Reversible water weakening of quartz

Caleb Holyoke
Andreas Kronenberg

Available at: https://works.bepress.com/caleb_holyoke/12/
Reversible water weakening of quartz
Caleb W. Holyoke III*, Andreas K. Kronenberg

Department of Geology and Geophysics, Texas A&M University College Station, TX 77843-3115, United States

ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form 23 April 2013
Accepted 24 May 2013
Editor: L. Sturkow
Available online 15 June 2013

Keywords:
water weakening
quartz
rheology

ABSTRACT

We have performed looped pressure-stepping deformation experiments at the same temperature (800 °C) and strain rate (2 × 10−6 s−1) on a milky quartz crystal and a quartzite that deform by dislocation creep. Our results demonstrate that flow strengths at fixed water content depend on fH2O, and that the dependence is reversible. Thus, rheology of quartzite can be predicted if fH2O is known. In addition, the effect of fH2O on strength of quartzite is greater than that of the milky quartz single crystal. The differing sensitivities are due to differing effects that water has on deformation and recovery within grain interiors and at (or near) grain boundaries. These results indicate that, as temperature increases with depth and the dominant recovery mechanism of dislocation creep changes from recrystallization at grain boundaries to intragranular recovery, dependence of quartz creep on fH2O may also decrease.

1. Introduction

Water weakening of quartz continues to be poorly understood because of differences in the mechanical properties of single crystals and polycrystals, differences in the types of water defects, and differences in conditions required for weakening. Griggs and Blacic (1964) first observed water weakening of dry natural quartz crystals deformed in the laboratory under hydrous conditions. However, most experimental data for quartz single crystals come from hydrothermally grown synthetic crystals with large initial water contents (Griggs and Blacic, 1965; Kokelwala et al., 1978, 1981; Kirby and McCormick, 1979; Linker and Kirby, 1981; Muto et al., 2011). Low strengths and evidence for water weakening in wet synthetic single crystals are observed at atmospheric pressure as well as high pressures (1500 MPa) and their strength appears to depend on water content rather than water fugacity (see review in Kronenberg (1994) and Muto et al. (2011)). These results may not be relevant to nature due to the difference in character of the water (free water in fluid inclusions in natural quartz versus gel-type nano-inclusions in synthetic quartz (Kekulawala et al., 1978, 1981; Kronenberg, 1994)). Furthermore, creep rates of synthetic quartz crystals are transient as fluid inclusions nucleate during deformation (Linker and Kirby, 1981). However, more recent results indicate that the rheology of natural milky quartz single crystals is also dependent on water content (Kronenberg et al., 2001).

In contrast to synthetic single crystals, experimentally deformed quartzites are strong at low Pc and progressively weaken with increasing Pc. The importance of elevated confining pressures to promote water weakening of natural quartzites was first reported by Mainprice and Paterson (1984) and confirmed by Kronenberg and Tullis (1984) for quartzites and fine-grained novaculites. Based on inferences of quartz defect chemistry (Hobbs, 1981) and comparisons with olivine deformed in a hydrous environment, the Pc effect on water weakening of quartzites was interpreted to result from the increase of water fugacity (fH2O) with increasing pressure (Kohlstedt et al., 1995). Individual deformation experiments on quartzites carried out at high Pc with varying fluid compositions and differing values of fH2O, fO2, and fH2O have confirmed this interpretation, showing that strength is reduced at high fH2O with little or no effect of other thermodynamic variables associated with fluid components (Post et al., 1996; Chernak et al., 2009).

The influence of fH2O on dislocation creep of quartz has been corroborated in naturally deformed rocks, in which crystal plastic deformation was documented in quartz of graphite-free schists, while quartz deformed by brittle cracking at the same temperature and pressure in graphite-bearing schists (Selverstone, 2005). Selverstone (2005) attributed this variation in quartz deformation mechanism to variations in local fH2O due to the localized presence of graphite in the embrittled schists. Based on fluids of the C–O–H system and equilibrium with graphite, Selverstone (2005) showed that dislocation creep was the predominant deformation mechanism at high fH2O, while brittle cracking replaced dislocation creep at low local values of fH2O. These results indicate that the strength of quartz may be extremely sensitive to changes in fH2O.

