

Fourier transform IR-determination of intragranular water content in quartzites experimentally deformed with and without added water in the ductile deformation field

Bas den Brok¹

HPT-laboratory, Institute of Earth Sciences, University of Utrecht, the Netherlands

Jörg Meinecke and Klaus Röller

Institute of Geology, Ruhr University, Bochum, Germany

Abstract. To test whether the weakening effect of added water in ductile deformation experiments on quartzite at high P-T conditions is associated with measurable changes in intragranular water content (c_w) we determined Fourier transform infrared (FTIR) spectra of single grains (grain size 150-250 μm ; IR spot size $\sim 70 \mu\text{m}$) in samples of Dongelberg quartzite experimentally deformed in a Griggs solid-medium deformation apparatus at a temperature of 800°C, a confining pressure of ~ 1200 MPa, and a strain rate of $\sim 10^{-7} \text{ s}^{-1}$, both with and without ~ 0.4 wt % added water. The added water caused a weakening effect of a factor ≥ 9 . Microstructural observations indicate that the dominant deformation mechanism in the weakened samples was solution-precipitation creep. The FTIR measurements showed that the starting material has a broad variation in c_w as well as in the type of OH absorption. The c_w of individual grains range from <200 -2900 molar ppm H/Si (measurement resolution: 100-1000 molar ppm H/Si; standard error of average c_w values 300-900 molar ppm H/Si). The experimentally deformed samples, whether deformed with or without added water, showed a broadly similar variation in c_w with similar types of OH absorption. Relatively "dry" grains (<100 -500 molar ppm H/Si) were still present in the samples deformed with added water, as well as relatively "wet" grains (>3000 molar ppm H/Si) in samples deformed without added water. We were unable to demonstrate any significant changes in average c_w after either of the treatments. Apparently, the water weakening effects seen in our experiments occurred without measurable changes in c_w .

Introduction

It is well known that addition of small amounts of water can strongly affect the flow behavior of natural quartzite in experiments at elevated P-T conditions. For example, samples of natural quartzite (grain size 100 to 250 μm), experimentally deformed at 800°C, a confining pressure of ~ 1500 MPa, with a strain rate of 10^{-6} s^{-1} , in the presence of ~ 0.4 wt % of added water, are ~ 10 times weaker than samples deformed without added water [Jaoul *et al.*, 1984]. Though poorly understood, it is widely assumed that this weakening effect is caused by bulk lattice and/or dislocation pipe diffusion of (a significant part of) the water into the original quartz grains and subsequent promotion of dislocation mobility (glide and climb) and/or dislocation multiplication [e.g., Paterson, 1989; Tullis and Yund 1989; Kronenberg *et al.*, 1990; Tullis, 1990; Tullis *et al.*, 1990].

Den Brok and Spiers [1991] recently proposed a different explanation for the weakening effect of added water in experiments on natural quartzite. According to these authors, the dominant deformation mechanism during macroscopic ductile deformation of the samples with added water is not dislocation creep, but solution precipitation creep plus microcracking, and they argued that these processes cause the

observed weakening effect. The reason that den Brok and Spiers [1991] came to this conclusion was that they observed that the dominant deformation microstructure in their samples deformed at a temperature of 800°C, a pressure of ~ 1200 MPa, a strain rate of 10^{-7} s^{-1} , and with ~ 0.4 wt % added water consisted of abundant small, new polygonal to euhedral quartz grains developed in axially oriented microfractures and grain boundaries. These axial arrays of small new grains contained abundant voids and channel structures, and it was inferred that the new grains were formed by precipitation from solution. The original grains showed abundant microscale subeuhedral syntaxial overgrowth features on grain boundaries oriented parallel to the shortening direction (Z); such features were conspicuously absent at grain boundaries oriented perpendicular to Z.

Two more observations were consistent with solution-precipitation creep plus microcracking which would be difficult to explain if dislocation-plastic mechanisms were assumed to be dominant. First, in samples deformed to ~ 40 and $\sim 46\%$ bulk finite strain, no significant lattice preferred orientation was developed [see also den Brok, 1992], and second, samples deformed with added water showed a stress-strain rate relationship fitting a power law with a stress exponent $n \leq 1.3$. Such very low n values were reported earlier (e.g., $n \approx 1.4$ by Jaoul *et al.* [1984]) and were considered enigmatic, since these were difficult to explain when weakening occurred by an intracrystalline dislocation-plastic mechanism. They are explained though, when it is assumed that solution-precipitation creep contributed significantly to the deformation.

¹Now at Department of Geology, University of Mainz, Germany.

Copyright 1994 by the American Geophysical Union.

Paper number 94JB01473.
0148-0227/94/94JB-01473\$05.00

In this paper we focus on another observation that is difficult to explain when the water-weakening effect in experiments on natural quartzite is assumed to occur by diffusional incorporation of water into the quartz grains followed by a promotion of the dislocation mobility and/or multiplication. This hypothesis predicts that the intragranular water content (c_w) of the grains in the quartzites deformed with added water should be higher than that of the grains in the undeformed starting material. Only one study in which the intragranular water content (c_w) of quartzite was actually measured after deformation has appeared in the literature [Kronenberg and Wolf, 1990]. In this case, determinations were made using Fourier transform infrared (FTIR) spectroscopy. The results showed that c_w of deformed material was similar to the starting value (~3800 molar ppm H/Si), even though the samples deformed in a ductile manner and were significantly weakened (by a factor ~10; see above) by the 0.5-0.6 wt % added water. This observation cannot easily be reconciled with the diffusion-based water weakening concept, since that requires quantities of water to enter the lattice that should be easily measurable [e.g., Blacic and Christie, 1984]. Water-weakening effects by a factor ~10 are caused by addition of 0.4 wt % water (equivalent to ~27,000 molar ppm H/Si), whereas the resolution of the IR measurements is usually of the order of 100-1000 molar ppm H/Si.

