

Water loss during dynamic recrystallization of Moine thrust quartzites, northwest Scotland

Andreas K. Kronenberg^{1*}, Kyle T. Ashley^{2†}, Matthew K. Francis^{2§}, Caleb W. Holyoke III^{1#}, Lynna Jezek^{1††}, Johannes A. Kronenberg^{1§§}, Richard D. Law² and Jay B. Thomas³

¹Center for Tectonophysics, Department of Geology and Geophysics, Texas A&M University, MS 3115, College Station, Texas 77843-3115, USA

²Department of Geosciences, Virginia Polytechnic Institute and State University, MC 0420, Derring Hall, RM 4044, Blacksburg, Virginia 24061, USA

³Department of Earth Sciences, Syracuse University, 204 Heroy Geology Laboratory, Syracuse, New York 13244, USA

ABSTRACT

Infrared absorption measurements of molecular water in sheared Cambrian quartzites in the footwall to the Moine thrust reveal a decrease in water content from 4080 to 1570 ppm with increasing recrystallization traced toward the overlying thrust at the Stack of Glencoul in northwest Scotland. These results are contrary to the expected correlation between shear strain and water content for quartz deformed by dislocation creep and water-weakening processes. The observed inverse correlation indicates that fluid inclusions and hydrous defects within grains were lost by mobile grain boundary sweeping and grain boundary diffusion. Although reduced water contents might lead to hardening as chemical weakening is diminished, quartz mylonites in the immediate footwall (5 mm) to the thrust are characterized by intense strain localization and contain the least water, and there is little evidence of shear zone widening. Water weakening appears to have been important throughout the quartz mylonites, controlled by the presence of water, not by water concentration. Fluids present within relict inclusions and at grain boundaries may have governed the high water fugacities critical for water weakening.

WATER WEAKENING

Deformation of quartz by dislocation creep at the temperatures and pressures of Earth's crust is widely believed to require water weakening, in which hydrogen defects help to break up fully linked silica tetrahedra at dislocations, subgrain walls, and grain boundaries, allowing dislocation glide and climb, intracrystalline recovery, and dynamic recrystallization

(Griggs and Blacic, 1965; Griggs, 1967; Paterson, 1989; Kronenberg, 1994). Dry varieties of quartz deformed in laboratory experiments are strong (Blacic and Christie, 1984), with inelastic deformations that require stresses far in excess of tectonic stresses. Varieties of quartz with molecular water contents >200 ppm (molar OH/10⁶ Si) deform by dislocation creep at lower laboratory stresses, and strain rates at a given stress are increased by higher water content and by higher water fugacity (Kronenberg, 1994). Flow laws of water-weakened quartzites with OH contents of 2000–4000 ppm, largely as fluid inclusions, match stress and strain rate estimates of quartz mylonites deformed at crustal temperatures, pressures, and water fugacities (Hirth et al., 2001; Stipp et al., 2010; Behr and Platt, 2011; Law, 2014; Togle et al., 2019).

Observed correlations among penetrative strain magnitudes, dislocation creep microstructures, and water contents of quartz in wet granitic shear zones (Kronenberg et al., 1990; Nakashima et al., 1995; Gleason and DeSisto,

2008) suggest that shear zone nucleation and strain localization may be due to water weakening. However, recent studies have revealed that water contents of highly deformed quartzofeldspathic rocks may also be small, with hydrous defects limited to hydrogen interstitials that are not known to weaken quartz (Kilian et al., 2016). Water contents of high-strain shear zones may show reductions toward the shear zone center (Finch et al., 2016), leading to hardening and shear zone broadening as water weakening becomes limited at the shear zone's center. Dislocation creep is generally accommodated by dynamic recrystallization that reduces dislocation densities and lowers thresholds for continued dislocation glide (Hirth and Tullis, 1992; Stipp et al., 2010); yet, intragranular water contents can be reduced during metamorphism and recrystallization (Nakashima et al., 1995; Seaman et al., 2013; Kilian et al., 2016), potentially leading to hardening.