We have performed two pressure-stepping experiments on a milky quartz crystal and a quartzite to answer the following questions:

(1) Does the strength of a single crystal oriented for slip on the basal (a) slip system depend on fH2O as observed for quartzites at a given water content?
Given that microcracking is promoted at high differential stresses anticipated at low $P_c$ and low $f_{H_2O}$, we applied high $P_c$ ($1.55 \pm 0.05$ GPa) at the beginning of each experiment, and performed constant strain rate tests at one or two more sequentially decreasing $P_c$. In between each deformation test, samples were unloaded and confining pressure was reduced over three hours. After these lower $P_c$ deformation steps, we tested reproducibility by duplicating the original, high $P_c$ deformation step. At the conclusion of the final step, the experiment was quenched to 300 °C to preserve the microstructures and then brought to room temperature and pressure over a period of 2 h.

Force and displacement data were corrected for changes in the loaded cross sectional area of the sample, assuming that it retained a right cylinder shape, and background friction to determine differential stresses and strains. The mechanical data was also corrected for load column friction and assembly strength according to the methods described in Holyoke and Kronenberg (2010) (Fig. 1). The same correction for load column friction and assembly strength was applied to the mechanical data of previous studies performed using a solid salt assembly in the Griggs apparatus (Kronenberg and Tullis, 1984; Post et al., 1996; Chernak et al., 2009) to determine stresses accurately (Holyoke and Kronenberg, 2010). Water fugacities were determined by the methods of Pitzer and Sterner (1994). The presence of salts (CaCl$_2$) in the fluid inclusions results in a very small decrease (0.01–0.05 in value of log $f_{H_2O}$, depending on concentration of salts), from the values of log $f_{H_2O}$ we calculated (Bakker, 1999).

Deformed samples were impregnated with epoxy and thin sections were prepared parallel to the compression direction for optical microscopy and infrared (IR) spectroscopy. IR spectra over the wavenumber range of 4000–1400 cm$^{-1}$ were collected from multiple spots of deformed single-crystal and polycrystalline samples, avoiding epoxy-filled cracks, using a Nic-Plan microscope attachment to a Thermo-Nicolet Magna 560 Fourier transform infrared (FTIR) spectrometer using unpolared light. FTIR measurements of water content were collected to confirm the presence of free intragranular water in the samples following the experiments and to confirm that water contents were similar to those observed in previous experiments using the same starting materials.

3. Experimental results

We performed deformation experiments on a natural milky quartz crystal and a natural quartzite, applying different $P_c$ sequentially during individual experiments at the same temperature (800 °C) and strain rate ($1.6 \times 10^{-5}$ s$^{-1}$). The presence of water in fluid inclusions of both natural quartz materials allows us to determine the fugacity of water from the pressure of the experiment through the activity coefficient ($f_{H_2O} = r_{H_2O} \times P_{H_2O}$; Pitzer and Sterner, 1994; Bakker, 1999). The strengths of both the Arkansas milky quartz single crystal and Black Hills quartzite increase with sequential decreases in $P_c$ (and $f_{H_2O}$) at constant temperature and strain rate. As expected, the strength of Black Hills quartzite was greater than the milky quartz oriented for easy slip at the same conditions. After yielding at 2–3% strain, the Arkansas milky quartz single crystal deformed at relatively constant differential stresses of 40, 60, and 100 MPa at $P_c = 1.58, 0.85$, and 0.61 GPa, respectively (Table 1, Fig. 1). In the final deformation test, the differential stress following yielding returned to 40 MPa, after $P_c$ was increased back to 1.5 GPa. Differential stresses in constant strain rate compression experiments on Black Hills quartzite increase from 70 MPa to 260 MPa with the drop in $P_c$ from 1.6 GPa to 0.85 GPa (Table 1, Fig. 1). In the final deformation test, differential stress decreased to 80 MPa upon returning $P_c$ to
1.56 GPa. While the increases in strength of the milky quartz single crystal and polycrystalline quartzite due to reduction in \( P_c \) and water fugacity differ significantly, both are reversible with differential stresses that are the same (within 10 MPa) during initial and final steps at the same \( P_c \) (and \( f_{H_2O} \)).

