Rheology and Microfabrics of Quartz: Experimental Deformation in Torsion

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Abstract

This study investigated the rheological, microstructural and textural evolution of quartz-rich aggregates at high temperature and high strain in torsion experiments using a Paterson gas-medium apparatus. Flow law parameters were derived from mechanical data. Textures and microstructures were studied using optical microscopy, X-ray texture goniometry, scanning electron microscopy including EBSD, synchrotron experiments and transmission electron microscopy.

Three different quartz-rich aggregates (Dover flint, Arkansas novaculite, hot-pressed silicic acid) were used as starting materials. Dover flint was deformed at temperatures of 1250-1400 K (977-1127 °C), 350 MPa confining pressure and constant twist rate (corresponding to maximum shear strain rate of $10^{-4}$ s$^{-1}$) under drained or undrained conditions. Heat-treatments were performed under drained conditions prior to deformation for different amounts of time (1/2 h up to 25 h) at 1300 K (1027 °C) and confining pressures of 150 MPa or 350 MPa. They resulted in an initial dilation with an isotropic distribution of water-filled pores followed by compaction by diffusive mass transfer processes. Deformation at 1300 K (1027 °C) was characterized by apparent steady-state behavior up to a shear strain of around $\gamma = 0.2$ followed by sudden hardening for shear strains up to $\gamma = 2.5$. During the apparent steady-state, the pores redistributed into an anisotropic arrangement in planes oriented at ± 25° to the maximum principal stress direction $\sigma_1$. The hardening was associated with the interconnection of some pores to form continuous bands in a synthetic Riedel (R1) orientation, but with no discernible lateral offset along them. These R1 bands are interpreted to serve as fluid pathways enhancing local drainage of the surrounding matrix, thus causing hardening by loss of pore pressure. Texture measurements in high strain samples indicated a weak lattice preferred orientation in the matrix with an oblique c-axis girdle opposite to the sense of shear. All microscopical evidence suggests that the dominant deformation mechanism was granular flow. Two samples were unloaded at a shear strain of $\gamma = 1.3$ and 2.5, respectively, and reloaded after 1/2 h annealing at the deformation temperature and pressure. Subsequent deformation occurred by sliding along pre-existing R1 bands. The microstructure showed the evolution of the R1 bands into shear planes with a visible displacement and grain-size reduction.

At 1400 K (1127 °C), the microstructure of samples heat treated for 1/2 h and deformed to low shear strains ($\gamma < 0.2$) under undrained conditions showed evidence of tensile fracturing, suggesting that the pore pressure exceeded the confining pressure. Drained samples showed no evidence of cracking. Other samples heat-treated for 1/2 h were deformed to high shear strains ($\gamma > 1.5$). These showed steady-state stresses up to a shear strain of $\gamma = 2$, then they progressively hardened. Strain hardening was primarily correlated with the development of cracks. Deformation
was strongly heterogeneous. Microstructural observations suggest that the strain accommodating mechanism was granular flow as in the experiments at 1300 K (1027 °C), probably enhanced by local melting along grain boundaries.

The instrumental setup for texture goniometry was optimized for small and fine-grained (<1 μm) quartz samples which are generally not accessible to EBSD analysis. Dover flint provides an isotropic standard to determine texture corrections for quartz. The dependence of texture index on the size of the sampled population was taken into account to quantitatively compare pole figures measured with X-ray texture goniometer, synchrotron experiments and EBSD analysis. This concept was demonstrated for weak and random textures in flint as well as for strong textures in natural quartz mylonites.

Synthetic quartz aggregates were produced by isostatic hot-pressing of predried or as-received silicic acid at 300 MPa confining pressure and 1300-1400 K (1027-1127 °C) for several hours under drained or undrained conditions. The microstructure of the synthesized samples was strongly influenced by the water content: low water content during hot-pressing led to incomplete crystallization with the presence of cristobalite and/or amorphous silica, whereas high water content promoted a strongly heterogeneous grain size and high porosity. Deformation experiments on hot-pressed silicic acid were performed at 1300 K-1400 K (1027-1127 °C), 300 MPa and strain rates of 1*10⁻⁴ to 1*10⁻⁵ s⁻¹ under drained or undrained conditions. The maximum attained shear strain was γ < 0.1 due to slippage at the sample-spacer interface.

Arkansas novaculite of two different grain sizes (1 and 30 μm) was deformed in torsion under drained conditions at 1300-1400 K (1027-1127 °C), 350 MPa and shear strain rates of 3*10⁻⁵ s⁻¹ and 5*10⁻⁶ s⁻¹. The samples deformed to less than γ = 0.1 before slippage at the sample-spacer interface. Thus novaculite is too strong to be deformed in torsion within the available range of experimental conditions and setup, probably due to the low initial water content.

In summary, the experimental deformation of quartz in torsion is very sensitive to the amount of water present in the samples. Water-rich quartz aggregates were successfully deformed by a grain size sensitive mechanism in the semi-brittle regime up to high shear strain. The starting materials and experimental conditions used in this study did not allow to attain the regime of crystal-plastic deformation. Dedicated heat-treatment of Dover flint enables to prepare excellent starting material for other deformation experiments with a well-defined range of grain sizes and water contents.
Kurzfassung

In dieser Arbeit wurde die Entwicklung der Rheologie und des Mikrogefüges von quarzreichen Aggregaten während der Deformation zu hohen Scherbeträgen mittels Torsionsexperimenten bei hohen Temperaturen untersucht. Fließgesetzparameter wurden aus mechanischen Daten hergeleitet. Texturen und Mikrostrukturen wurden mittels Lichtmikroskopie, Texturgoniometrie, Rasterelektronenmikroskopie mit integrierter Elektronenrückstreubeugung (EBSD), Synchrotronexperimenten und Transmissionselektronenmikroskopie analysiert.


Bei 1400 K (1127 °C) zeigte die Mikrostruktur von nicht entwässernden Proben (1/2 Std. getempert und zu niedrigem Scherbetrag (γ < 0.2) verformt) Dehnungsbrüche, was darauf
schliesst, dass der Porendruck höher als der Umgebungsdruck war. Demgegenüber zeigten entwässernde Proben keine Rissbildungen. Andere Proben, die während 1/2 Std. getempert wurden, wurden zu hohen Scherbeträgen verformt ($\gamma > 1.5$). Sie zeigten eine scheinbar stationäre Fließspannung bis zu einer Scherung von $\gamma = 2$, gefolgt von einer progressiven Verfestigung. Die Verfestigung war hauptsächlich auf die Bildung von Rissen zurückzuführen. Die Verformung war sehr heterogen. Mikrostrukturbildliche Beobachtungen lassen darauf schliesen, dass analog zu den Experimenten bei 1300 K (1027 °C) der hauptsächliche Deformationsmechanismus "Granulares Fließen" war, wahrseheinlich unterstützt durch Schmelzanteile, welche lokal entlang von Korngrenzen vorhanden waren.


Synthetische Quarzaggregate wurden mittels heiss-isostatischem Pressen (HIP) von unbehandelter oder vorgetrockneter Kieselsäure während mehreren Stunden unter entwässernden oder nicht entwässernden Bedingungen bei 300 MPa Umgebungsdruck und 1300 oder 1400 K (1027-1127 °C) hergestellt. Die Mikrostruktur der synthetisierten Proben war stark vom Wassergehalt beeinflusst: ein niedriger Wassergehalt während dem HIP-Verfahren führte zu unvollständiger Kristallisation (neben Quarz waren Cristobalit sowie amorphe Kieselsäure vorhanden), während ein hoher Wassergehalt eine stark heterogene Korngrösse sowie eine hohe Porosität bewirkte. Verformungsexperimente an synthetisierten Proben wurden bei 1300 und 1400 K (1027-1127 °C), 300 MPa und Scherraten von $1 \times 10^{-4}$ bis $1 \times 10^{-5}$ s$^{-1}$ unter entwässernden und nicht entwässernden Bedingungen durchgeführt. Der höchstmögliche Scherbetrag war nur gerade $\gamma < 0.1$ bevor der Reibungskontakt an der Stirnfläche der Probe verloren ging.

Proben von Arkansas Novakulit mit zwei unterschiedlichen Korngrössen (1 und 30 μm) wurden in Torsion unter entwässernden Bedingungen bei 1300 und 1400 K (1027-1127 °C), 350 MPa und Scherraten von $3 \times 10^{-5}$ s$^{-1}$ und $5 \times 10^{-6}$ s$^{-1}$ deformiert. Die Proben verformten weniger als $\gamma = 0.1$ bevor der Reibungskontakt an der Stirnfläche der Probe verloren ging. Novakulit ist demzufolge innerhalb der erreichbaren experimentellen Bedingungen zu hart, um in Torsion verformt zu werden, wahrscheinlich aufgrund des niedrigen Wassergehaltes.
1 Introduction

1.1 General background

Quartz is a major constituent of the Earth’s crust. It has been assumed that the flow strength of the upper and middle continental crust below the brittle-ductile transition can be described by the flow law for polycrystalline quartz aggregates deforming by dislocation creep processes (Fig. 1.1) (Fliervoet 1997 and references therein). The understanding of its rheological and microfabric (texture and microstructure) behavior is therefore of prime importance not only in the interpretation of geological structures, but also in the large scale geophysical interpretations of flow strengths and dynamics of the continental crust.

