added samples (Fig. 3).

We interpret that the strain weakening of samples with 2 wt. % water added arises from the presence of pressurized fluids in the fault zones. In lower pressure experiments (≤ 300 MPa), strain weakening of sheet silicates during frictional sliding sometimes occurs during fabric development (e.g., Morrow and Byerlee, 1989). This weakening arises from the rotation of grains into a preferred orientation that aligns the weak basal planes (Haines et al., 2013). Indeed, water saturated antigorite gouge exhibits strain weakening during fabric development in some low pressure experiments (e.g., Moore et al., 1997). However, in other low pressure experiments strain weakening does not occur (e.g., Behnsen and Faulkner, 2012; Takahashi et al., 2011); the reasons for the differences between these low-pressure experiments are not clear. Nonetheless, because the room-dry sample of Proctor and Hirth (2016) and our sample # 2055 show alignment of antigorite basal planes (Fig. 5), but these samples did not strain weaken, we infer that fabric development is not the primary cause of strain weakening for samples with 2 wt. % water.

We assume that the differences in strength between the room-dry and water added samples arise from pore fluid pressurization, and evaluate the fluid pressure necessary to cause the observed strain weakening of antigorite with 2 wt. % added water. Proctor and Hirth (2016) showed that the steady-state strength of room-dry serpentinite is achieved by a strain of $\gamma = 0.7$; we assume that $\alpha_P = 0$ in the room-dry experiments and that weakening of samples with 2 wt. % added water is due to pore fluid pressurization at $\gamma \approx 0.7$. To estimate the magnitude of $\alpha_P$, we use a Mohr circle analysis and published strength data for serpentinite (Fig. 8). We assume that the strength at high effective pressure follows the failure envelope from Proctor and Hirth (2016) and that the strength at low effective pressure follows the failure envelopes from Takahashi et al. (2011) and Okazaki and Katayama (2015). We then calculate the evolution of $\alpha_P$ that is required for the Mohr circle to remain tangent to the failure envelopes throughout strain weakening. This analysis indicates that in samples with 2 wt. % water, $\alpha_P$ increases with displacement from $\sim 550$–$600$ MPa just past peak strength ($\gamma = 0.7$) to $\sim 650$–$700$ MPa at steady-state (Fig. 9a). The trend that $\alpha_P$ increases with strain is independent of the failure envelopes that we use for the analysis, although the absolute values of $\alpha_P$ do depend on the failure envelope. For instance, if we use a failure envelope corresponding to a frictional relation with $\mu = 0.36$ (e.g., Proctor and Hirth, 2015), $\alpha_P$ evolves from 50–100 MPa just past peak strength to $250$–$300$ MPa with increasing strain.

Given the calculated values of $\alpha_P$, we examine two end-member scenarios for the values of $\alpha$ and $P_f$ and evaluate the implications of both on weakening processes during deformation: (1) $\alpha$ is constant and equal to 1 and (2) $P_f$ is equal to $\alpha_0$. If $\alpha = 1$ throughout strain weakening, pore fluid pressure must increase with strain (Fig. 9b). This, in turn, requires compaction and a net volumetric strain up to $\epsilon_V = 0.001$ for constant water mass (Fig. 9c). In contrast, if $\alpha$ remains approximately constant and equal to $\alpha_0$ throughout weakening, then $\alpha$ must increase (Fig. 9d) and the total pore volume in the sample must remain approximately constant to maintain near-constant pore pressure.

Our microstructural observations are most consistent with an increase in $\alpha$ during deformation (Scenario 2). Although there are no published pore volume measurements at these experimental pressures to help us evaluate which of the two scenarios is correct, measurements from experiments conducted at pressures up to 300 MPa consistently show that the greatest compaction occurs during initial strain hardening, and that strain weakening corresponds most often with dilation, and rarely minor compaction (Morrow and Byerlee, 1989; Marone, 1991; Lockner and Byerlee, 1994). In our experiments, such volume strain would lead to significant weakening of the peak strength potentially followed by a small additional strain weakening or hardening (e.g., Faulkner et al., 2018). However, we find that the elastic loading curves are nearly independent of water content (Fig. 2). In addition, we observe only a small (14%) decrease in peak strength relative to room-dry experiments and a greater decrease in the nominally steady state strength (30%) in experiments with 2 wt. % water. Furthermore, if $\alpha$ remains constant (Scenario 1), the compaction necessary to explain weakening (Fig. 9b) is at odds with the concomitant development of a localized fracture zone, which is usually associated with dilatant deformation. It is more consistent with our understanding of fracturing to assume that the increase in pore volume associated with microfracturing resulted in a pressure drop within the fault zone. This, in turn, implies that weakening was not due to fluid pressurization, as the pore fluid pressure in the fault zone actually decreased slightly, which promotes fluid flow into the fault zone. Therefore, we interpret that the most likely cause of strain weakening was due to increasing $\alpha$ during development and deformation of the fracture zone. Given that the experiments are undrained, we acknowledge that a range of conditions with $\alpha < 1$ and $P_f < \alpha_0$ are possible.