In this study, we revisit the classic mylonitic Cambrian quartzites in the footwall to the Moine thrust (defined by the Cambrian quartzite–Neoproterozoic Moine schist contact; Peach et al., 1907; Christie, 1963; Law et al., 2010) exposed at the Stack of Glencoul in the Assynt region of northwest Scotland (Fig. 1) in order to measure molecular water contents as a function of structural level, from 70 m below the principal thrust surface to within 5 mm of the thrust contact. Earlier, exploratory infrared (IR) absorption measurements of Moine thrust mylonites revealed significant quartz water contents (Kronenberg and Wolf, 1990), which were presumed, but not demonstrated, to correspond to dislocation creep and strain localization. In contrast to the expected correlation between creep strain and intragranular water, rounded elliptical

*E-mail: kronenberg@geo.tamu.edu

†Current address: Department of Geology and Environmental Science, University of Pittsburgh, 4107 O'Hara Street, Pittsburgh, Pennsylvania 15260, USA

§Current address: Tessella, 10777 Westheimer Road, Suite 1025, Houston, Texas 77042, USA

#Current address: Department of Geosciences, University of Akron, Akron, Ohio 44325-4101, USA

††Current address: Ball Aerospace and Technologies Corp., 1600 Commerce Street, Boulder, Colorado 80301, USA

§§Current address: Walgreens Corporate, 1425 Lake Cook Road, Deerfield, Illinois 60015, USA

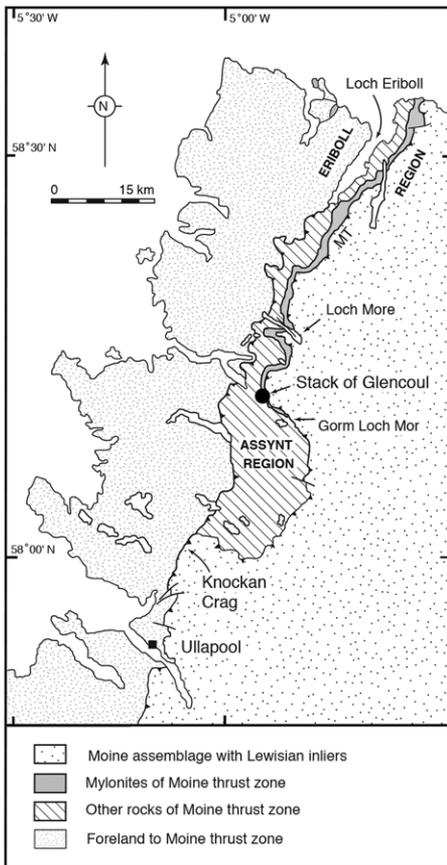


Figure 1. Location map of Moine thrust (MT), northwest Scotland, with samples collected from its footwall at the Stack of Glencoul (after Law et al., 2010).

quartz grains of sedimentary origin in the least-deformed protolith rocks below the thrust show the highest water contents, while highly sheared quartz ribbons and recrystallized grains of mylonites directly below the thrust surface have the lowest water contents.

MICROSTRUCTURES

Mylonitic Cambrian quartzites (Figs. 2A–2C) are exposed up to 10 m beneath the Moine thrust at the Stack of Glencoul (see the GSA Data Repository¹) and are separated from underlying weakly deformed quartzites (Fig. 2D) along an unexposed thrust (Law et al., 2010). Microstructural deformation features in the mylonites include intensely sheared ribbon quartz grains (Fig. 2C), dynamic recrystallization, and strong crystallographic fabrics (Christie, 1963; Law et al., 2010) that reflect large penetrative strains by regime 2 dislocation creep (Hirth and Tullis,

¹GSA Data Repository item 2020168, data files and a readme file for the IR data presented in Figure 3, details of methods of observation and measurement used in this study, Figure DR1, and Tables DR1–DR3, is available online at <http://www.geosociety.org/datarepository/2020/>, or on request from editing@geosociety.org.