As an alternative interpretation, Kronenberg and Wolf [1990] suggested that the added water could have buffered the original c_w , so that the original intragranular water could have allowed the easy movement of the dislocations. They proposed that if no water had been added, then the original intragranular water might have diffused out of the grains, and the samples would have been stronger; however, they did not test their explanation by measuring a loss of water from the grain interiors when samples were deformed without added water. We decided to conduct a similar, but more systematic study, of water contents in deformed quartzite with the aim of testing previous hypotheses of the weakening effect of added water in experiments on quartzites.

It should be emphasized that the present study concerns the weakening effect of added water only, and not (1) the weakening effect associated with grown-in water in synthetic quartz [e.g., McLaren *et al.*, 1989], (2) the weakening effect of water present in as-received material (compared to vacuum heated samples that are almost completely dry) [e.g., Jaoul *et al.*, 1984], or (3) the weakening effect of dehydrating talc, as has been used repeatedly in experiments in the Griggs solid medium deformation apparatus as a confining medium [e.g., Koch *et al.*, 1989].

Deformation Experiments and Conditions

All of the experiments reported in the present paper were carried out on Dongelberg quartzite, described previously by den Brok and Spiers [1991] and den Brok [1992]. The Dongelberg quartzite is a very dense material (porosity < 0.1%) consisting of ~97 vol % quartz with a grain size of 150-250 μm . The quartzite contains ~2 vol % white micas (probably phengitic) and ~1 vol % Fe-(hydr)oxides. The weight loss, determined by thermo gravimetry (measured by heating the samples for 30 hours in nitrogen gas at 800°C), is about 0.3 wt %. This value includes the water made available from dehydration of micas and Fe hydroxides, plus the intergranular and intragranular water present in the quartzite.

Cylindrical specimens of this material, measuring 6 mm in diameter and 12 ± 1 mm in length, were cored from a single block at 45° to the bedding, using a diamond coring tool with water as a lubricant. The ends of the sample were then ground flat and parallel to within 30 μm measured parallel to the sample length. The samples were subsequently oven dried at 150°C for 12 hours to remove any surficial water.

As described in detail by den Brok [1992], the samples were deformed using a Tullis-modified Griggs apparatus with NaCl as the confining medium. Temperature and pressure were raised simultaneously in order to follow the water isochore of 1 Mg/m^3 as closely as possible. The deformation experiments were performed at constant displacement rates corresponding to a strain rate of $\sim 10^{-7} \text{ s}^{-1}$ to total strains of 5 to 15%. After deformation, samples were unloaded at rates $< 3 \times 10^{-6} \text{ m/s}$, and the temperature and pressure were lowered, once again following the water isochore of 1 Mg/m^3 as closely as possible. Cooling times varied from 0.3 to 2.2 hours.

The raw data were processed, correcting the axial displacement for apparatus distortion, and loads for friction [see den Brok, 1992]. To determine the axial load supported by the sample, it was assumed that the "take-off force record" (i.e., when the inner piston is advanced through the upper lead disk of the sample assembly) could be linearly extrapolated. The extrapolation would thus give an estimate of the load required to push against the pressure plus the friction, while the sample is axially loaded. The load supported by the sample is obtained by subtracting the extrapolated values from the total measured load. It should be noted, however, that load or displacement variations with confining pressure, as well as variations in friction between the inner and the outer piston, may cause deviations in the linearity of the extrapolated values.

Differential stresses were calculated using the initial cross section of the samples. Axial strain was computed using the initial sample length at ambient P-T conditions. The resolution of the stress measurement is believed to be approximately 25 MPa, a figure that is comparable with that obtained in previous work using the Griggs apparatus [e.g., Jaoul *et al.*, 1984].

Quartzite samples GRU11 and 26 (see Table 1) [see also den Brok and Spiers, 1991; den Brok, 1992] were weld sealed in Au capsules together with ~0.4 wt % of added water, and deformed at a temperature of 800°C, a confining pressure of ~1200 MPa, and a strain rate of $\sim 10^{-7} \text{ s}^{-1}$ to 11 (± 1) and 14 (± 1)% bulk finite strain, respectively. Sample GRU39 was jacketed in gold without added water, and held at a temperature of 800°C and a confining pressure of ~1200 MPa for ~5.5 days. Samples GRU31 and 41 were also jacketed in gold without added water, but experimentally deformed, at a temperature of 800°C, a confining pressure of ~1200 MPa, a strain rate of $\sim 10^{-7} \text{ s}^{-1}$, to a finite strain of 10 (± 1)%. The durations of the tests were ~12.3 and ~14.8 days, respectively. Sample GRU40 was also jacketed in gold without added water, but first held at 800°C and ~1200 MPa for ~13.5 days (without deformation). It was then deformed to 7 (± 1)% strain at 10^{-7} s^{-1} for a further ~8.1 days before termination of the test.