To investigate Scenario (2) further, we determine whether the evolving value of $\alpha$ is consistent with theory. $\alpha$ is proposed to be controlled by the real area of grain contact, where $\alpha = 1 - \chi/\alpha_0$, where $\alpha_0$ is the real area of contact (Boitnott and Scholz, 1990; Scholz, 2002). Thus, the increase in $\alpha$ implied by Scenario (2) requires a reduction of the real area of contact within the fracture zones. Hirth and Beeler (2015) and Beeler et al. (2016) hypothesized that if $\alpha$ is controlled by plastic yield at microscopic contacts then $\alpha = 1 - \sigma_0/\sigma_f$, where $\sigma_f$ is the effective normal stress, $\chi = \cos (\tan^{-1}(\mu)/2\mu$ and $\sigma_f$ is the contact-normal yield stress. Using this formulation and calculated values of $\alpha$ (Fig. 9d), we calculate $\sigma_f$ during strain weakening and compare it to experimental measurements for antigorite. We find that the yield strength required to maintain $P_f = \sigma_f$ is approximately 1.9 GPa, and that it increases slightly (3%) with
increasing strain (Fig. 9e). The compressive yield strength of antigorite is estimated from the indentation hardness, $H$, measured by D. L. Goldsby and reported by Kohli et al. (2011). At room temperature, $H$ is 4 GPa and scaling to 500 °C using the activation energy for low-temperature plasticity of Hilairet et al. (2007) (59.9 kJ/mol) results in $H = 2$ GPa. Overall, the agreement between calculated and previous measurements of $\sigma_y$ offers support for an adhesion theory control of $\alpha$. Because the plastic yield strength of antigorite should not vary with strain, the 3% evolution could represent error in our assumption of constant $P_f$. Specifically, if the fluid pressure decreased due to dilation of the pore space, the assumption of constant fluid pressure causes the yield strength to appear to increase.

Application of adhesion theory also suggests that the real area of contact is greatest during the initial hot pressing stage of our experiment, when the shear strain rate is zero (Beeler et al., 2016) (Fig. 10a). At this stage, undrained consolidation of the serpentinite powder is expected to create fluid pressure equal to $\sigma_2$. As shear stress increases, crystal plasticity alone cannot accommodate deformation of the antigorite, because von Mises strain compatibility criterion is not satisfied in antigorite (e.g., Chernak and Hirth, 2010). As a result, distributed deformation during strain hardening occurs by a combination of low temperature plasticity and microcracking, as well as elasticity (Figs. 4a and 10b). Despite microcracking, previous experiments at lower pressure show that this stage corresponds to very small net compactive deformation because microcracks preferentially form along basal planes well-oriented for shear not dilatant opening (Escartin et al., 1997; French and Zhu, 2017). We, therefore, predict that $A_\alpha$ may decrease slightly, but $P_f$ remains high during strain hardening in these experiments. The fact that the strain hardening curve is nominally independent of water content, and therefore fluid pressure, supports the hypothesis that $A_\alpha$ is high and $\alpha$ is correspondingly low at this stage.

During the early stage of strain weakening and localized fracturing, pore space and connectivity increase by transgranular fracturing (Figs. 4b–d and 10c). The onset of localization corresponds to a reduction in strength with a locally increasing water content, and subsequent weakening increases with increased localization (Figs. 2 and 3). That localization and enhanced fracturing are associated with weakening, but only in the presence of pore fluids, provides some insight into
the weakening process. Fracturing is a dilatant process that results in at least a small local fluid pressure drop. Thus, the observation that the onset of fracturing results in strain weakening in the presence of fluids - and an apparent increase in $\alpha P_f$ - leads us to hypothesize that localized fracturing promotes an increase in $\alpha$, which can be explained by a decrease in $A_s$ using adhesion theory. This process is consistent with the ‘dilatancy weakening’ scenario proposed by Hirth and Beeler (2015).