![Fig. 1.1 Strength profile for continental lithosphere; frictional regime data from Kohlstedt et al. (1995); plastic strength is based on wet quartzite flow law from Luan and Paterson (1992). The dashed line indicates the brittle-ductile transition.](image)

In general, deformation in the Earth’s crust tends to localize into narrow zones. Deformation in such high-strain zones is usually non-coaxial (i.e., the principal axes of finite strain do not lie parallel to those of successive strain increments); this type of high-strain zone, called shear zone, probably accommodates important tectonic displacements. The large magnitude of deformation often led to characteristic rocks (mylonites), whose microfabrics are very different from their protoliths (e.g., Etheridge and Wilkie, 1979), suggesting that there is an evolution of rheology, texture and microstructure with progressive strain. A steady-state configuration may possibly be reached at high strains. When deformation conditions change, it takes time (and further strain) until the system adjusts to the changed conditions, perhaps into a new steady-state. Numerous studies have focused on microfabrics of natural quartz mylonites, since they reflect information about the thermal, kinematic and mechanical evolution of a shear zone. Although a lot of data is available in the geological literature, their interpretation remains ambiguous because it is very
difficult to isolate the influence of each of the variables that contribute to the overall final pattern of the microfabric (Schmid, 1994).

One possible approach to study systematically the influence of some of the variables is to perform experimental rock deformation studies. The aim of such experiments is to activate the same processes that occur in nature, but under scaled and well-constrained conditions. The microstructure of samples experimentally deformed by dislocation creep have been correlated with recrystallization microstructures of natural mylonites (e.g. Stipp, 2001), showing that experimental rock deformation is a valuable tool for the interpretation of microfabrics preserved in naturally deformed rocks.

1.2 Problem definition

One of the main problems concerning the comparison between experimentally and naturally deformed rocks is that most experimental studies to date have been conducted in axial compression (i.e., coaxial deformation), whereas in nature, deformation is commonly non-coaxial. Noncoaxial high strain experiments (shear strain $\gamma < 3$) on quartz were performed using diagonal saw cut tests under axial compression (Dell’Angelo and Tullis, 1989). This study showed the importance of non-coaxial experiments for the investigation of microfabrics which are similar to those in naturally sheared rocks, but are absent in axial compression experiments. However, the disadvantages of diagonal saw cut tests are that (1) lateral offsets complicate the derivation of accurate strength data at higher strains, and (2) the deformation contains a flattening strain component.

Another important problem with axial compression experiments is that they involve small sample strains (typically around 45% at maximum, corresponding to a shear strain of $\gamma \approx 1$). In natural shear zones strains of at least $\gamma = 10 - 20$ are commonly reported (e.g. Ramsay and Graham, 1970). Pieri et al. (2001) clearly showed that the rheology and microfabric of Carrara marble still evolve in simple shear at shear strains much higher than $\gamma \approx 1$, suggesting that previous observations on mechanical and microfabric steady-state based on compression tests should be reconsidered. For quartz, no high strain data are available except those of Dell’Angelo and Tullis (1989).

Most of the experimental studies on quartz were performed in the dislocation creep regime (see Chapter 3). Grain size sensitive mechanisms, which are generally believed to be important in fine-grained quartz aggregates at high temperatures, are still under investigation (e.g. Brodie and
Rutter, 2000). Microfabric development in such aggregates has not been investigated in detail, and no simple shear experiments have been reported.

1.3 Present aims

From the above considerations it is clear that there is a need for experimental studies on the deformation of quartz aggregates under high strain simple shear. The torsion testing system is a reliable tool for such a goal since (1) it allows non-coaxial deformation with or without an axial deformation component, and (2) there is no theoretical limit on the amount of deformation that may be applied to the sample. The technique is often used in material sciences as well as in experiments on analogue materials. In experimental rock deformation it has been successfully applied to various rock-forming minerals, but not yet to quartz.

The aim of this research was to explore the rheological and microfabric development of quartz aggregates over a much larger strain range than previously investigated. High temperature simple shear experiments were performed to strains an order of magnitude larger than those obtained in conventional axial compression tests. Complete texture analyses of the deformed samples were carried out by using electron backscatter diffraction techniques, X-ray texture goniometry and synchrotron experiments. Microstructures were examined by means of optical microscopy and transmission electron microscopy.

1.4 Structure of the thesis

Some general information about occurrence, polymorphism, structure and chemistry of quartz is given in Chapter 2, and a review about previous experimental studies on quartz in the brittle and plastic fields is presented in Chapter 3. Chapter 4 provides details on techniques and analyses used in this study. Chapter 5 describes the rheological and microfabric evolution of Dover flint deformed to high shear strains (up to $\gamma = 4$) in torsion at temperatures of 1250 K, 1300 K, and 1400 K. The first part of this chapter is submitted for publication. Investigations on an optimized instrumental setup for texture goniometry of weak textures in fine-grained quartz aggregates are discussed in the first part of Chapter 6. The second part deals with a quantitative comparison of textures by means of the texture index obtained from quartz aggregates measured by X-ray goniometry, EBSD and synchrotron diffraction, and is being prepared for publication. Chapter 7 describes experiments on two other starting materials, namely fabrication and deformation of
hot-pressed silicic acid (synthetic quartz-rich aggregate) and deformation of Arkansas novaculite (natural quartz-rich aggregate). Chapter 8 provides a summary with some geological implications.
2 Structure and chemistry of the low-pressure silica polymorphs

2.1 Introduction: Occurrence of quartz-rich rocks

Quartz is the most abundant rock-forming mineral in the continental crust and occurs as an important mineral of many igneous, metamorphic and sedimentary rocks. It is common in hydrothermal veins where it is often associated with ores (Heaney, 1994). It also occurs as a secondary mineral, often forming a cementing matrix in sediments. Quartz has also been found in meteorites (Deer et al., 1963).

Rocks of granitic composition (granites, granodiorites, tonalites, granite pegmatites) consist of 55-60 weight percent of SiO₂ (Foucault and Raoult, 1984).

In metamorphic rocks, quartz dominates in quartzites and other rocks saturated in silica (migmatites, phyllites, mica schists), occurring as metamorphic product of quartz-bearing sediments and igneous rocks but also as reaction product by the release of SiO₂ which takes place during metamorphism.

Quartz is abundant in detrital sediments (sandstones, sands) because of its chemical and physical resistance to erosion. Authigenic quartz is formed by chemical, biological or biochemical processes and consists typically of compact microcrystalline varieties of silica (Deer et al., 1963). Principal rocks of this type are diatomite, agate, chert (flint, jasper) and radiolarite (Foucault and Raoult, 1984).

2.2 Polymorphism: phase equilibria and occurrence

2.2.1 The system SiO₂

Quartz shows polymorphism with increasing pressure and/or temperature. The more important SiO₂ polymorphs and their temperature ranges of stability are (Sosman, 1927) (Fig. 2.1):

α-Quartz is stable up to 846 K at atmospheric pressure.

β-Quartz is stable from 846 K to 1143 K at atmospheric pressure. It can exist metastably above 1143 K. The α-β transition occurs at higher temperatures for higher pressures.

Tridymite is observed in nature and can be synthesized in experiments, but it is not clear whether tridymite has a stability field in the pure SiO₂ system (Navrotsky, 1994). It was suggested that β-tridymite is the stable form from 1143 K to 1743 K at atmospheric pressure (Deer et al., 1996).
Above 1743 K it can exist metastably. α-tridymite can exist metastably at atmospheric temperatures and down to 390 K.

β-Cristobalite is stable from 1743 K to the melting point at 1986 K at atmospheric pressure. It can exist metastably above 473-548 K.

Coesite is a high-pressure phase, under experimental conditions produced at 723-1073 K and 38 kbar pressure (Coes, 1953; Sosman, 1954).

Stishovite is a high-density form of silica, synthesized at 1473 K to 1673 K and at pressures around 130 kbar.

![Pressure-temperature diagram for low-pressure SiO$_2$ polymorphs (dry conditions). Modified after Deer et al. (1996).](image)

The crystal structure of the five principal polymorphs are quite different (Tab. 2.1). However, in each case, the structure is built by SiO$_4$ tetrahedra, which are linked by sharing each of their corners with another tetrahedron. The transformation kinetics from one polymorph to another are slow, so that the higher temperature forms cristobalite and tridymite can exist metastably below their respective inversion temperatures (Deer et al., 1996).