The optical and TEM scale microstructures observed in both samples are consistent with dislocation creep with slip dominantly on the basal (a) slip system (Table 1, Fig. 2). Coarse, optical-scale fluid inclusions of the staring materials are replaced by extremely fine, distributed fluid inclusions by processes documented by Tarantola et al. (2010, 2012). Recovery in the milky quartz single crystal occurs by dislocation climb and recovery in the quartzite is dominated by grain boundary bulge recrystallization with a component of dislocation climb (Stipp et al., 2010). Water concentrations determined from the area of absorbance beneath the broad water band (3700–3000 cm\(^{-1}\)), using the Stipp et al. (2006) calibration, are 8460 H/10\(^6\) Si (±1980) for the Arkansas milky quartz crystal and 2630 H/10\(^6\) Si (±670) for the Black Hills quartzite (Fig. 3). The character of their absorption bands is consistent with OH stretching of liquid molecular water in distributed fluid inclusions. The concentrations of water in our samples are consistent with previous measurements of water contents in deformed samples of the Arkansas milky quartz crystal (Kronenberg et al., 2001) and Black Hills quartzite (Stipp et al., 2006).

### 4. Discussion

#### 4.1. Reversibility of water weakening

The pressure-stepping results for single crystal milky quartz demonstrate that water weakening by hydrogen defects, which accelerate dislocation processes (i.e. glide and climb) in grain...
where \( \dot{\epsilon} \) is the strain rate, \( \sigma_{\text{diff}} \) is the differential stress, \( Q \) is the activation energy, \( R \) is the gas constant, \( T \) is the absolute temperature, and \( A, r, s, n \) are constants. The \( P_s \)-stepping experiments also demonstrate the reversibility of the \( \sigma_{\text{diff}}-f_{\text{H}_2\text{O}} \) relation of Eq. (1). However, the dependence of strength on \( f_{\text{H}_2\text{O}} \) differs between the natural quartz single crystal and quartzite. We do not know the exact nature of the critical hydrogen (or hydrogen-bearing) defects that are responsible for increasing dislocation mobility or enhance grain boundary mobility. However, deformation microstructures of the single crystal and quartzite indicate that both deform by climb-accommodated dislocation creep with slip on the (a) slip system. Therefore, the differing \( \sigma_{\text{diff}}-f_{\text{H}_2\text{O}} \) relations suggest that some form of hydrogen defects enhance recovery processes that differ in single crystals and polycrystalline samples.