The relevant mechanical data appear in Table 1 and have been presented as axial stress versus strain graphs in Figure 1. Samples GRU11 and 26 (both deformed with added water) had strengths that remained below the stress resolution of the Griggs apparatus (i.e., <25 MPa). Due to failure of the force measurement system, no stress/strain curve was determined for

Table 1. Summary of Experimental Data

Sample	Condition	-Log strain rate, s ⁻¹	Finite strain, %	P _c , MPa	LTC, °C	UTC, °C	t ₁ , hours:min	t ₂ , hours	t ₃ , days	t ₄ , hours:min	Yield stress, MPa	Maximum stress, MPa	Average c _w ± SE, ppm H/Si
DBQ16	as-rec	0.0	0	0	0	0	0:00	0	0.0	0:00	—	—	1250 ± 300
GRU11	wet	7.0	11	1040	784	800	2:20	19	13.5	2:40	?	<25	1900 ± 500
GRU26	wet	7.0	14	1130	798	800	4:30	144	22.2	0:20	?	<25	1200 ± 300
GRU39	as-rec	0.0	0	1170	774	815	34:45	133	5.5	1:50	—	—	2000 ± 500
GRU31	as-rec	7.0	10	1160	776	800	21:10	78	14.8	0:50	140	210	2450 ± 900
GRU41	as-rec	7.0	10	1200	816	800	25:55	17	12.3	0:22	?	?	1400 ± 400
GRU40	as-rec	7.0	7	1190	788	815	30:20	324	21.6	0:17	225	225	1850 ± 400

"Wet" refers to 0.4 wt % water added, while "as-rec" refers to as-received (i.e., without added water); LTC, lower thermocouple temperature; UTC, upper thermocouple temperature; t₁, elapsed time to reach P-T conditions; t₂, time at P-T conditions before deformation; t₃, total time at P-T conditions; t₄, elapsed time after deformation to reach room P-T conditions; c_w, intragranular water content (average c_w values are tabulated together with their standard error).

experiment GRU41 (deformed without added water). Experiment GRU31 (without added water) showed macroscopic yielding at ~140 MPa and ~2% strain, followed by strain hardening. After ~10% strain the differential stress was ~210 MPa. Sample GRU40, deformed without added water after a preheating stage of ~13.5 days, yielded at ~225 MPa, after which the sample appeared to approach steady state flow. The samples deformed with added water were ≥9 times weaker than the samples deformed without added water.

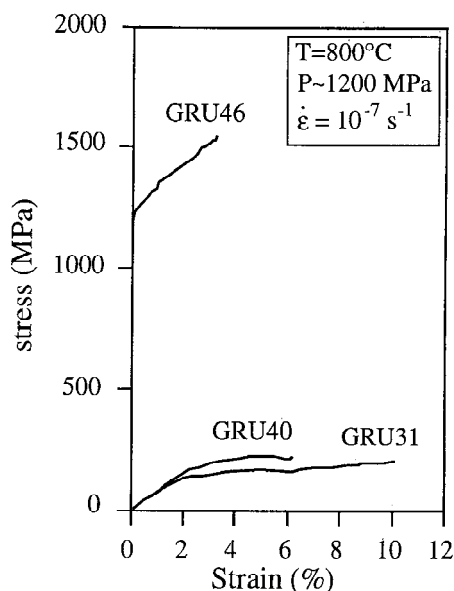


Figure 1. Stress/strain curves obtained for samples GRU31 and GRU40. The curves of samples GRU11 and GRU26 deformed with 0.4 wt % added water could not be determined (stresses measured were below the resolution limit of the Griggs apparatus, i.e., lower than ~25 MPa). For comparison, we also plotted the curve of Dongelberg quartzite sample GRU46, which was vacuum heated for ~12 hours at 800°C prior to deformation and contained <200 molar ppm H/Si. Sample GRU46 was deformed under otherwise similar conditions (i.e., a temperature of 800°C, a confining pressure of ~1200 MPa, and a strain rate of 10⁻⁷ s⁻¹).

FTIR Measurement Technique

The IR spectra were obtained using an IFS-48 Bruker Fourier transform infrared spectrometer with IR microscope (Bruker). The spectroscope is equipped with a globar (SiC) infrared source, a HgCdTe IR detector with ZnSe window, a germanium-coated KBr beam splitter, and has a wavenumber resolution of 4 cm⁻¹. The microscope allows direct observation of the measurement area by optical microscopy. Using the infrared optics of the microscope, reproducible spectra were obtained from selected spots. A spot size of ~70 μm was sufficient to measure intragranular water contents of single grains of the Dongelberg quartzite (grain size 150-250 μm). The microscope was equipped with a vacuum cooling stage allowing low-temperature measurements to 77 K.

Samples were prepared as unsupported longitudinal sections through the cylindrical samples, with a thickness of 50-240 μm. They were polished on both sides using SiC powder with grit sizes down to 0.3 μm. FTIR transmission spectra from single grains were obtained by accumulating 128 scans in the wavenumber range of 5000 to 1700 cm⁻¹. Room temperature (~295 K) and low-temperature (~77 K) spectra were taken at every measuring spot. About 2-20 spectra were taken for each sample.

Determination of water content was carried out after the method favored by Paterson [1982]. This method determines the OH concentration by integrating over the OH absorption band using a wavenumber-dependent absorption coefficient. Absorption was assumed to be isotropic (i.e., independent of crystallographic orientation). Only the room temperature spectra were used for this determination. The detection limit for the OH broadband absorption, dominating in all spectra, varies between 100 and 1000 molar ppm H/Si, depending on the thickness of the samples. For graphical presentation the spectra were baseline corrected to eliminate individual scattering and reflection effects; the baseline was assumed to be linear.

Optical Microstructures

The microstructures of samples GRU11 and 26 (deformed with added water) were described in detail by den Brok and Spiers [1991] and den Brok [1992]. In these samples the most conspicuous microstructural features are the abundant small,

new polygonal to euhedral quartz grains, developed in axially oriented microfractures and grain boundaries. The original grains show abundant microscale syntaxial overgrowth features on grain boundaries oriented parallel to the shortening direction, and are almost free of intracrystalline deformation features. Deformation lamellae are present in less than ~5% of the original grains. *Den Brok and Spiers* [1991] argued that these samples were deformed predominantly by solution-precipitation creep plus stable microcracking. A sample deformed to ~46% bulk strain under otherwise similar conditions shows no significant *c* axis preferred orientation [*den Brok, 1992*].