The predominant polymorph within the crust is α-quartz, since it is stable at temperatures and pressures typical for most of the crust. The polymorphs β-quartz, β-tridymite and β-cristobalite usually are transient forms that may crystallize during cooling of igneous bodies (Heaney, 1994). Alternatively, tridymite and cristobalite may form stably in tectonically active zones or in regions associated with contact metamorphism, and they may convert to quartz with decreasing temperature (Moehlman, 1935; Van Valkenburg and Buie, 1945; Green and Fitz 1993). Coesite and stishovite are both high-pressure phases found in rocks subjected to the impact of large meteorites (Heaney, 1994). Coesite also occurs in xenoliths in kimberlites and in ultra-high
pressure terrains in mountain belts, e.g. Dora Maira (W-Alps) (Chopin et al., 1991) and Himalaya
(Pakistan) (Treloar et al., 2001).

This study focuses on the behavior of the polymorph quartz which will be reviewed in the
following.

Table 2.1 Symmetry, cell parameters and density (at room conditions) of polymorphic forms of sil¬
lica. Z is number of formula units per unit cell (SiO\textsubscript{2}). After Heaney (1994) and Deer et
al. (1996).

<table>
<thead>
<tr>
<th>Form of SiO\textsubscript{2}</th>
<th>System</th>
<th>Space Group</th>
<th>Z</th>
<th>a (Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>ρ (g cm\textsuperscript{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Quartz</td>
<td>Trigonal</td>
<td>P\textsubscript{3}1\textsubscript{2}1 or P\textsubscript{3}2\textsubscript{1}1</td>
<td>3</td>
<td>4.91</td>
<td>-</td>
<td>5.40</td>
<td>2.65</td>
</tr>
<tr>
<td>β-Quartz</td>
<td>Hexagonal</td>
<td>P6\textsubscript{4}22 or P6\textsubscript{2}22</td>
<td>3</td>
<td>5.01</td>
<td>-</td>
<td>5.47</td>
<td>2.53</td>
</tr>
<tr>
<td>α-tridymite</td>
<td>Orthorhombic</td>
<td>C\textsubscript{2}22\textsubscript{1}</td>
<td>8</td>
<td>5.04</td>
<td>8.74</td>
<td>8.24</td>
<td>2.27</td>
</tr>
<tr>
<td>β-tridymite</td>
<td>Hexagonal</td>
<td>P\textsubscript{6}3/mmc</td>
<td>4</td>
<td>5.05</td>
<td>-</td>
<td>8.27</td>
<td>2.18</td>
</tr>
<tr>
<td>α-Cristobalite</td>
<td>Tetragonal</td>
<td>P4\textsubscript{1}2\textsubscript{1}2 or P4\textsubscript{3}2\textsubscript{1}2</td>
<td>4</td>
<td>4.97</td>
<td>-</td>
<td>6.92</td>
<td>2.33</td>
</tr>
<tr>
<td>β-Cristobalite</td>
<td>Cubic</td>
<td>Fd\textsubscript{3}m</td>
<td>8</td>
<td>7.13</td>
<td>-</td>
<td>-</td>
<td>2.21</td>
</tr>
<tr>
<td>Coesite</td>
<td>Monoclinic</td>
<td>C\textsubscript{2}/c</td>
<td>16</td>
<td>7.17</td>
<td>12.38</td>
<td>7.17</td>
<td>2.93</td>
</tr>
<tr>
<td>Stishovite</td>
<td>Tetragonal</td>
<td>P4/mmm</td>
<td>2</td>
<td>4.18</td>
<td>-</td>
<td>2.67</td>
<td>4.35</td>
</tr>
</tbody>
</table>

2.2.2 Crystal structures of α- and β-quartz

Quartz is made up of SiO\textsubscript{4} tetrahedra, with Si atoms at the centre of each tetrahedron. Tetrahedra
are linked by sharing each of their corners with another tetrahedron. Thus every silicon has four
oxygens and every oxygen has two silicons as nearest neighbours (Deer et al., 1963). Each of the
four oxygens of a tetrahedron is shared with another tetrahedron.

In β-quartz, tetrahedra are grouped to form regular hexagonal helices parallel to the c-axis (Deer
et al., 1963). Depending on the handedness of the helices, the space group is either P6\textsubscript{4}22 (for
left-handed helices) or P6\textsubscript{2}22 (for right-handed helices) (Heaney, 1994). The structure of α-quartz
can be regarded as a distortion of the β-polymorph (Fig. 2.2). The polymorphic change is a
displacive transformation corresponding to minor atomic movements without any rupture of
bonds. By a slight rotation of the tetrahedra about the (1010) axis, the six-fold axis becomes a
three-fold axis, decreasing the space group symmetry from P6\textsubscript{4}22 to its subgroup P\textsubscript{3}1\textsubscript{2}1 (or from
P6\textsubscript{2}22 to P\textsubscript{3}2\textsubscript{1}1) (Nicolas & Poirier, 1976). The handedness of the helices can be visualized as
follows: If the height markings 1/3 and 2/3 in Fig. 2.2 were interchanged this would transform it
to the structure of opposite „hand“. Left- and right- handed forms are related by the inversion,
which is not a symmetry operation of the crystal lattice, a phenomenon called enantiomorphism.
The two enantiomorphs of α-quartz, which are associated with the 3\textsubscript{1} and 3\textsubscript{2} screw symmetries,
are generally known as the Brazil twins. These twins are related by reflection across \( \{11\bar{2}0\} \) which inverts the handedness of the crystal (Fig. 2.3). Another important twin of \( \alpha \)-quartz is the Dauphiné twin. It involves a \( 60^\circ = 180^\circ \) rotation about the [0001] axis without changing the handedness of the crystal (Heaney, 1994).

**Fig. 2.2** Crystal structure of a) \( \alpha \)- and b) \( \beta \)-quartz projected on (0001). From Deer et al. (1963).

**Fig. 2.3** Crystal faces and directions in quartz. a) Crystal morphology with crystallographic axes and faces for left- and right-handed quartz. b) Upper-hemisphere equal-angle projection of the poles to crystallographic planes (dots) in quartz. After Twiss and Moores (1992) and Heaney (1994).
2.2.3 The system SiO₂–H₂O:

2.2.3.1 Phase relationships

Several studies showed the large effect of H₂O on the SiO₂ melting point (Kennedy, 1950; Morey and Hesselgesser, 1951; Tuttle and England, 1955; Tuttle and Bowen, 1958; Stewart, 1957; Kennedy et al., 1962). The system SiO₂–H₂O is characterized at high temperatures and pressures by a three–phase region in which one H₂O rich vapor phase and one rich in SiO₂ melt are in equilibrium with pure SiO₂ solid (Fig. 2.4a).

If the system SiO₂–H₂O is in equilibrium, the crystallization point of SiO₂ is lowered from 1993 K at 0 kbar to 1373 K at 3 kbar. With increasing pressure the melting point decreases further.

![Fig. 2.4 The system SiO₂–H₂O. Experimental conditions of this study indicated as stars. a) Melting conditions of SiO₂ with excess H₂O. b) Weight percent compositions along the upper three-phase boundary in the system SiO₂–H₂O at 1373 K. After Kennedy et al. (1962).](image)

2.2.3.2 Solubilities

Several studies have examined the composition of the different phases in the three-phase and the two-phase regions (for reviews, see Anderson and Burnham, 1965; Paterson, 1986; Watson and Wark, 1997).

In the three-phase region, the composition of the water – rich vapor and the silica – rich melt in equilibrium with a quartz phase is shown in Fig 2.4b. The solubility of SiO₂ in vapor increases
steadily with increasing pressure at constant temperature. At 3.5 kbar, almost 10 weight percent SiO₂ can be dissolved in vapor. A small drop in pressure will cause the precipitation of SiO₂. In the silica–rich melt, an initial H₂O pressure introduces a relatively large amount of water into the melt. At 3.5 kbar, the melt contains approximately 5 weight percent water at around 1373 K.

a) SiO₂ in H₂O. In the two–phase region, the solubility of quartz in water has been studied over a wide range of conditions (for review, see Fournier and Potter, 1982; Paterson, 1986). The solubility of SiO₂ in H₂O vapor is known to be quite high at low pressures (Kennedy et al., 1962; Anderson and Burnham, 1965). Fournier and Potter (1982) developed an empirical relation to correlate the solubility of quartz in water from 298 K to 1173 K at pressures up to 10 kbar. The values calculated for temperatures up to 1400 K are in good agreement with the solubility values from Paterson (1986). In general, the predicted solubility increases with both temperature and pressure.

b) H₂O in SiO₂. On the other extreme, dissolved water in quartz causes hydrolytic weakening of quartz. Because of the slow kinetics, this solubility is not well determined experimentally (Paterson, 1986).