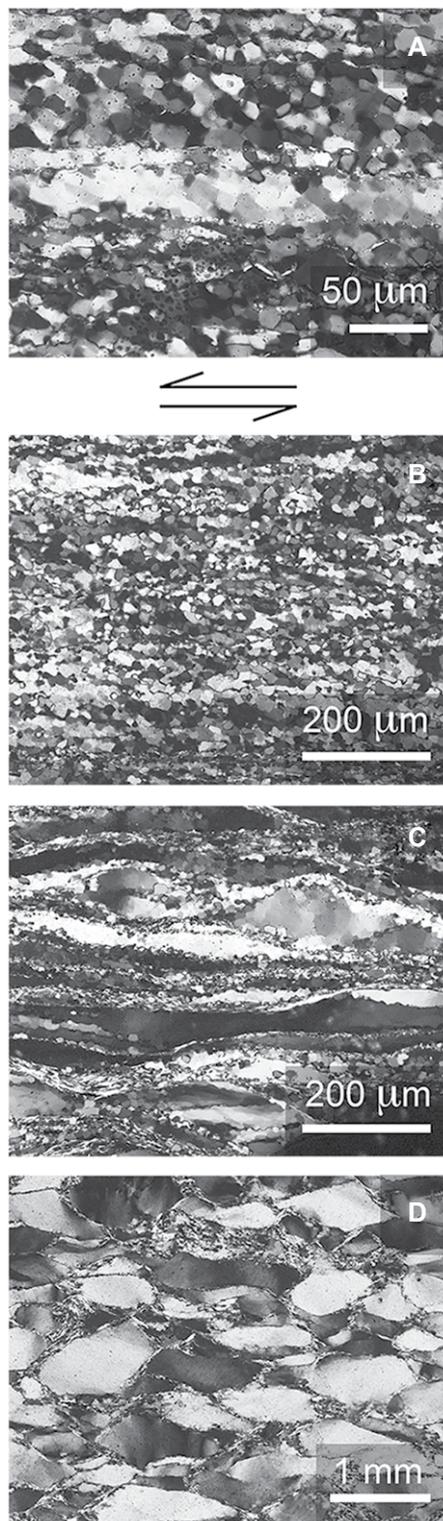


Figure 2. Optical deformation and recrystallization microstructures of Cambrian quartzites from the Moine thrust (northwest Scotland) footwall (crossed polarizers, sections cut perpendicular to foliation and parallel to lineation, with top-to-left, west-northwest shear sense). (A,B) Fully recrystallized mylonite SG-1, collected 5 mm below the Moine thrust, with aligned recrystallized grain and subgrain boundaries (thin section thickness $t = 12 \mu\text{m}$). (C) Larger sheared ribbon quartz grains with undulatory extinction and subgrains, and

1992) accommodated by a combination of subgrain rotation (SGR) and bulge nucleation (BLG) recrystallization (Stipp et al., 2010; Law, 2014).

Strain magnitudes based on original detrital quartz grain shapes (Fig. 2D) are relatively uniform in the mylonites (Fig. 2C), and a general shear-dominated deformation (with estimated vorticity numbers, W_m , ranging between 0.00 and 0.73) is indicated by the relatively minor external and internal asymmetries in c -axis fabrics measured on these relic detrital grains (Law, 2010; Law et al., 2010). However, much larger shear strains are inferred directly below the Moine thrust, where the quartzites are extensively recrystallized, and c -axis fabrics of recrystallized grains are markedly asymmetric (W_m numbers ranging between 0.90 and 0.99). We use the extent of recrystallization of quartzites below the Moine thrust as a proxy for shear strain, with shear strain magnitudes dropping off as recrystallization drops from 97% by volume for mylonites directly below (5 mm) the Moine thrust (Figs. 2A and 2B) to 17% for quartzites 70 m below, in which new, recrystallized grains are restricted to the margins of original detrital grains (Fig. 2D; see the Data Repository).