The microstructure of sample GRU39, hydrostatically loaded without added water for ~5.5 days, is similar to that of the starting material, except for the presence of a single sample-scale fracture oriented perpendicular to the sample axis. This crack was presumably introduced during depressurization.

Sample GRU41, which was deformed to ~10% strain without added water, shows (subbasal) deformation lamellae developed in 30-60% of the grains. Deformation bands are also present, and are mostly associated with bending of the lamellae. Abundant axially oriented microfractures are present on the sample scale. These appear to have propagated from a sample-scale shear fault oriented at ~30° to the shortening direction (*Z*). Many finely spaced fractures appear oriented perpendicular to *Z*, presumably due to unloading. (Note that the presence of the sample-scale axial and shear fractures under the experimental conditions at which sample GRU41 was deformed is quite unusual.)

The deformation microstructures seen in samples GRU31 and 40, which were also deformed without added water, are similar to those observed in sample GRU41, except that no sample-scale axial or shear fractures are present, and that the number of unloading fractures is small.

FTIR Results

The samples in which the intragranular water content (c_w) was measured are listed in Table 2. DBQ16 is the starting material. In all, 67 spectra were measured for 63 original (i.e., non recrystallized) grains, located in the seven samples. The c_w obtained for each grain are listed in Table 2 and in Figure 2. The average c_w with their standard errors are given for each sample in Table 1. A typical collection of base-line corrected absorption spectra is shown in Figure 3. A complete reproduction of all of the determined spectra can be found in the work by *den Brok* [1992].

The FTIR spectra show a wide variation of OH absorption type and intensity. Typical for the room temperature spectra is a broadband absorption with an intensity maximum around 3400 cm^{-1} . Additionally, many spectra show a more or less intense absorption band at around 3620 cm^{-1} . In most cases, low-temperature ($T \approx 77$ K) spectra reveal a shift and modification of the broad absorption band, with a new maximum at 3200 cm^{-1} . The new absorption maximum is caused by the overlapping structure of three bands. This is due to the formation of ice in submicroscopic fluid inclusions [e.g., *Aines and Rossman, 1984*]. Extremely sharp bands occur at 3565 and 3685 cm^{-1} ; these are due to OH-related point defects [*Kats et al., 1962*].

The absorption band at 3620 cm^{-1} remains unaffected by freezing and is probably caused by submicroscopic mica inclusions [*Kronenberg and Wolf, 1990*]. In addition, a

fraction of the broadband absorption does not change with cooling. The nature of water defects causing this absorption type remains unclear (see discussion by *McLaren et al.* [1984]). A discussion of the problematic interpretation of IR spectra of natural quartz is in preparation (*K. Röller et al.*, manuscript in preparation, 1994). By comparing the spectra with that of pure ice, the total amount of freezable water can be estimated (Table 2). In all but one of the grains more than 40% of the water is freezable.

The spectra also show absorption bands that are not related to OH. Very weak absorption near 3200 and 3300 cm^{-1} was attributed to Si-O bonds [*Kats et al., 1962*], and in sample GRU11 (grains 8, 11 and 12), absorption bands are present around 2850 to 2950 cm^{-1} that are most likely due to organic material, very probably the araldite used in thin-section preparation.

The type of spectrum varies from grain to grain, and the variation in c_w is remarkably large, both in the starting material as well as in the experimentally treated samples. For instance, there are "dry" grains containing <200 molar ppm H/Si and "wet" grains containing >3000 molar ppm H/Si. This heterogeneity in type of spectrum and the quantity of c_w is typical for quartzites composed of quartz grains of different origin, as has been demonstrated recently by *Stöckhert et al.* [1990], *Meinecke et al.* [1991], and *Röller et al.* [1993], who determined the type, the quantity, and the distribution of water-related defects and submicroscopic inclusions in many different well-characterized natural quartz rocks.

The intragranular water content of our samples also varies within single grains. For example, in one grain in the deformed sample GRU40 a relatively "dry" portion contains ~600 ppm H/Si whereas a relatively "wet" part contains ~2900 molar ppm H/Si. "Wet" grains, or parts of grains, invariably contain very fine (<1 μm), but optically visible fluid inclusions. These are mostly heterogeneously distributed (i.e., planar arrays of fluid inclusions are relatively rare). Unfortunately, the number of grains that could be measured in each sample is insufficient to enable a well-balanced average c_w for each sample (standard errors of the calculated average c_w fall in the range 24-40%, corresponding to 300-900 molar ppm H/Si). For the two to 20 grains per sample, the spread in c_w was simply too large.

It should be noted that the reported c_w refer to the bulk c_w minus the water believed to be present in micas. The reason for this correction is that the mica-bound water is not believed to play a significant role during the deformation of the quartz grains because most of the micas are still present after deformation.