Hydrothermal experiments (i.e. experiments in the presence of heated water) on dry quartz using a solid-medium apparatus indicated a strong penetration of water into quartz at 1000–1600 MPa pressure and 1100–1300 K temperature (Griggs and Blacic, 1964; Blacic, 1975; Blacic, 1981; Mackwell and Paterson, 1985; Ord and Hobbs, 1986). The depth of penetration appeared to correspond to a diffusion coefficient of the order of 10⁻¹² to 10⁻¹¹ m²s⁻¹, and the solubility was determined to be around 1'000 H/10⁶ Si (about 0.015 weight percent) at 1173 K, 1500 MPa with no melt present (Mackwell and Paterson, 1985). In contrast to these observations, no significant penetration of water into quartz has been detected in similar hydrothermal experiments in a gas-medium apparatus at 300 to 500 MPa pressure (Paterson and Kekulawala, 1979). These results suggest that the diffusion coefficient of water in quartz is very strongly pressure dependent. However, several solid-medium experimental studies by Kirby and Kronenberg (1984), Kronenberg et al. (1986), Rovetta et al. (1986) showed that earlier determinations of solubility and diffusivity made in solid-medium apparatus are affected by microcracking with the accompanying introduction of molecular water inclusions.

Other estimations of solubility of water in quartz were made by determining the water content of quartz crystals grown commercially under hydrothermal conditions (Lias et al., 1973; Barns et al., 1976). At 600–700 K and 100–300 MPa, 13 H/10⁶ Si (about 0.0002 weight percent) were detected. However, since synthetic crystals often seem to be supersaturated with respect to water,
this value probably represents an upper limit for the solubility under growth conditions (Paterson, 1989).

A thermodynamic treatment of the solubility of water in quartz was discussed by Doukhan and Trépied (1985) and Paterson (1986). The calculations indicate that the solubility is relatively low, less than 100 H/10^6 Si (about 0.0015 weight percent), even at the highest temperatures and pressures (1300 K and 1500 MPa; Paterson, 1986). The predictions give a monotonously increasing solubility with increasing temperature at given pressure, and an increase in solubility with increasing pressure at given temperature up to a critical pressure. Above this pressure solubility decreases again with further increase in pressure (Fig. 2.5). The theoretical considerations indicate a small dependence of the predicted solubility on water fugacity and oxygen fugacity, which was observed experimentally (Ord and Hobbs, 1986; Post and Tullis, 1996).

![Fig. 2.5](image)

*Fig. 2.5  Calculated solubility of water in quartz at relatively high oxygen fugacity. a) Temperature-solubility diagram for various pressures. b) Pressure-solubility diagram for various temperatures. From Paterson (1986).*
2.2.3.3 Diffusivity

Measurements of transport properties (viscosity and solute diffusivity) at the pressure-temperature conditions of the mid-crust to upper mantle are rare (for review, see Watson and Wark, 1997).

The diffusivity \( D \) of dissolved \( SiO_2 \) in quartz-saturated \( H_2O \) at 1 GPa was recently determined to follow an Arrhenius-type dependence of \( D^{SiO_2} \) (m\(^2\)/s) upon \( T \) (K):

\[
D = 2.8 \times 10^{-5} \exp(-6271/T)
\]

(Watson and Wark, 1997). The authors suggested little dependence of \( D^{SiO_2} \) upon pressure.

2.2.4 Chemistry

Quartz incorporates only few impurities into its lattice. Therefore the composition of quartz is close to 100% \( SiO_2 \) (Deer et al., 1996). However, a limited amount of substitutional solid solution may occur, mainly by the trivalent \( Al \) and \( Fe \) and the monovalent \( Li, Na \) and \( K \) (Heaney, 1994). The most abundant impurity is \( Al \), which can be present up to 15'000 ppm in natural quartz (Smith and Steele, 1984) and up to 17'500 ppm in synthetic crystals (Ono, 1979). The substitution of \( Al \) or \( Fe \) for \( Si \) appears to be accompanied by the introduction of the alkali ions \( Li, Na \) and \( K \) in order to maintain electrical neutrality (Dennen, 1966). However, an important role in maintaining charge balance is played by monovalent \( H \) (Kronenberg, 1994). Hydrogen occurs as: (1) molecular water aggregates or adsorbed species; (2) water species in solid solution, and (3) species in dislocation cores (Paterson, 1989). The possible effects of water species on the rheological behavior of quartz is discussed in Chapter 3.
Chapter 3

3 Previous laboratory studies on the deformation of quartz

In this chapter, the deformation behavior of experimentally deformed quartz is reviewed. The terminology of Rutter (1986) is followed, where the change in failure mode (localized versus ductile) is termed the 'brittle-ductile transition' (BDT) and the change in dominant deformation mechanisms (cataclastic deformation vs. intracrystalline plasticity vs. diffusive mass transfer) is termed the 'brittle-plastic transition' (BPT). Deformation involving together plastic and brittle mechanisms is called 'semibrittle flow'.

3.1 Brittle deformation

Brittle deformation involves creation of new fractures, loss of cohesion and frictional sliding along grain boundaries and fractures (Knipe, 1989). Paragraph 3.1.1 reviews the genesis of fractures in quartz. Paragraphs 3.1.2 to 3.1.4 treat the macroscopic behavior of quartz (single crystals and polycrystalline quartz) in the brittle field with a review of the three important deformation styles: macroscopic fracturing, frictional sliding and cataclastic flow. In paragraph 3.1.5 the semibrittle field is discussed, where brittle deformation mechanisms together with intracrystalline plasticity and/or diffusive mass transfer processes have been reported for quartz.

3.1.1 Fracture mechanics

The atoms of silicon and oxygen in quartz are bonded by forces that have the character of ionic as well as covalent bonds. This leads to a strong and highly brittle behavior of quartz. The theoretical shear strength $\tau_m$ of a perfect quartz crystal is around 4.4 GPa (Lawn and Wilshaw, 1975). The strength of a real quartz crystal is controlled by the initial presence of microcracks (Griffith, 1920, 1924). By applying a mechanical stress to quartz, the following processes can initialize microcracks (Krantz, 1983): (1) twin interactions with grain boundaries and other twins (Martin and Durham, 1975), (2) release of stored energy associated with kink bands (Christie et al., 1964) and deformation lamellae (Heard and Carter, 1968), and (3) stress concentration at grain boundaries (Hallbauer et al., 1973) or intracrystalline pores (Wong, 1982).

Crack growth velocity during slow strain rate experiments on quartz single crystals is enhanced in the presence of water, and this effect becomes stronger with increasing temperature (Scholz, 1972; Martin, 1972). This can be explained by a "stress corrosion": since water weakens Si-O bonds, pore fluids can have an important role in promoting crack growth by the corrosion of crack tips (so-called 'stress corrosion'; Michalske and Freiman, 1982): strong Si-O-Si bonds are replaced across the crack tip by weaker Si-OH: HO-Si links. Crack growth then proceeds by breaking the
weak hydrogen bonds. This time-dependent process is thermally activated and has a strong
influence on quartz strength below a certain 'subcritical' crack propagation velocity (about 1
cm sec$^{-1}$). Therefore, the fracture strength of a wet sample is lower than of a dry one at slow strain
rates. Values for the activation enthalpies of crack growth by stress corrosion in quartz range
between 46 and 99 kJ mol$^{-1}$ (Kronenberg, 1994).

For polycrystalline quartz, a compilation of subcritical crack growth data for Arkansas novaculite,
Tennessee sandstone and Mojave quartzite is given in Atkinson and Meredith (1987). The
influence of temperature was only studied for novaculite and showed effects similar to those for
quartz single crystals.

Different chemical compositions of water can induce different fracture strength during crack
propagation by stress corrosion (see references cited in Paterson, 1978, and review by Anderson
and Grew, 1977). For example, alkaline solutions lower the fracture strength of both quartzite and
quartz single crystals (Griggs and Bell, 1938; Fairbairn, 1950).

The opposite effect to stress corrosion microcracking is crack healing. The amount of healing in
samples of single quartz crystals with added water is a function of temperature, time, initial
concentration of silica in the pore fluid, the initial crack dimensions and fluid chemistry (Smith
and Evans, 1984; Brantley et al., 1990). Typical values for the activation enthalpy are similar to
those measured for stress corrosion microcracking (35 to 80 kJ mol$^{-1}$; Kronenberg, 1994). These
low values suggest that fluid-filled intracrystalline microcracks in quartz will not persist long in
geological timescales at temperatures above 473 K (Smith and Evans, 1984).

3.1.2 Macroscopic fracturing

Bulk rock fracturing in quartz is commonly associated with dilatancy and strong strain softening
(Edmond and Paterson, 1972). Throughgoing shear fractures typically develop in samples with
macroscopic displacement. For bulk mechanical behavior, the strength of quartz is mainly
affected by confining pressure, strain rate, water content and pore pressure, porosity and
crystallographically controlled anisotropy.