Despite the strong gradient in extent of recrystallization with structural level, the mean sizes of recrystallized quartz grains over the interval sampled beneath the Moine thrust are nearly constant ($21.7 \pm 1.8 \mu\text{m}$), much as reported by Weathers et al. (1979). Based on microstructural paleopiezometers of Twiss (1977) and Stipp and Tullis (2003; corrected, see the Data Repository), the shear stress magnitudes implied by these recrystallized grain sizes are $\sim 61 \text{ MPa}$ and $\sim 46 \text{ MPa}$, respectively. Irrespective of the piezometer relationship used, shear stresses throughout the footwall mylonites do not appear to have varied by more than 10%.

Fine white micas in the mylonites (1%–5%) appear as isolated plate-like grains aligned parallel to foliation, with departures in orientation associated with quartz grain boundaries and subtle S-C fabric. Qualitative estimates indicate that feldspars represent at most 1%–3% of the mylonites. Determinations of white mica crystallinity imply peak temperatures of 300–350 °C (Johnson et al., 1985), lower than deformation temperatures indicated by detrital grain quartz c -axis fabric opening angles (390–440 °C; Law et al., 2010). While thermal gradients may be generated by mass flow in large-displacement shear zones at larger length scales (Behr and Platt, 2011), the close spacing of the

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finely recrystallized grains of SG-7 (2.5 m below thrust, $t = 8 \mu\text{m}$). (D) Least-deformed quartzite protolith SG-15 (70 m below the Moine thrust, $t = 30 \mu\text{m}$) with undulatory extinction of original (now-elliptical) detrital quartz grains and fine recrystallized grains and white micas at original grain margins.

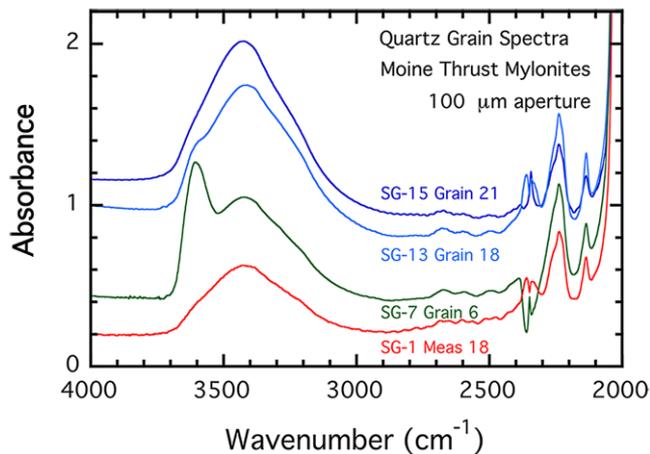


Figure 3. Infrared (IR) absorption spectra of deformed Cambrian quartzites in the Moine thrust (northwest Scotland) footwall at the Stack of Glencoul, with broad OH absorptions at $\sim 3400\text{ cm}^{-1}$ due to fluid inclusions within deformed quartz grains of samples SG-7, SG-13, and SG-15 (measured using an IR microscope and $100\text{ }\mu\text{m}$ aperture) and in domains of finely recrystallized quartz of SG-1. The secondary sharp band of variable size at 3620 cm^{-1} is due to finely dispersed

micas. Absorbance values were normalized to sample thickness of 1 mm.

mylonites sampled here suggests that temperatures during deformation were relatively uniform, if somewhat uncertain (see Law et al., 2010, discussion on p. 569–572).