Discussion

The FTIR measurements show that the spread in c_w determined in the starting material (DBQ16) and in the differently treated samples (GRU11, 26, 31, 39, 40, 41) is broadly similar. "Dry" grains (<100-500 molar ppm H/Si) and "wet" grains (>3000 molar ppm H/Si) were present in all of the experimentally treated samples, whether deformed with added water (even after a test duration of ~3 weeks at 800°C and 1200 MPa), or without added water (test duration up to ~15 days). Apparently, no pervasive equilibration of c_w occurred. Moreover, the different water species (freezable and non-freezable, molecular water and hydroxyl; see above) were all present in the starting material as well as in the treated

Table 2. Summary of c_w Determinations

Sample	Grain	Sample thickness, μm	H/Si, ppm			freezable, %	non-freezable, %
			Bulk	Mica	Quartz		
DBQ16	1	200	500	<200	300-500	*	*
	2	200	<200		<200	*	
	3	200	600		600	50%	50%
	4	200	700	<200	500-700	*	*
	5	200	1700	200	1500	40%	60%
	6	200	1900	200	1700	40%	60%
	7	200	2300	500	1800	*	
	8	200	800	100	700	*	
	9	200	11000	7800	3200	*	*
	10	200	700	<100	600-700	*	*
	11	200	200		200	*	*
	12	200	5600	2700	2900	*	†
	13	200	3500	1500	2000	*	
GRU11	1	90	<500		<500		
	2	90	4600		4600	60%	40%
	3	90	500		500	*	
	4	90	6100		6100	*	†
	5	90	3000	200	2800	*	
	6	90	<500		<500	*	
	7	270	1100		1100	*	
	8	270	1800		1800	*	
	9	270	2200		2200	*	
	10	270	500	<100	400-500	*	
	11	270	1400		700	*	
	12	270	2900	1300	1600	*	
GRU26	1	220	400		400	*	
	2	220	300		300	*	
	3	220	1300	<200	1100-1300	*	*
	4	220	2100	200	1900	*	
	5	220	800		800	*	*
	6	220	1700		1700	*	
	7	220	3000	<200	2800-3000	*	
	8	220	900	<200	700-900	*	
GRU39	1	140	4300		4300	30%	70%
	2	140	700		700	*	
	3	240	800		800	*	
	4	240	5700	1900	3800	*	
	5	240	3900	1700	2200	*	
	6	240	1200	100	1100	*	
	7	240	1900	100	1800	*	
	8	240	1300	<100	1200-1300	*	
GRU31	1	110	3700		3700	*	†
	2	110	800		800	*	
	3	50	1600		1600	*	
	4	50	6200		6200	60%	40%
	5	50	<1000		<1000	*	
	6	50	1400		1400	*	
GRU41	1	240	3000		3000	*	
	2	240	4300	2300	2000	*	†
	3	240	200	100	100	*	†
	4	240	2100	1000	1100	*	†
	5	240	800		800	*	†
	6	240	4200	2800	1400	*	†
GRU40	1	180	2900	<200	2700-2900	40%	60%
	2	180	600	<200	400-600	*	
	3	180	1100		1100	*	
	4	180	1700		1700	*	
	5	180	4700	200	4500	*	
	6	180	400	<200	200-400	*	
	7	180	4000		4000	*	
	8	180	2100	<200	1900-2100	70%	30%
	9	180	400	<200	200-400	60%	40%
	10	180	1300		1300	*	†
	11	180	2300	700	1600-2300	*	
	12	180	2000		2000	*	
	13	180	1500	100	1400	*	†
	14	180	2100	1000	1100	*	
	15	180	3500		3500	*	*

* Presence of (non)freezable water is indicated by IR spectrum,

† Only small amounts of (non)freezable water indicated by IR spectrum; for further explanation, see text.

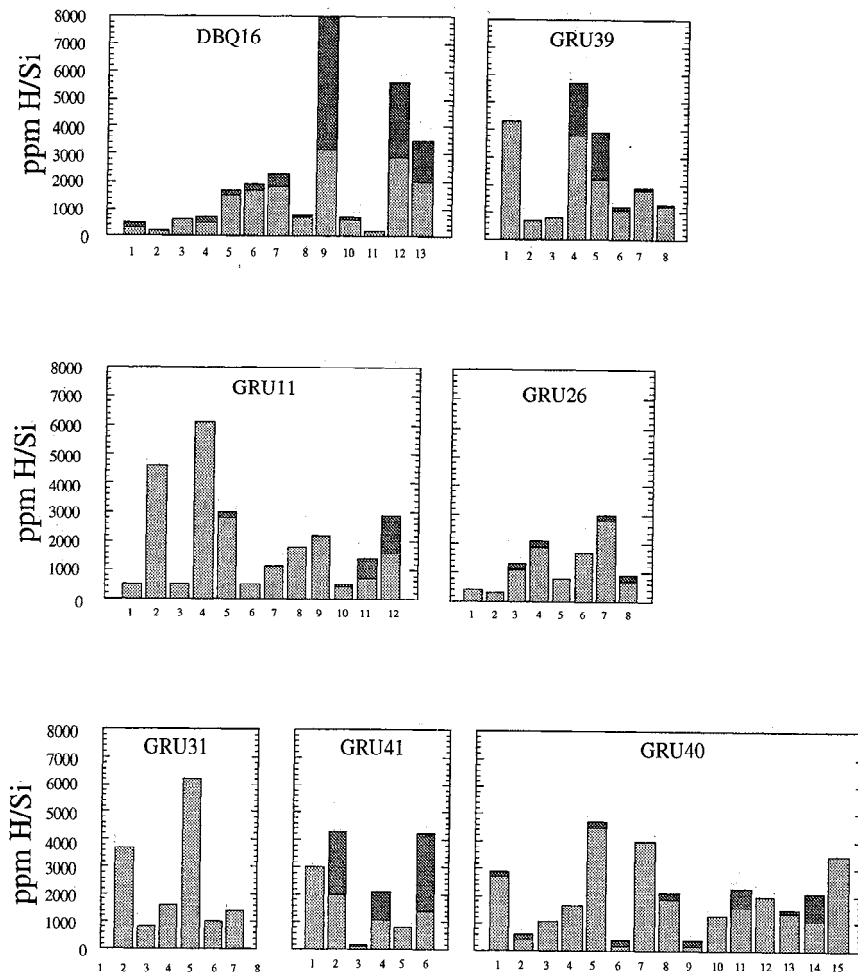


Figure 2. Histograms showing intragranular water content (c_w in molar ppm H/Si). Each histogram refers to one sample (sample number is indicated). Each column refers to one grain (grain numbers are also indicated). The darker shaded part of the columns is the contribution of absorption attributed to mica.