Our results differ from those obtained for synthetic quartz crystals. First, steady strengths are achieved at low strains (~5%) at fixed \( T, \dot{\epsilon}, \) and \( f_{\text{H}_2\text{O}} \) while synthetic quartz crystals deformed in axial compression work harden at all conditions (Kirby and McCormick, 1979, Kekulawala et al., 1979, 1981). Synthetic quartz crystals deformed at high pressures in general shear ultimately reach steady state conditions but only at large shear strains of 1–4 after a period of transience (Muto et al., 2011). The predominant slip system activated for the milky quartz crystal is basal (a) (Table 1, Fig. 1); whereas, the predominant slip system activated in synthetic single crystals deformed at 1 atm in uniaxial compression is prism (c) (Kirby and McCormick, 1979). Results for synthetic single crystals deformed at high confining pressure (~1.5 GPa) are more similar to our results for milky quartz with basal (a) slip being weaker than prism (c) slip (Muto et al., 2011). Previous results for quartz single crystals indicate that strengths depend on the water content, either as non-freezable water clusters in synthetic quartz crystals (Griggs and Blacic, 1965; Kekulawala et al., 1978, 1981; Muto et al., 2011) or freezable fluid inclusions in Arkansas milky quartz (Kronenberg et al., 2001). However, the creep strength dependence of quartz single crystals on \( f_{\text{H}_2\text{O}} \) has not been reported. Prior studies of synthetic quartz have not been performed over varying \( f_{\text{H}_2\text{O}} \), and large variations in water content of individual cores of milky quartz may have obscured this effect. Differences in mechanical properties measured for synthetic quartz crystals deformed at low \( f_{\text{H}_2\text{O}} \) and our results for milky quartz deformed at high \( f_{\text{H}_2\text{O}} \) may be due to differences between their fluid inclusion populations and distributions. Transient creep observed for synthetic quartz crystals has been linked to increasing diffusion distances as fluid inclusions coarsen and become widely spaced (Kronenberg, 1994). For the case of milky quartz, transient strain weakening may be expected during early deformation as large fluid inclusions are replaced by fine fluid inclusions (Kronenberg et al., 2001). However, we observe constant stress deformation at constant strain rate in the first step, which is reproduced in the final step. Thus, any large changes in populations or spacing of fluid inclusions must occur at very low strains (<1%) in the first deformation step of each pressure-stepping experiment. This is consistent with the early collapse of large, optical-scale fluid inclusions under non-hydrostatic stresses, and the formation of a secondary generation of fine, TEM-scale inclusions (Tarantola et al., 2010, 2012). Flow strengths measured during pressure-stepping experiments correspond to deformation at comparable populations of fine fluid inclusions. Given that fluid inclusions serve as sources of hydrogen defects to dislocations and grain boundaries, the dependence of milky quartz and quartzite rheologies on \( f_{\text{H}_2\text{O}} \) represent reversible responses in hydrogen defect concentrations that can be applied to models of the strength of the Earth’s crust based on thermodynamic conditions of pressure (i.e. \( f_{\text{H}_2\text{O}} \)) and temperature, without knowledge of water content or geologic history.

### 4.2. Water fugacity dependence

The increase in strength of the Arkansas milky quartz crystal from 40 to 100 MPa at confining pressures of 1.58 and 0.61 GPa, respectively, is consistent with Eq. (1), if we assume that freezable H2O in fluid inclusions fix \( f_{\text{H}_2\text{O}} \) at the experimental pressure and buffered \( f_{\text{H}_2\text{O}} \). If \( T \) and \( \dot{\epsilon} \) are constant, then the relationship between \( \sigma_{\text{diff}} \) and \( f_{\text{H}_2\text{O}} \) can be described by

\[
\Delta \log \sigma_{\text{diff}} = \frac{r}{n} \Delta \log f_{\text{H}_2\text{O}}.
\]

and the \( f_{\text{H}_2\text{O}} \) exponent \( r \) can be determined from the slope of this relationship (r/n) if \( n \) is known. Although the value of \( n \) for basal (a) slip in wet single crystals has not been determined, the value of \( n \) for first-order prism slip, which has the same Burgers vector (a), is 3.4–5.3 (Kirby and McCormick, 1979; Linker and Kirby, 1981) and the value determined for quartzites deforming predominantly on the basal (a) slip system is 4 (Luan and Paterson, 1992; Gleason and Tullis 1995). Therefore, if the value of r/n is 0.37 and we assume \( n = 4 \) for basal (a) slip in milky quartz, then \( r = 1.5 \).

Our pressure-stepping results for Black Hills quartzite are in excellent agreement with previous studies of individual samples of natural polycrystalline aggregates (quartzites and novaculites) deformed over a wide range in \( P_c \) and \( f_{\text{H}_2\text{O}} \) (Kronenberg and Tullis, 1984; Post et al., 1996; Chernak et al., 2009; data corrected according to Holyoke and Kronenberg (2010)). The best fit to the corrected data from experiments performed on Black Hills quartzite (Chernak et al., 2009) and novaculite (Kronenberg and Tullis, 1984) (Fig. 4) gives \( r/n = 0.63 \), or \( r = 2.5 \) if \( n = 4.0 \) (Luan and Paterson, 1992; Gleason and Tullis, 1995). This value is consistent with values of \( r = 2.1 \) and 2.8 determined for the Heavitree quartzite using the piston-cylinder and gas deformation apparatus (Post et al., 1996, M. Paterson, personal communication in Post