INFRARED SPECTROSCOPY

Fourier transform infrared (FTIR) microscope measurements of Stack of Glencoul quartz mylonites are dominated by two OH absorption bands, a broad absorption at a wavenumber of $\sim 3400\text{ cm}^{-1}$ characteristic of molecular water in fluid inclusions and a sharper absorption band of variable size at 3620 cm^{-1} due to finely dispersed white mica inclusions (Fig. 3). After separating these absorptions, integrating the 3400 cm^{-1} OH absorption, and applying the IR calibration of Aines et al. (1984), broad-band OH contents of quartz grains vary widely within individual samples (see the Data Repository), much as documented by recent FTIR imaging studies (Kronenberg et al., 2017). However, variations in OH content show no apparent correlation with deformed detrital grain shape. High-strain ribbon quartz grains have large variations in water content that broadly overlap the similarly scattered water contents of moderately sheared and low-strain quartz grains (standard deviations, s , approach mean values for $N = 22\text{--}39$ individual measurements of a given sample). OH contents also do not show clear correlation with grain size of porphyroclasts; OH contents of large grain interiors vary significantly and are not readily distinguished from those of smaller porphyroclasts, the IR spectra of which may, in part, represent vicinal or grain boundary water. Mean quartz OH contents can be distinguished for samples collected at different structural distances below the Moine thrust, with significance given by smaller standard errors of the mean (s/\sqrt{N}) than by s .

WATER LOSS DURING DYNAMIC RECRYSTALLIZATION

Moine thrust quartz mylonites are marked by extensive recrystallization that overprints

highly sheared quartz ribbons and deformation microstructures at the locus of major tectonic displacement. Following up on work of Weathers et al. (1979), our measurements of volume fractions of recrystallized quartz vary from 17% to 97% (Fig. 4A; see the Data Repository) for footwall samples collected at 70 to 0.005 m, respectively, below the Moine thrust. Quartz water contents of these same samples show significant variations as well, with reductions in mean OH contents from 4080 ± 1400 ppm in the quartzite protolith at 70 m below the thrust (SG-15) to less than half this value (1570 ± 1070 ppm; SG-1) directly below the thrust (Fig. 4B). This trend is opposite to the positive correlation between shear strain and OH content expected for water weakening. Instead, water contents as a function of structural level are correlated inversely with the extent of recrystallization (Fig. 4C).