In contrast to halite or calcite, quartz never becomes ductile at room temperature just by increasing
the confining pressure; its strength even increases with pressure (e.g., Griggs and Bell, 1938;
Bridgman, 1952; Christie et al., 1964b). For example, the strength of unconfined quartzites is
about 300 MPa, while at 100 MPa confining pressure, the strength ranges from 500 to 1000 MPa
(Paterson, 1978).
The effect of strain rate on fracture strength is strongly dependent on water content (Tab. 3.1, Fig. 3.1a).

**Table 3.1 Effect of strain rate on fracture strength**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Material</th>
<th>wet/dry</th>
<th>Strain rate (s⁻¹)</th>
<th>Temp (K)</th>
<th>Confining Pressure (MPa)</th>
<th>Fracture strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heard (1962)</td>
<td>Quartzite</td>
<td>wet</td>
<td>10⁻⁵</td>
<td>773</td>
<td>500</td>
<td>2500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>dry</td>
<td>10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bernabe and Brace (1990)</td>
<td>Sandstone</td>
<td>wet</td>
<td>10⁻⁴</td>
<td>room</td>
<td>various</td>
<td>see Fig. 3.1a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>dry</td>
<td>10⁻⁴</td>
<td>room</td>
<td>various</td>
<td></td>
</tr>
<tr>
<td>Rutter and Mainprice (1978)</td>
<td>Sandstone</td>
<td>dry</td>
<td>10⁻⁷</td>
<td>573</td>
<td>1500</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wet</td>
<td>10⁻⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>wet</td>
<td>10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 3.1** Effect of water pore pressure on deformation of porous Berea sandstone at room temperature at different strain rates and effective pressures (Pc − Pp). Diamonds indicate dry samples and stars samples fractured by increasing the pore pressure. Squares and triangles respectively indicate tests run at 2×10⁻⁴ and 2×10⁻⁵ s⁻¹ with distilled water as pore fluid. The approximate ranges of the brittle, transitional and ductile regimes are indicated. **a)** The peak stress (solid symbols) and the yield stress (open symbols) as a function of effective pressure. Dry samples are slightly stronger than water saturated ones. Samples deformed slower are slightly weaker. **b)** The friction stress as a function of effective pressure. The straight line corresponds to Byerlee’s relation (τ = 0.85σN, with τ = shear stress, σN = normal stress; Byerlee, 1968) for a single fault inclined at 30° to σf. Dashed line represents Coulomb’s law for Berea sandstone (τ = 24.1MPa + 0.49σN). The intersection of the two lines corresponds to the brittle-ductile transition (BDT). Note the good fit with Byerlee’s relation in the brittle field and the deviation of the data in the transitional regime. After Bernabe and Brace (1990).
Rutter and Mainprice (1978) showed a strong decrease of fracture strength in wet Tennessee sandstone with decreasing strain rates less than $10^{-6}$ s$^{-1}$ concluding that deformation was controlled by the kinetics of water assisted stress corrosion. Thus, there is a remarkable influence of strain rate on brittle fracture in wet quartz in the presence of thermally activated processes like stress corrosion.

Pore fluids can influence fracture strength through a direct mechanical pressure effect as well as through chemical interactions with the rock (Lockner, 1995). The chemical interactions have already been discussed in the context of fracture mechanics. Additionally, physico-chemical actions of the pore fluid at grain boundaries, grouped together under the general descriptive term 'Rehbinder effect' (Rehbinder and Lichtman, 1957), can also reduce the ultimate and residual (frictional sliding) strength of quartz-rich rocks (Boozer, Hiller and Serdengecti, 1963; Colback and Wiid, 1965; Rutter and Mainprice, 1978). The mechanical effect of pore pressure in drained experiments on sandstones has been shown to be roughly opposite to that of confining pressure. Therefore, Terzaghi’s concept of effective pressure can be applied in the case of porous sandstone (Handin et al., 1963; Murrell, 1965; Byerlee, 1975; Bernabe and Brace, 1990). The differential stress for shear failure is approximately constant at the same 'effective pressure' when the latter is the total confining pressure minus the pore pressure (Fig. 3.2). In undrained experiments on sandstone at atmospheric temperature, confining pressures up to 500 MPa and variable pore pressures, dilatancy produced by cracking resulted in dilatancy hardening. This prevented or delayed mechanical instability and counteracted the formation of major faults (Ismail and Murrell, 1976).
Porosity exerts a major influence on fracture strength (e.g., Dunn et al., 1973; Hirth and Tullis, 1989; Wong, 1990). A strong inverse relationship between fracture strength and porosity was observed in sandstones at room temperature (Dunn et al., 1973). A compilation of the unconfined compressive strength at room temperature for quartz rich rocks with different porosities in comparison with other rock types is given in Fig. 3.3. The high variability in strength can be correlated to variations in porosity (up to 16% for sandstone compared with 1-2% for quartzite), but also grain size, grain shape and cementation.
Chapter 3

Fig. 3.3  Unconfined compressive strength at room temperature for different rock types. Each box represents ±25% of the data about the mean value (shown as vertical line). Error bars represent the full range of data (exceptions are plotted as individual circles). From Lockner (1995)

Quartz single crystal is one of the strongest minerals with a compressive strength of 2.4 GPa at atmospheric pressure and room temperature (Sosman, 1927). Studies on the anisotropic behavior of fracture strength of single quartz crystals were performed by Griggs and Bell (1938), Griggs et al., (1960), and Christie et al. (1964b): faulting occurred at lowest shear stress on the basal (0001) plane, than on rhombohedral \{10\overline{1}1\} and \{01\overline{1}1\} planes and highest on \{10\overline{1}0\} and \{11\overline{2}0\}. Samples oriented normal to the (0001)-plane were stronger than samples oriented normal to the \{10\overline{1}1\} rhombohedral plane.

3.1.3 Frictional sliding

The resistance to sliding at an interface (coefficient of friction, $\mu$) in quartz and quartz rich rocks is mainly influenced by normal effective stress, temperature, strain rate, pore fluid and chemical environment. As an approximate estimation for different conditions, the following values of $\mu$ are typical (Paterson, 1978):

Sandstone and quartzite: $\mu = 0.5\text{--}0.7$

Quartz single crystal: $\mu = 0.1\text{--}0.2$

In general, the dominant variable for frictional strength is normal effective stress at pressures below 1000 MPa or at temperatures below 673 K (Stesky, 1978). A linear increase of frictional strength is observed with an increase in normal stress (Fig. 3.1b). Frictional strength of sandstone has been shown to follow Terzaghi’s concept of effective stress (Byerlee, 1975).
Fig. 3.4 Frictional sliding resistance of surfaces of Eureka quartzite deformed at room temperature in air (hydrous environments) and in dry argon atmosphere (anhydrous environments). a) Effect of environment. Sliding velocity 1.0 \( \mu \text{m/s} \). Larger shear stresses \( \tau \) are required to start sliding along surfaces in anhydrous than in hydrous environments. b) Effect of velocity and environment. Variations in shear resistance \( \tau \) during velocity-stepping experiments. Velocity weakening is observed in humid environments but not in dry environment. After Dieterich and Conrad (1984).

The effect of temperature and time on purely brittle sliding is difficult to assess due to the possible interaction with thermally activated processes like diffusive mass transfer, subcritical stress corrosion or intracrystalline plasticity. For example, a significant reduction of the friction coefficient occurs if dissolution and precipitation processes due to the presence of fluids are involved (Chester and Higgs, 1992; Chester, 1995).

At low temperature, brittle fracturing and comminution (i.e., reduction in grain size) of grains are probably the controlling mechanisms of frictional sliding at low and intermediate pressures in the laboratory (e.g., Friedman et al., 1974; Yund et al., 1990). Rutter and Mainprice (1978) found no effect of temperature on residual strength up to 573 K in sandstone for high strain rates where thermally activated processes were probably negligible. However, amorphous material on sliding surfaces at low temperature was often observed in experimental studies (Yund et al., 1990 and references herein). The formation of amorphous material can lead to an increase of the coefficient of friction (Friedman et al., 1974). There is some discussion whether the amorphous material at slow displacement rates is formed by melting due to frictional heating (Stesky, 1974; Engelder, 1978) or to comminution of crystalline fragments (Yund et al., 1990).