samples, and in broadly similar amounts. Hence, no significant changes in the distribution of the different water species occurred. There is also no indication that the average starting c_w was significantly altered by either of the treatments (though the standard errors in the average c_w values are quite large). The observed water-weakening effect (of a factor ≥ 9) therefore occurred without the uptake of significant and measurable amounts of water by the quartz grains. This result is in excellent agreement with results of *Kronenberg and Wolf* [1990] for samples deformed with added water (i.e., there is no significant increase in c_w). The present findings are inconsistent, however, with the suggestion of *Kronenberg and Wolf* [1990] that the original intragranular water would diffuse out of the grains when the samples are deformed without added water. Our results show that large quantities of intragranular water in the samples deformed without added water do not diffuse out of grain interiors.

Mainly on the basis of microstructural evidence, *den Brok and Spiers* [1991] concluded that the water-added samples (GRU11 and 26) were deformed predominantly by solution-precipitation creep plus microcracking. Our FTIR results are qualitatively consistent with this hypothesis, since diffusion

of water into or out of the original grains is not required for solution-precipitation creep to occur.

At broadly similar P-T conditions the weakening effect of added water observed in previously reported experiments on natural quartzite were mostly assumed to be of an intracrystalline nature, caused by diffusion of the added water into the quartz grains and subsequent promotion of dislocation mobility [e.g., *Mainprice and Paterson*, 1984; *Jaoul et al.*, 1984; *Koch et al.*, 1989; *Tullis*, 1990; *Ralser et al.*, 1991]. The weakening effects seen in these experiments were caused by addition of 0.1 to 0.5 wt % water. If all of this would have entered the quartz grains by diffusion, then c_w values should have been increased by several 10000 molar ppm H/Si. This is not compatible, however, with our present results on a comparable starting material, at similar P-T conditions, with similar amounts of added water, and for much longer time spans (up to 3 weeks). Our results suggest that any increases in c_w must be less than about 1000 molar ppm H/Si.

One explanation for this might be that significant fractions of the added water in many of the previous water-weakening experiments may have been lost by diffusional transport of hydrogen out of the metal sample capsules. Thus, only a

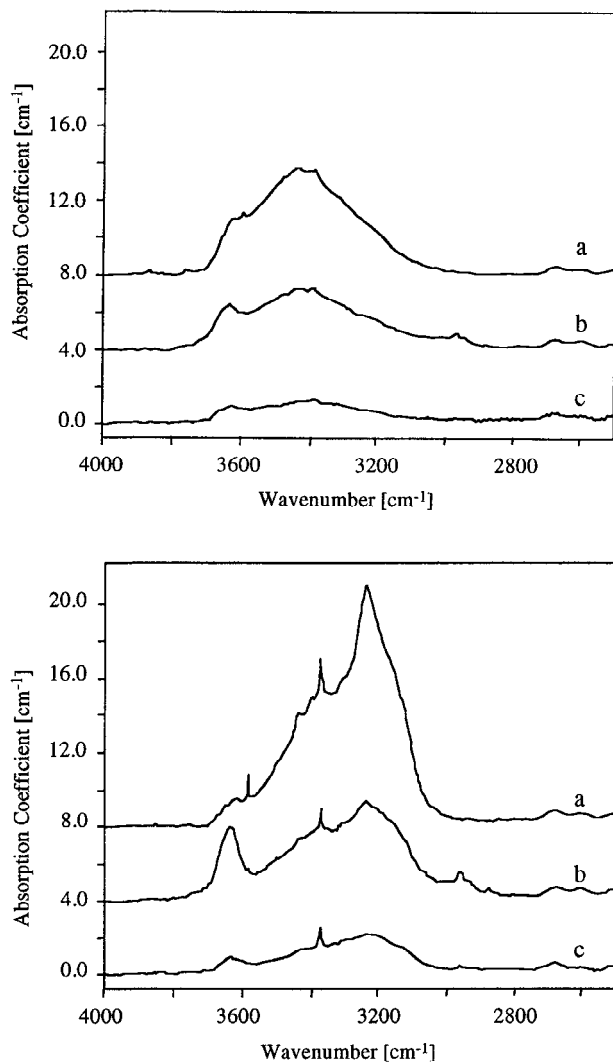


Figure 3. Typical examples of some baseline-corrected FTIR transmission spectra measured in three different grains: (a) spectra determined at room temperature and (b) spectra determined at low temperature (~ 77 K). Curves "a" were measured in grain number 1 of sample GRU41, curves "b" in grain number 8 of sample GRU11, and curves "c" in grain number 1 of sample DBQ16. Sample thicknesses are indicated in Table 3. In order to compare the different baseline-corrected spectra, they were shifted vertically by four units relative to each other.

remnant of the added water (<1000 molar ppm H/Si) may have been available and caused an intracrystalline weakening effect. In the present experiments, Au capsules were used with a wall thickness of 0.7 mm, and diffusion of hydrogen through Au capsules of this thickness can be considered negligible at the present experimental conditions. The capsules were also weld sealed, thus preventing any loss of water during pressurization of the sample. One problem that remains in this case is that in spite of differences in jacket materials used, the stress versus strain rate data of *Jaoul et al.* [1984] and of *den Brok and Spiers* [1991] for similar experimental conditions are comparable, even though *Jaoul et al.* [1984] used Pt capsules through which diffusion of hydrogen should be much faster than through gold, and their capsules were only mechanically sealed. The close fit

of the mechanical data obtained with quite different capsule materials would indicate that diffusion of hydrogen out of the sample capsules was probably not very important.