---

**Fig. 4.** Results of pressure-stepping experiments conducted on Arkansas milky quartz single crystal and Black Hills quartzite, displayed as \( \log \sigma_{\text{diff}} \) versus \( \log f_{\text{H}_2\text{O}} \). Results are also shown for published results of individual experiments performed over a wide range of \( P_c \) for Black Hills quartzite (Chernak et al., 2009) and Arkansas novaculite (Kronenberg and Tullis, 1984). Pressure-stepping results for Arkansas milky quartz single crystal define a slope (~0.37); or \( r = 1.5 \) for \( n = 4 \) that is significantly lower than defined by the quartzite data (~0.63; or \( r = 2.5 \) for \( n = 4 \); using pressure-stepping results of this study and previous results). Individual experiments performed using Heavitree quartzite (Post et al., 1996) are offset from the Black Hills quartzite and novaculite results, but have a similar slope (~0.53; or \( r = 2.1 \) for \( n = 4 \)).
et al. (1996)). This value is considerably larger than $r$ inferred for milky quartz crystal ($r$=1.5).

4.3. Differing recovery mechanisms in quartz single crystal and quartzite

Comparing either the ratio ($r/n$) or the inferred values of $r$, the effect of $f_{H_2O}$ on creep of quartzite is larger than we find for single crystal milky quartz shortening at the same experimental conditions (Fig. 4). Basal deformation lamellae and microstructures of both deformed milky quartz and quartzite samples indicate that basal (a) slip is predominant and that internal recovery occurs by dislocation climb. In the case of single crystals, dislocation creep may depend on $f_{H_2O}$ through the influence of hydrogen (water-related) defects that increase the rates of diffusion and dislocation climb (Tullis and Yund, 1989). However, the large creep dependence of quartzite on $f_{H_2O}$ may be due to effects of water at grain boundaries, in addition to internal recovery. Water appears to increase grain boundary mobility (Tullis and Yund, 1982), leading to rapid grain growth and perhaps enhanced recrystallization, even while it does not change the grain size-stress relationship of steady-state creep (Stipp et al., 2006).

Hirth and Tullis (1992) demonstrated that at colder temperatures or higher strain rates (i.e. stresses $>$ 220 MPa), dislocation climb is limited in quartzites and the dominant recovery process is strain-induced grain boundary migration (Regime 1 of Hirth and Tullis (1992)). At stresses $<$ 220 MPa, Hirth and Tullis (1992) found that subgrains begin to form at the TEM scale and they concluded that dislocation climb is the dominant recovery process with recrystallization occurring by subgrain rotation (Regime 2 of Hirth and Tullis (1992)). However, they also observed microstructures due to strain-induced grain boundary migration, much as observed in the quartzite deformed in this study, which deformed at differential stresses of 70–260 MPa.

In a recent study of microstructures of naturally deformed quartzites, Stipp et al. (2010) found that strain-induced grain boundary bulge-migration is the dominant recrystallization process at low temperatures (400°C) and geologic strain rates, corresponding to Regime 2 and most of Regime 3 dislocation creep of Hirth and Tullis (1992). Stipp et al. (2010) concluded that, although dislocation climb is important at the conditions of Regime 2 creep, strain-induced recrystallization is important to defect reduction in all three creep regimes. The difference in $f_{H_2O}$ exponents for milky quartz and polycrystalline quartzite may therefore reflect the effect of hydrogen defects on internal recovery by climb in both single crystals and polycrystals, while water and/or hydrogen defects facilitate quartzite deformation further by accelerating grain boundary migration.

Water concentration data also point to the importance of processes operating at grain boundaries during deformation of quartzites. The average water concentration in the Black Hills quartzite sample from this study (2630 ± 670 H/10^6 Si) is similar to the average concentrations of water observed in deformed samples of Black Hills quartzite with 0.2 wt% water added (2860 ± 680 H/10^6 Si) and with no water added (2250 ± 290 H/10^6 Si) prior to the experiment by Stipp et al. (2006), Post et al. (1996) and Stipp et al. (2006) found that water-added samples do not have significantly more water in grain interiors than measured for samples deformed without adding water. These results indicate that the decrease in the strength of quartzites with added water relative to the strength of quartzites without water added and deformed at the same conditions is due to water at (or near) grain boundaries, which may enhance rates of grain boundary migration, which may enhance rates of recovery by recrystallization processes.