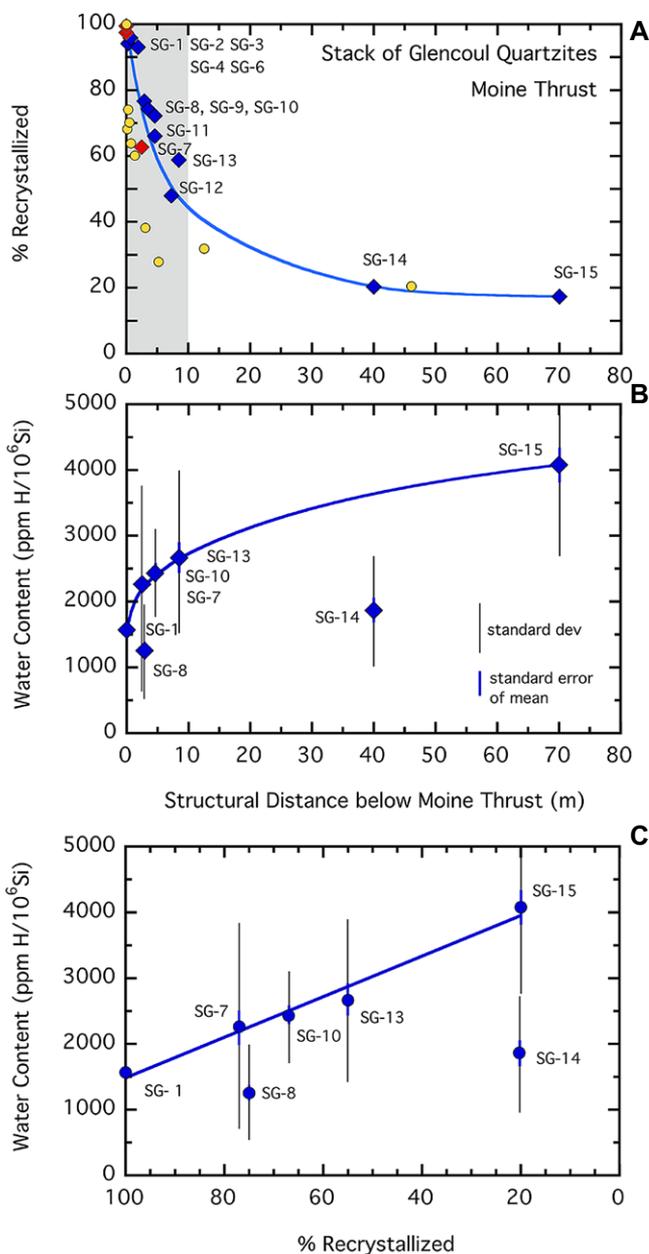


Figure 4. Variations in extent of dynamic recrystallization and OH content of quartz as a function of structural level beneath the Moine thrust (northwest Scotland) at the Stack of Glencoul. (A) Recrystallized quartz grains (% by volume) versus structural distance below the thrust (blue diamonds represent section-wide measurements, excluding horizons with white micas; red diamonds give measurements for samples in which micas were unavoidable; yellow circles represent measurements of Weathers et al. [1979]). (B) Quartz water contents due to fluid inclusions (ppm, molar H/10⁶ Si) versus structural distance beneath the Moine thrust. (C) Cross-plot of quartz water content (ppm) versus recrystallization (vol%). Mean OH contents, standard deviations, and standard errors of mean OH contents are given in the Data Repository (Table DR3 [see footnote 1]). Smooth nonlinear curves in A and B (blue) are intended for illustration purposes only, without any claim of functional dependence. Line in C is least-squares fit to data.

IMPLICATIONS

Water contents of relict sedimentary grains of the least-deformed quartzite protolith at 70 m below the Moine thrust at the Stack of Glencoul are large (4080 ppm; Fig. 4B), and comparable to those of quartz deformed in laboratory experiments by water-weakening processes. The inverse correlation between water and extent of recrystallization (Fig. 4C) suggests loss of water during deformation and recovery processes. The IR character of OH bands and prior observations of Moine thrust mylonites (Ord and Christie, 1984) indicate that most of the intragranular water lost during recrystallization originally occurred as fluid inclusions. H₂O loss from detrital grain interiors may have been due to pipe diffusion (Cordier et al., 1988; Bakker and Jansen, 1994) during SGR recrystallization or decrepitation of inclusions (Tarantola et al., 2010), with delivery to grain boundaries. Once at grain margins, continued loss of H₂O from the deforming quartzites may have proceeded by grain boundary diffusion and impurity sweeping by mobile grain boundaries during BLG recrystallization (Palazzin et al., 2018).

Water contents of 1570 ppm in highly sheared mylonites directly below the Moine thrust (Figs. 2B and 4B) were apparently sufficient for continued deformation. There is no evidence of changing deformation mechanisms, work hardening, or shear zone broadening as observed for other mylonites (Finch et al., 2016). Water weakening may have continued throughout the footwall mylonites, owing to the presence of water within inclusions and grain boundaries at all structural levels, thus maintaining an elevated fugacity of water (Kohlstedt et al., 1995; Hirth et al., 2001; Holyoke and Kronenberg, 2013). Yet, the observed loss of water associated with (and presumably due to) deformation and recovery processes indicates that water weakening was not the cause of strain localization. Instead, penetrative strain (or strain rate) variations at constant shear stress in the mylonites must have been governed by proximity to the overlying ductile fault plane, along which mylonitic Precambrian rocks have been displaced laterally by many tens of kilometers (Peach et al., 1907) and thrust over the similarly mylonitic, but more foreland-positioned, Cambrian quartzites.

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