Another explanation for why the weakening effect of added water in previously reported experiments on quartzite was mostly assumed to be of intracrystalline signature, and not due to solution-precipitation creep and microcracking, might be that in these experiments the contribution of crystal plastic processes (inferred from the optical and transmission electron microscopical deformation microstructures) was overestimated, and accordingly the contribution of solution-precipitation processes underestimated, such as previously suggested by *den Brok* [1991, 1992] and *den Brok and Spiers* [1991]. Following these authors, the typical "crystal plastic" deformation features (such as undulatory extinction, subgrains, and recrystallized grains) could equally well result by a combination of microcracking plus solution-precipitation processes. These features should therefore not be used as criteria for crystal plastic deformation.

Our results do not rule out that amounts smaller than ~ 1000 molar ppm H/Si diffused into the quartz grains and eventually affected the dislocation substructure. *Farver and Yund* [1991] observed that the oxygen lattice diffusivity at a temperature of 700°C and pressures in the range 5-350 MPa increased with increasing water fugacity, thus suggesting that (at least some) water diffused into the quartz lattice under these P-T conditions. At 800°C and at the much higher pressures attained in the present experiments, this might have occurred as well. *Tullis and Yund* [1989] demonstrated that water at 800°C and 1500 MPa can promote dislocation climb. They deformed a natural quartzite sample without added water at a temperature of 700°C , a pressure of 1500 MPa, and a strain rate of 10^{-5} s^{-1} . A differential stress of 2100 MPa was reached. After deformation, the sample contained a very high and heterogeneous dislocation density (10^{11} - 10^{12} cm^{-2}). Annealing of this sample at a temperature of 800°C and pressures of 550 and 1500 MPa, for 1 and 4 days, with and without added water, showed that water promoted dislocation climb. Dislocation climb did not occur in samples annealed without added water. In our experiments, the added water may also have promoted dislocation climb, though without having a dominant effect on the strength of the samples. Our results suggest that it is the larger portion of the added water (i.e., the part that did not diffuse into the grains) that caused the weakening effect.

The results of the present study may be consistent with the model proposed by *Fitz Gerald et al.* [1991] for the weakening effect of added water seen in the experiments on natural single crystals of quartz. These authors assumed that water would only enhance intracrystalline deformation indirectly, namely, by the promotion of stress corrosion cracking and associated healing and/or sealing processes. This would promote the nucleation of dislocations, and enhance intracrystalline deformation processes. In the quartzite experiments, relatively large amounts of added water might have controlled the number of cracks that developed; only small (or negligible) amounts of water may have been incorporated into the grains. However, there is no direct evidence for this occurring in experiments on quartzite. In addition, natural quartzites commonly already show moderate (starting) dislocation densities (e.g., $\sim 10^8 \text{ cm}^{-2}$ in the case of the Dongelberg quartzite, whereas the dislocation density in natural Brazilian quartz is commonly of the order of 10^3 cm^{-2}); thus, nucleation of dislocations does not appear to be essential for the weakening of quartzites.

Conclusion

We have reported FTIR determinations of intragranular water content in natural quartzite samples (grain size 150-250 μm) experimentally deformed both with and without 0.4 wt % added water at a temperature of 800°C, a confining pressure of ~1200 MPa, and a strain rate of $\sim 10^{-7} \text{ s}^{-1}$. Though the water-added samples were maintained for 14-22 days under high P-T conditions and were ≥ 9 times weaker than samples deformed without added water, added water did not diffuse into the quartz grains within measurement resolution (≤ 1000 molar ppm H/Si). Similarly, no evidence was found for any diffusion of water out of the grains in samples deformed without added water during experiments of 6-22 days. Because the amount of water that needs to be added in order to obtain a significant weakening effect is much larger than the measurement resolution (namely, of the order of several tens of thousands of molar ppm H/Si when diffused into the grains), it is concluded that the water that remains present at grain boundaries and/or in open fractures (i.e., the water that does not diffuse into the grains) plays an essential role in the weakening process. This supports the suggestion of *den Brok and Spiers* [1991] that the weakening effect of added water seen in such experiments on natural quartzite may be caused mainly by solution-precipitation creep and microcracking.

Acknowledgments. We wish to thank Chris Spiers for carefully reviewing earlier versions of the manuscript, and Jim Boland and John Fitz Gerald for some valuable comments. Reviews and comments by Andy Kronenberg, Stephen Mackwell, and Jan Tullis very significantly improved the content and readability of the final manuscript. B. den Brok received financial support from the Netherlands Organisation for Scientific Research (NWO) (AWON project 751.353.017). The Deutsche Forschungsgemeinschaft (DFG) provided financial support and sponsored J.M. and K.R. with a grant.