4.4. Naturally deformed quartzites

Naturally deformed quartzites commonly contain aqueous fluid inclusions, indicating deformation in the presence of free water (Kronenberg, 1994). The direct response to changes in $f_{H_2O}$ imposed by pressure-stepping experiments on Black Hills quartzite and milky quartz and the reversibility of these responses indicate that changes in the rheology of naturally deforming quartzites can be modeled without knowledge of the specific water content as long as free water is present. Previous determinations of quartzite flow laws (Gleason and Tullis, 1995; Kohlstedt et al., 1995; Hirth et al., 2001) have favored a linear dependence ($r=1$) on $f_{H_2O}$, particularly at low stresses. However, the best-fit value of $r/n$ (0.63) across the measured range of stresses and water fugacities (Fig. 4) and the reported value $n=4$ requires that $r$ is much greater than unity ($r=2.5$). The activation energy ($Q=135$ kJ/mol, Hirth et al., 2001) and stress exponent ($n$) of Eq. (1) are not affected by this change in $r$ value since they are determined at constant $f_{H_2O}$ conditions, but the pre-exponential term ($A$) must be recalculated due to the change in the value of $r$ (recalculated log $A=-13.2 \pm 0.6$ MPa^{-1}s^{-1}$ in the Hirth et al. (2001) flow law). We expect that this rheology will govern quartzite deformation at conditions where strain-induced grain boundary migration is the predominant recovery mechanism ($T<400$ C, Stipp et al., 2002, 2010). However, studies of naturally deformed quartzites indicate that the dominant recovery mechanism at elevated temperatures of the lower crust changes to subgrain rotation recrystallization, which has not been replicated in the laboratory (Stipp et al., 2002, 2010). Our single-crystal pressure-stepping results indicate that quartz deformation, in the absence of grain boundary recovery mechanisms, is less sensitive to $f_{H_2O}$ than observed in quartzite experiments. Water contents in the mid to lower crust appear to decrease with increasing temperature (Nakashima et al., 1995; Yardley and Valley, 1997; Thust et al., 2011). Thus, water fugacities may decrease once H2O is no longer present as a separate phase. Yet, quartz may remain weak given that intragranular recovery mechanisms have a weaker $f_{H_2O}$ dependence than determined for grain boundary bulging recovery.

5. Conclusions

On the basis of pressure-stepping experiments performed on natural quartz single and polycrystalline samples with spectroscopically similar types of water, residing primarily in freezeable fluid inclusions, we find that:

(1) Water weakening of quartz during dislocation creep depends on the fugacity of water $f_{H_2O}$ and this dependence is reversible in both single and polycrystals.

(2) The influence of $f_{H_2O}$ on dislocation creep strength of quartzite deformed at conditions that favor basal (a) slip and recovery by grain boundary bulging is stronger than observed for milky quartz single crystals deforming by basal (a) slip in the absence of grain boundary recovery processes.

(3) The water fugacity dependence observed in Regime 2 dislocation creep for quartzite is likely due to effects of water-derived defects that enhance recovery processes within grains and recrystallization processes at grain boundaries.

Acknowledgments

This study was inspired by discussions about hydrolytic weakening mechanisms in milky quartz single crystals between Renee C.W. Holyoke III, A.K. Kronenberg / Earth and Planetary Science Letters 374 (2013) 185–190 189
Heilbronner, Holger Stuenitz, Anja Thust, AK and CH. CH and AK thank Linda Chernak and Jan Tullis for generously providing the Black Hills quartzite starting material. We thank Linda Chernak, Greg Hirth, Julie Newman, Dave Prior, Jan Tullis and Rachel Wells for valuable discussions of these results, and Jane Selverstone, Jan Tullis, Michael Stipp and an anonymous reviewer for constructive reviews, which significantly improved this manuscript.

References