Wetting of the sliding surfaces has not a straightforward effect on friction (Paterson, 1978): sometimes, wetting has no effect. Possibly more often, there is a decrease in the coefficient of friction. For example, friction coefficients determined for quartzite surfaces in dry argon ranged from 0.85 to 1.0, while surfaces exposed to air or other humid environments had friction
coefficients of 0.55 to 0.70 (Fig. 3.4a). Friction coefficients $\mu$ exposed to humid environments also vary slightly as a function of time and sliding velocity (Fig. 3.4b) (Dieterich and Conrad, 1984). The mechanisms influencing time-dependent frictional properties of humid quartz surfaces remain unclear. Hydrogen species may affect cracking at asperity contacts by stress corrosion processes, or they may change adhesion between surfaces which are in contact (Kronenberg, 1994). Chester (1994) found that friction coefficients for water saturated quartz gouge were slightly lower than dry quartz gouge at 297 K, 330 K, and 355 K. His observations are consistent with processes of subcritical crack growth and crack healing by diffusive mass transfer. Velocity-stepping experiments on quartzite in a dry argon-environment showed small, instantaneous changes of shear stresses as sliding velocities were changed, while velocity-weakening occurred in humid environments (Fig. 3.4b) (Dieterich and Conrad, 1984).

The role of the chemical environment on frictional sliding is complex. Data suggest that chemically assisted comminution may be important at high and low ionic concentration because it may reduce the effective viscosity and the shear strength of fault gouge (Dunning et al., 1994). At intermediate ionic concentration the role of pH appears to be important because it changes the coefficient of friction by enhancing or diminishing crack propagation in asperities.

### 3.1.4 Cataclastic flow

'Cataclastic flow' involves only brittle mechanisms like microcracking and intergranular sliding, but strain is macroscopically not localized (review by Evans et al., 1990). Mechanically, brittle faulting is associated with strain softening, while cataclastic flow is a strain hardening process (Fig 3.5).

The dominant role of effective pressure in controlling the transition from brittle faulting to cataclastic flow (brittle-ductile transition BDT) has been shown in several studies at room temperature (e.g., Edmond and Paterson, 1972; Scott and Nielsen, 1991, for sandstone; Hadizadeh and Rutter, 1983, for quartzite). The effective pressure where the BDT in sandstone occurred was consistent with the predictions of Byerlee (1968): for any rock type the intersection of the Mohr-Coulomb criterion with Byerlee’s friction law defines the effective pressure for the BDT (Fig. 3.1b).

Cataclastic flow is not only promoted by an increase in effective pressure, but also by porosity (Tab. 3.2). In contrast to porous rocks, non-porous quartzite faults unstably even at high confining pressure. Therefore Hirth and Tullis (1989) suggested that cataclastic flow is a transient phenomenon which is related to porosity changes.
Fig. 3.5  Deformation of porous sandstone. a) Mechanical data for Adamswiller sandstone (22.6% porosity). Differential stress and porosity decrease versus axial strain. Effective pressures as indicated. The solid curves are for samples which failed by shear localization, and the dashed curves for samples which failed by cataclastic flow. b) Critical effective pressure for the onset of grain crushing under hydrostatic loading as a function of the product of initial porosity and grain radius. From Wong et al. (1997)

Table 3.2  Effect of porosity on cataclastic flow.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Starting Material</th>
<th>Porosity (%)</th>
<th>Confining Pressure (MPa)</th>
<th>Strain (%)</th>
<th>Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jones (1980)</td>
<td>Sandstone</td>
<td>24</td>
<td>50</td>
<td>up to 90%</td>
<td>cataclastic</td>
</tr>
<tr>
<td>Hadizadeh and Rutter (1983)</td>
<td>Quartzite</td>
<td>7</td>
<td>600</td>
<td>&lt;25</td>
<td>cataclastic</td>
</tr>
<tr>
<td>Hirth and Tullis (1989)</td>
<td>Quartzite</td>
<td>7</td>
<td>600</td>
<td>&gt;25</td>
<td>faulting</td>
</tr>
<tr>
<td>Hirth and Tullis (1989)</td>
<td>Quartzite</td>
<td>0</td>
<td>1000</td>
<td>&lt;5</td>
<td>faulting</td>
</tr>
</tbody>
</table>

Different models were used to explain the microstructural behavior at the BDT: (1) Edmond and Paterson (1972) concluded that the transition from faulting to cataclastic flow can be attributed to a stabilization of microcracking with increasing pressure. Throughgoing shear planes were observed in low-porosity sandstones only after many grains were fractured (Dunn et al., 1973). In terms of fracture mechanics, coalescence of stress-induced microcracks would lead to shear localization, whereas during cataclastic flow homogeneously distributed microcracking would occur (Hirth and Tullis, 1989). (2) In the model of Hadizadeh and Rutter (1983), fault localization occurs due to the growth of grain boundary cracks. These cracks loosen the microstructure so much that axial transgranular cracks can develop. The authors discussed two main reasons for which the microstructure is responsible for hardening and thereby for stabilizing the flow. First,
very small gouge fragments are produced, and further grain size reduction requires increasingly higher energies because increasingly more surfaces are created. Second, the small grains around each grain core are like a buffer that spreads the load around the core boundary and inhibits axial crack formation. (3) Several studies pointed to the influence of porosity: (3.i) Gowd and Rummel (1980) suggested that compaction during ductile deformation is due to collapse of pore space and a subsequent readjustment of grains into a denser packing, which leads to strain hardening. (3.ii) Hirth and Tullis (1989) proposed that the transition to cataclastic flow is due to the changing influence of pores. According to them the transition from faulting to cataclastic flow corresponds to the initiation of pore collapse: when the critical stress for pore collapse is achieved before the stress required to nucleate axial cracks at the tips of pores, compaction will stabilize the flow. If dilatancy due to continued microcracking becomes dominant, deformation will be localized on faults. (3.iii) The influence of porosity on stabilizing deformation was confirmed by Bernabe and Brace (1990): they proposed that compaction due to fragmentation of grains and rearrangement of these fragments in the pore space allowed distributed deformation in Berea sandstone. When all available pore space has been filled with fine fragments, this stabilizing mechanism should stop and dilatancy with shear localization would be expected.

A relatively complete set of mechanical data (including stress, strain, porosity change and acoustic emission activity) for six sandstones with porosities ranging from 15% to 35% was acquired by Wong et al. (1997). For all of the studied sandstones, the transition from brittle faulting to compactive cataclastic flow occurred at a critical effective pressure $P^*$ at which grains were crushed and pores collapsed. This resulted in an overall decrease in porosity. The influence of grain size was shown in an earlier study: Gu and Wong (1994) deformed ultrafine and coarser quartz samples under similar conditions. Shear localization was observed only in the ultrafine samples. The authors suggested that comminution, which is easier in coarse grains, resulted in homogeneous cataclastic flow. Shear localization in the coarse gouge only developed after significant compaction and grain-size reduction. Zhang et al. (1990) formulated a Hertzian fracture model that predicts the critical pressure $P^*$ to be

$$
P^* = \frac{2.2(1 - v^2)}{E^2(1 - 2v)^3} \frac{K_{IC}^3}{(\alpha \Phi R)^{3/2}} \tag{3.1}
$$

where $v$ is the Poisson’s ratio, $K_{IC}$ is fracture toughness, $E$ is the Young’s modulus, $\alpha$ is the ratio of the initial crack length to grain radius, $\phi$ is initial porosity, and $R$ is grain radius. The magnitude of the critical effective pressure is therefore primarily controlled by the porosity and grain size: with increasing porosity and grain size, the transition pressure for the BDT decreases (Fig. 3.5b).
(Zhang et al., 1987). A water-weakening effect by 20% to 70% was observed in water-saturated samples of Darley Dale sandstone at effective pressures ranging from 10 MPa to 300 MPa (Wong and Baud, 1999).

Compression tests can only attain a limited amount of strain. It remains therefore unclear whether higher strains can be accommodated by cataclastic flow. Information on high strain behavior can be obtained by shearing experiments: Marone and Scholz (1989) sheared layers of quartz sand between steel surfaces under drained and water saturated conditions at room temperature and 100 MPa effective normal stress. At shear strains $\gamma$ of less than 0.8, strain hardening and compaction was observed. Afterwards dilatancy with increase in porosity occurred and the rate of strain hardening decreased. After a shear strain $\gamma$ of 1.3-1.65 the deformation localized into shear bands. The authors concluded that initial porosity reduction (compaction) and strain hardening were due to changes in grain sorting, and that shear localization initialized as soon as dilatancy began.

Near the brittle-ductile transition, an intermediate mechanical and microscopic behavior was observed (Scott and Nielsen, 1991) (Fig. 3.6): the stress-strain curves showed apparent steady-state stable sliding. The samples revealed a network of small shear zones with concentrated cataclasis along them and negligible shear displacement. These shear zones were described as "Lüders’ bands" (Friedman and Logan, 1973).