References

- Aines, R.D., and G.R. Rossman, Water in minerals? A peak in the infrared, *J. Geophys. Res.*, **89**, 4059-4071, 1984.
- Blacic, J.D., and J.M. Christie, Plasticity and hydrolytic weakening of quartz single crystals, *J. Geophys. Res.*, **89**, 4223-4239, 1984.
- den Brok, S.W.J., Development of apparent crystal plastic deformation microstructures in quartz by stable extensional microcracking plus solution-precipitation creep, *Terra Nova*, **3**, *Abstr. Suppl.*, **5**, 33, 1991.
- den Brok, S.W.J., An experimental investigation into the effect of water on the flow of quartzite, *Geol. Ultraiectina*, **95**, 178 pp., 1992.
- den Brok, S.W.J., and C.J. Spiers, Experimental evidence for water weakening of quartzite by microcracking plus solution-precipitation creep, *J. Geol. Soc. London*, **148**, 541-548, 1991.
- Farver, J.R., and R.A. Yund, Oxygen diffusion in quartz: Dependence on temperature and water fugacity, *Chem. Geol.*, **90**, 55-70, 1991.
- Fitz Gerald, J.D., J.N. Boland, A.C. McLaren, A. Ord, and B.E. Hobbs, Microstructures in water-weakened single crystals of quartz, *J. Geophys. Res.*, **96**, 2139-2155, 1991.
- Jaoul, O., J. Tullis, and A.K. Kronenberg, The effect of varying water content on the creep behavior of Heavtree quartzite, *J. Geophys. Res.*, **89**, 4298-4312, 1984.
- Kats, A., Y. Haven, and J.M. Stevels, Hydroxyl groups in α -quartz, *Phys. Chem. Glasses*, **3**, 69-75, 1962.
- Koch, P.S., J.M. Christie, A. Ord, and R.P. George Jr., Effect of water on the rheology of experimentally deformed quartzite, *J. Geophys. Res.*, **94**, 13,975-13,996, 1989.
- Kronenberg, A.K., and G.H. Wolf, Fourier transform infrared spectroscopy determinations of intragranular water content in quartz-bearing rocks: Implications for hydrolytic weakening in the laboratory and within the earth, *Tectonophysics*, **172**, 255-271, 1990.
- Kronenberg, A.K., P. Segall, and G.H. Wolf, Hydrolytic weakening and penetrative deformation within a natural shear zone, in *The Brittle-Ductile Transition in Rocks: The Heard Volume*, *Geophys. Monogr. Ser.*, vol. 56, edited by A.G. Duba, W.B. Durham, J.W. Handin, and H.F. Wang, pp. 21-36, AGU, Washington, D.C., 1990.
- Mainprice, D.H., and M.S. Paterson, Experimental studies on the role of water in the plasticity of quartzites, *J. Geophys. Res.*, **89**, 4257-4269, 1984.
- McLaren, A.C., R.F. Cook, S.T. Hyde, and R.C. Tobin, The mechanisms of the formation and growth of water bubbles and associated dislocation loops in synthetic quartz, *Phys. Chem. Miner.*, **9**, 79-94, 1984.
- McLaren, A.C., J.D. Fitz Gerald, and J. Gerretsen, Dislocation nucleation and multiplication in synthetic quartz: relevance to water weakening, *Phys. Chem. Minerals*, **16**, 465-482, 1989.
- Meinecke, J., K. Röller, B. Martin, O.W. Flörke, and B. Stöckhert, "Water" species in quartz related to the microfabric of metamorphic rocks (abstract), in European Union of Geosciences EUG VI, *Terra Abstr.*, **3**, 74, 1991.
- Paterson, M.S., The determination of hydroxyl by infrared absorption in quartz, silicate glasses and similar materials, *Bull. Mineral.*, **105**, 20-29, 1982.
- Paterson, M.S., The interaction of water with quartz and its influence in dislocation flow - An overview, in *Rheology of Solids and of the Earth*, edited by S.I. Karato and M. Toriumi, pp. 107-142, Oxford University Press, New York, 1989.
- Ralser, S., B.E. Hobbs, and A. Ord, Experimental deformation of a quartz mylonite, *J. Struct. Geol.*, **13**, 837-850, 1991.
- Röller, K., J. Meinecke, R. Wirth, O. Flörke, and B. Stöckhert, Water in rock-forming quartz (abstract), in European Union of Geosciences EUG VII, *Terra Abstr.*, **5**, 296-297, 1993.
- Stöckhert, B., K. Röller, B. Martin, and O.W. Flörke, Hydrolytic weakening in nature - A FTIR microspectrometric study of water in quartz from metamorphic rocks (abstract), in Conference on Crustal Dynamics, Pathways and Records, 21-24 Feb. 1990, Bochum, RFG, *Terra Abstr.*, **2**, 21, 1990.
- Tullis, J., Experimental studies of deformation mechanisms and microstructures in quartz-feldspathic rocks, in *Deformation Processes in Minerals, Ceramics and Rocks*, edited by D.J. Barber and P.G. Meredith, pp. 190-227, Unwin Hyman, London, 1990.
- Tullis, J., and R.A. Yund, Hydrolytic weakening of quartz aggregates: The effects of water and pressure on recovery, *Geophys. Res. Lett.*, **16**, 1343-1346, 1989.
- Tullis, J., L. Dell'Angelo, and R.A. Yund, Ductile shear zones from brittle precursors in feldspathic rocks: The role of dynamic recrystallization, in *The Brittle-Ductile Transition in Rocks: The Heard Volume*, *Geophys. Monogr. Ser.*, vol. 56, edited by A.G. Duba, W.B. Durham, J.W. Handin, and H.F. Wang, pp. 67-81, AGU, Washington, D.C., 1990.

B. den Brok, Tectonophysics laboratory, Department of Geology, University of Mainz, 55099 Mainz, Germany. (e-mail: denbrok@dagobert.zdv.uni-mainz.de)

J. Meinecke and K. Röller, Institute of Geology, Ruhr University, 44780 Bochum, Germany.

(Received March 29, 1993; revised May 27, 1994; accepted June 7, 1994.)