4.3. Localized deformation at geologic conditions

4.3.1. Fracture-induced dehydration

Previous experiments on serpentine, lawsonite, and analog materials conducted outside the stability field for these phases have documented localized deformation associated with dehydration and phase transitions, which led to the conclusion that the reactions cause faulting (Jung et al., 2004; Chernak and Hirth, 2011; Brantut et al., 2011; Proctor and Hirth, 2015; Okazaki and Hirth, 2016). In some cases, faulting during phase changes can be dynamic, which is a process known as ‘dehydration embrittlement’ and a leading hypothesis to explain intermediate depth seismicity (e.g., Raleigh and Paterson, 1965; Brantut et al., 2017). Whether or not frictionally-unstable dehydration embrittlement occurs in serpentinite is subject to debate over apparently contradictory experimental observations (Raleigh and Paterson, 1965; Jung et al., 2004; Chernak and Hirth, 2011; Proctor and Hirth, 2015). Our results demonstrate that localization can actually precede and promote dehydration of antigorite, and in a stable manner. If the coupled process of fracture and reaction is active in subduction zones, then the reaction likely has sufficient time to go to completion in regions of intense fracturing before reaching conditions thought to favor dehydration embrittlement (e.g., Raleigh and Paterson, 1965; Dobson et al., 2002; Jung et al., 2009). Therefore, unstable slip may be unlikely in pre-existing fracture zones. Although the reaction in our experiments did not result in dramatic weakening, this does not preclude the possibility that the reaction product and the pore water produced could significantly weaken the rock if weak reaction products develop in greater abundance over larger time scales or over the larger strains expected in-situ.

On the basis of microstructures in naturally-deformed serpentinites, some workers have inferred that evidence of brittle deformation associated with antigorite dehydration products is the result of dehydration-induced brittle deformation (Auzende et al., 2015). Our results call into question how we might distinguish between dehydration-induced faulting and faulting-induced dehydration in the rock record. In particular, evidence of localized deformation and dehydration is likely the result of fracture-induced dehydration at lower pressure and temperature conditions than predicted from hydrostatic experiments of antigorite (Ulmer and Trommsdorff, 1995; Perrillat et al., 2005).

4.3.2. Pore fluid weakening

We show that localized deformation under undrained conditions causes moderate strain weakening in serpentinite shear zones, despite the dilatant nature of the localized fracturing which is often associated with pore pressure drop and hardening (e.g., French and Zhu, 2017). Previous experimental work indicates that semi-brittle deformation of antigorite prevails at the pressures, temperatures, and strain rates at which transient deformation events like slow slip and low-frequency earthquakes occur (Chernak and Hirth, 2010; Proctor and Hirth, 2016). However, structural observations of naturally deformed serpentinites and limited experimental evidence suggest that at the lower strain rates (which may prevail during inter-event periods), viscous deformation mechanisms and distributed deformation are more likely (Hilairet et al., 2007; Auzende et al., 2015; Amiguet et al., 2014). Thus, we expect that the weakening process that we document could occur during transitions from distributed to localized deformation due to, for instance, a transient increase in strain rate.

Beeler et al. (2016) used adhesion theory to show that, during localized deformation, strain rates are high enough that the time-dependent yielding of asperities cannot reach the condition of $A_s = A$. As a result, $\alpha > 0$ and localized deformation results in more efficient pore fluid pressure weakening than distributed deformation. Therefore, if adhesion theory controls the value of $\alpha$, the unique material properties that cause an inverse ‘ductile to brittle’ transition with increasing depth may also result in a transition from fluid pressure-insensitive distributed deformation to fluid pressure-sensitive localized deformation with depth. Although the lithologies that accommodate slow slip deformation are not known, the weakening effects of fluid pressure that we document are likely important for other lithologies that exhibit a transition from distributed to localized deformation as well. For example, talc exhibits a transition back to localized deformation at conditions above its brittle-ductile transition (Escartín et al., 2008), suggesting that this may be a general property of highly anisotropic phyllosilicates. Notably, both the subduction interface and the deep San Andreas fault are thought to be rich in phyllosilicate-rich phases, including talc and serpentinite.

5. Conclusions

We present a suite of deformation experiments that indicate weakening effects associated with pore fluids and the onset of dehydration reactions in antigorite serpentinite, both triggered by the localization of deformation with strain. At all fluid conditions, the serpentinite undergoes strain hardening to a peak strength followed by strain weakening, coincident with localization of deformation to a fracture zone. The addition of pore fluids results in a small reduction in the peak strength when deformation is distributed, and a much greater reduction in shear strength during localized deformation, but no change in the deformation mechanism which remains frictional. We evaluate two end-member scenarios that could explain weakening (1) that $\alpha = 1$ and $P_f$ increases with fracture zone development; and (2) that $P_f = P_s$ and increases with fracture zone development. Although (2) is better supported by previous experiments at lower pressure, both scenarios indicate that weakening can occur during localized deformation at high pore fluid pressures and slow-slip strain rates. Dehydration of antigorite to form nanocrystalline talc-like phase and olivine occurs within the fracture zone at all fluid conditions and at pressure and temperature conditions where antigorite is typically considered stable. We attribute the enhanced reaction kinetics to an increase in nucleation sites and fast diffusion along lattice defects caused by fracturing and low-temperature plasticity. In addition, low normal stress along fracture faces due to locally low fluid pressures may also promote dehydration. The extent of the reaction was not sufficient to measurably affect the strength, but it likely is at the larger times scales of in-situ deformation.

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