In conclusion, the transition from shear localization to cataclastic flow is promoted in sandstone by an increase in the effective pressure, porosity and grain size (e.g. Dunn et al., 1973; Wong, 1990; Bernabe and Brace, 1990; Scott and Nielsen, 1991). The compactive process causes strain hardening. A rock can only compact over large strains, if the increasing number of microcracks do not coalesce. This inhibits the onset of shear localization (Wong and Baud, 1999). An overview of the brittle-ductile transition in porous sandstones is given in Fig. 3.6. Non-porous quartz-rich rocks have not yet been experimentally deformed in the cataclastic field.
3.1.5 Semibrittle deformation

Semibrittle flow involves cataclasis as well as intracrystalline plasticity and/or diffusive mass transfer. First, some studies are reviewed where cataclasis together with intracrystalline plasticity occurred: in a recent study by Hirth and Tullis (1994) using a solid-medium apparatus, the brittle-plastic transition (BPT) for non-porous Heavitree quartzite (~0.1 wt% H₂O, grain size ~200 μm) involved at least three transitions in deformation mechanism that occur with increasing temperature and/or pressure (Fig. 3.7).

First there was a transition from cataclastic faulting to semibrittle faulting. In the cataclastic faulting regime a large drop in stress was associated with localized, unstable faulting. Very few or no dislocations occurred. In the semibrittle faulting regime significant inelastic deformation (up to 12%) occurred prior to weakening associated with localization of deformation into stable faulting. Localized microcracking led to the formation of a fault zone. Faulting was stabilized due to dislocation glide which lowered the stresses at the advancing fault tip. However, the accessible strain was not higher than 44%.

Fig. 3.6 Stress-strain curves for porous sandstones deformed at room temperature. Effective confining pressures and initial porosities as indicated. Open square marks stable sliding on shear fracture, triangle is brittle-ductile transitional behavior, solid circle is ductile cataclastic flow. Note large stress drop associated with brittle failure and continuous hardening during cataclastic flow. Inset: Macroscopic characteristics over the brittle-ductile transition. After Scott and Nielsen (1991).
Second, there was a transition from semibrittle faulting to semibrittle flow, corresponding to the BDT of Evans et al. (1990). For semibrittle flow, modest strain weakening was associated with distributed microcracking and deformation, respectively. A relatively strong LPO developed at 44% shortening with a tight small circle girdle of c-axes. The authors suggested that localized deformation was avoided because the microcracks were not able to propagate across grain boundaries. The transition was grain size sensitive: At conditions, where Heavitree quartzite (initial grain size ~200 µm) deformed by semibrittle flow, fine-grained novaculite (~5 µm) still underwent semibrittle faulting. A third transition occurred from semibrittle flow to dislocation creep (the BPT of Evans et al, 1990). There was no microcracking in the dislocation creep regime and the LPO was similar to that observed in the semibrittle flow regime with the addition of a c-maximum component parallel to \( \sigma_1 \) (see also Gleason et al., 1993). It was suggested that the transition was due to an increase of grain boundary mobility with increasing temperature. In gas-medium apparatus, the semibrittle faulting and flow regimes occurred at higher temperatures but lower pressures (Fig. 3.7; Mainprice and Paterson, 1984). Semibrittle flow was only observed in the samples with water added and only to less than 10% shortening. In summary, the transition from brittle faulting to intracrystalline plastic flow in experimentally deformed quartz aggregates seems to occur over a wide range of conditions.

A systematic study on semibrittle flow involving cataclasis as well as diffusive mass transfer in quartz-rich rocks was performed on wet Tennesse sandstone (grain size ~150 µm) in a series of stress relaxation experiments at 573 and 673 K, 150 MPa confining pressure and strain rates as low as \( 10^{-10} \) s\(^{-1} \) in a gas-medium apparatus (Rutter and Mainprice, 1978; Rutter and White, 1979;
Maddock et al. (1987). A dramatic weakening was observed when strain rate was progressively lowered below ca. \(10^{-6} \text{ s}^{-1}\). The experimental data were fitted with a theoretical model for deformation controlled by pressure solution (Rutter and Mainprice, 1978). Examination of pre-faulted samples by HVTEM revealed brittle as well as plastic features: (1) the gouge zones consisted of angular fragments (<1 µm); (2) fractures which terminated in grains were characterized by strained tips but no dislocation generation; (3) grains away from the gouge zone showed coarse subgrains and dislocations, and (4) overgrowths by new grains, corrosion microstructures as well as cementation of void space indicated mass transfer with increasing experimental duration. On the basis of the theoretical model and the observed microstructures, Maddock et al. (1987) suggested that reduction in strength at low strain rates is due to a transition in deformation mechanism from cataclasis to water-assisted grain boundary diffusion. By using water-saturated ultrafine quartz gouge (<1 µm) at 150 MPa confining pressure and 100 MPa pore pressure, Higgs (1981) and Chester and Higgs (1992) noticed a transition from a low-temperature regime (up to 573 K) characterized by heterogeneous cataclastic deformation to a high-temperature regime (723 K to 873 K) characterized by distributed cataclastic flow assisted by solution-precipitation. Substantial weakening occurred during relaxation to shear strain rates of \(10^{-3}\) to \(10^{-6} \text{ s}^{-1}\) in the high-temperature regime. The samples showed a lattice preferred orientation (due to anisotropic growth) and vein formation which were taken as evidence for solution transfer processes (Higgs, 1981; Power and Tullis, 1989). In dry tests and in tests at 296 K, the weakening was not observed.

The interactions of cataclastic and dissolution-precipitation processes in promoting slip localization were further investigated by Kanagawa et al. (2000) on synthetic quartz gouges of different grain sizes at a temperature of 1200 K, a confining pressure of 300 MPa, a pore water pressure of 200 MPa and strain rate of about \(10^{-4} \text{ s}^{-1}\). For conditions favoring the activity of dissolution-precipitation processes, i.e. for fine gouge (grain size ~2 µm) or at slower displacement rates, slip hardening and a high friction coefficient were observed (Fig.3.8a). Abundant features suggesting the activity of dissolution-precipitation processes were present, but only minor evidence of cataclastic processes was found, and the deformation was distributed across the whole gouge layer. In contrast, slip softening after initial hardening occurred for coarse gouge (grain size ~45 µm) and at faster displacement rates with a lower friction coefficient (Fig. 3.8a, b). Shear strength depended on effective pressure, suggesting that cataclastic processes predominated, and deformation localized along the gouge-forcing block interface with subsequent quasi-stable sliding.
The authors proposed that in strain-hardened samples, dissolution-precipitation processes were sufficiently fast to partly accommodate the shear strain leading to compaction and granular flow. Compaction increased the number of grain-to-grain, load-bearing grain contact area resulting in strain hardening. In strain-softened samples, cataclastic processes were more active than dissolution-precipitation resulting in strongly compacted samples. For further strain accommodation, slip localization was thereby necessary. The transition from hardening to softening is therefore influenced by the compaction rate and the role of cataclastic processes (Kanagawa et al., 2000).

Hence, all studies show the dependence of shear strength on the interactions between cataclastic and diffusive mass transfer processes: In hydrothermal environments (i.e. in the presence of heated water) increasing temperature, decreasing displacement rates and decreasing grain sizes favor the activity of dissolution-precipitation processes.

In summary, cataclastic flow in the semibrittle field in quartz-rich rocks can be accompanied by intracrystalline plasticity or diffusive mass transfer processes. The latter ones are favored by high water pore pressures.
3.2 Plastic deformation

Plastic deformation is meant here in the loose sense of nondilatant processes, and includes intracrystalline plasticity as well as diffusive mass transfer processes (Rutter, 1986). It is characterized by motion of point defects, dislocations, twins, and ions, or by grain boundary sliding (Evans and Kohlstedt, 1995). The following two deformation mechanisms can be recognized in the plastic field: diffusive mass transfer and intracrystalline plasticity. In diffusive mass transfer, the deformation takes place either by diffusional mass transfer (‘diffusional flow’, ‘pressure solution’ and ‘grain growth’) or by sliding along grain boundaries (‘grain boundary sliding’). Intracrystalline plasticity involves internal distortion or recovery of crystalline grains as a result of slippage of crystallographic planes with respect to one another (Rutter, 1993). Motion of dislocations may occur by glide, climb, or cross-slip, recovery by climb and cross-slip (Evans and Kohlstedt, 1995). Both regimes were observed to occur in experimental deformation of quartz and they are reviewed in the following.

3.2.1 Diffusive mass transfer processes

Diffusive mass transfer processes were observed in quartz by conducting either compaction or deformation experiments. An overview of the conditions for the different processes (pressure solution, grain growth, diffusional flow) is given in Tab. 3.3.

3.2.1.1 Pressure solution

Various attempts have been made to study diffusive mass transfer processes, and especially pressure solution, in quartz by experimental methods. Microstructural evidence for pressure solution has been found in compaction experiments under hydrothermal conditions (Maxwell, 1960; Ernst and Blatt, 1964; Cox and Paterson, 1991) or in compression (De Boer et al., 1977; Rutter and Mainprice, 1978; den Brok, 1992). Typical features are interpenetration of grains with the formation of sutured grain boundaries, overgrowths, corrosion microstructures, reduction in grain angularity, reduction of porosity, cementation of void space and truncation of grain shapes.

Experiments at temperatures below 931 K at various pressures showed that pressure solution in quartz-rich rocks is enhanced by (1) a high water content, (2) the presence of a highly soluble source of silica, (3) small grain size, (4) high temperature, (5) saline or alkaline water composition, and (6) an increased pore pressure (Maxwell, 1960; Ernst and Blatt, 1964; Renton et al., 1969; Sprunt and Nur, 1976; de Boer et al., 1977). Rutter and Mainprice (1978) derived a
Table 3.3  Conditions for diffusive mass transfer processes observed in laboratory experiments on quartz

<table>
<thead>
<tr>
<th>Reference</th>
<th>Type of quartz aggregate</th>
<th>Type of experiment</th>
<th>Process</th>
<th>Strain rate (s⁻¹)</th>
<th>Temp (K)</th>
<th>Confining Pressure (MPa)</th>
<th>Pore pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutter and Mainprice (1978)</td>
<td>Sandstone wet</td>
<td>Stress relaxation</td>
<td>Pressure solution</td>
<td>10⁻⁹</td>
<td>573</td>
<td>1500</td>
<td>?</td>
</tr>
<tr>
<td>Cox and Paterson (1991)</td>
<td>Sandstone wet</td>
<td>Isostatic hot pressing</td>
<td>Pressure solution</td>
<td>-</td>
<td>1200</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td>Den Brok (1992)</td>
<td>Quartzite (coarse, wet)</td>
<td>Axial compression</td>
<td>Pressure solution + microcracking</td>
<td>10⁻⁷</td>
<td>1073</td>
<td>1200</td>
<td>?</td>
</tr>
<tr>
<td>Karato and Masuda (1989)</td>
<td>Agate, wet</td>
<td>Axial compression</td>
<td>Grain growth</td>
<td>10⁻⁴ - 10⁻⁶</td>
<td>973-1273</td>
<td>400</td>
<td>?</td>
</tr>
<tr>
<td>Green et al. (1970)</td>
<td>Flint, wet</td>
<td>Axial compression</td>
<td>Grain growth</td>
<td>10⁻⁵ - 10⁻⁶</td>
<td>1223-1573</td>
<td>~1500</td>
<td>?</td>
</tr>
<tr>
<td>Brodie and Rutter (2000)</td>
<td>Synthetic, ultrafine, wet</td>
<td>Axial compression</td>
<td>Diffusional flow</td>
<td>10⁻⁷</td>
<td>1273-1473</td>
<td>300</td>
<td>0</td>
</tr>
</tbody>
</table>

constitutive flow law for pressure solution from stress relaxation experiments on Tennessee sandstone. Based on the experiments, an activation enthalpy of ~31 kJmol⁻¹ was obtained, and the constitutive flow law predicted no pronounced grain size effects but a strong dependence on temperature and pore fluid pressure. From creep experiments on pre-faulted Tennessee sandstone, the activation enthalpy was estimated to be ~36 kJmol⁻¹ (Rutter and White, 1979).

One of the major problems in studying pressure solution is the slow kinetics of fluid-assisted mass transfer in quartz. The kinetics can be accelerated by increasing the temperature: rapid compaction creep has been achieved in initially porous, fine-grained quartz powder during hydrothermal isostatic pressing at 1200 K, a confining pressure of 300 MPa and a pore water pressure of 200 MPa (Cox and Paterson, 1991). Based on microstructural observations, Cox and Paterson (1991) suggested that the fluid distribution during compaction creep changed continuously and was not controlled entirely by equilibrium wetting angles. The high temperatures and pressures substantially increased the solubility of quartz and also enhanced reaction kinetics and diffusivity in the pore fluid.

Den Brok (1992) deformed Dongelberg quartzite in a Griggs solid-medium deformation apparatus at a temperature of 1073 K, a confining pressure of ~1200 MPa, and a strain rate of ~10⁻⁷ s⁻¹, both with and without ~0.4 wt.% added water. He observed (1) abundant small, new polygonal to
euhedral quartz grains developed in microfractures and grain boundaries, which were parallel to the compression axis, (2) subeuhedral syntaxial overgrowth features on original grains, (3) no significant lattice preferred orientation after a strain of ~46%, (4) samples deformed with added water showed a stress exponent $n \leq 1.3$, and (5) water-added samples were $\geq 9$ times weaker than samples deformed without added water, but added water did not diffuse into the quartz grains within measurement resolution ($\leq 1000 \text{ H}/10^6 \text{ Si}$). Den Brok and Spiers (1991) and den Brok (1992) concluded that the dominant deformation mechanism was pressure solution creep associated with stress corrosion microcracking. According to them, the weakening effect of added water observed in various studies at similar conditions on natural quartzite (Jaoul et al., 1984; Mainprice and Paterson, 1984; Koch et al., 1989; Tullis and Yund, 1989) is not an intracrystalline process influencing crystal-plasticity, but it is caused by water remaining at grain boundaries and/or in open fractures. The experimental data of den Brok (1992) could be best fitted by a model assuming water-assisted solid state grain boundary diffusion occurring at the crackbound island-island contacts ('Gratz model', Gratz, 1991; den Brok, 1992; den Brok, 1998). The model predicts that the rate of pressure solution depends strongly on (1) the possibility of microcracking and (2) the intensity of microcracking (den Brok, 1998).

While water-rich fluids promote processes of dissolution, precipitation, and silica transport, they also accelerate rates of grain growth resulting in increasing grain sizes (Tullis and Yund, 1982). Increasing grain sizes tend to decrease creep rates of diffusive mass transfer processes and may therefore change the rate-controlling mechanisms (Kronenberg, 1994).

### 3.2.1.2 Grain growth

Grain growth in quartz is strongly affected by the presence of fluid (Tullis and Yund, 1982). Substantial grain growth was observed during deformation of wet fine-grained natural quartz aggregates like agate or flint at various conditions (see Tab. 3.3). (Green et al., 1970; Masuda and Fujimura, 1981; Karato and Masuda, 1989). Two deformation regimes were distinguished by the resulting microstructures (Karato and Masuda, 1989): (1) at relatively low temperature, high strain rates and high differential stresses, a clear foliation developed normal to the compression direction defined by highly flattened grains with irregular grain boundaries. A maximum of $c$-axes formed parallel to the compression direction. (2) At relatively high temperature, low strain rates and low differential stresses, grain shape was nearly isotropic and very weak foliation developed. The $c$-axes tended to lie at 40-50° to $\sigma_1$ and a maximum of the rhombohedron $r$ pole developed parallel to $\sigma_1$. Different explanations for the two regimes exist: (1) Karato and Masuda (1989) suggested that the observed foliation at high differential stresses was due to anisotropic grain
growth caused by anisotropic water distribution. At low differential stresses, grain growth was isotropic due to an isotropic fluid distribution controlled by dihedral angle. (2) According to Green et al. (1970), the LPO in the low stress regime was caused by strain-induced recrystallization, and in the high stress regime by stress controlled grain growth.

### 3.2.1.3 Diffusional flow

Brodie and Rutter (2000) deformed hot-pressed, ultrafine-grained (grain size <4 μm) quartz aggregates at 300 MPa confining pressure at temperatures between 1273 K and 1473 K. No grain growth was observed, grains remained equigranular, no LPO was produced, the stress exponent n was 1, and the strain rate was approximately proportional to d^{-2}. The rheological behavior could be fitted to the theoretical flow law for diffusion-accommodated grain-boundary sliding of Ashby and Verrall (1973).

### 3.2.2 Intracrystalline plasticity

#### 3.2.2.1 Hydrolytic weakening of quartz

In natural quartz-rich rocks, there is abundant microscopic evidence that quartz has deformed plastically and was weaker than other minerals (such as feldspars) (Blacic and Christie, 1984). In contrast, quartz single crystals and aggregates are very strong and brittle in laboratory deformation experiments (see section 3.1.2). This phenomenon could be explained by the model of hydrolytic weakening by Griggs and Blacic (1965). The model of hydrolytic weakening led to numerous studies on the plastic deformation of quartz. Extensive reviews on hydrolytic weakening of quartz were given by Aines and Rossman (1984), Blacic and Christie (1984), Paterson (1989) and Kronenberg (1994).

Since the beginning of this century, several attempts have been made to induce plastic flow in quartz crystals by applying a high confining pressure (Adams, 1910; Griggs, 1936; Griggs and Bell, 1938; Bridgman, 1952; Carter et al., 1961; Christie et al., 1964b). The first microstructural evidence of plastic deformation of quartz was obtained in experiments using quartz sand compressed in an anvil device (deformed at >298 K and >500 MPa) by Carter et al. (1961) and later in single crystals at >673 K and 1500-3000 MPa using a Griggs’ apparatus (Carter et al. 1964). Griggs and Blacic (1964) discovered that natural crystals deformed at stresses an order of magnitude lower than in previous studies if they had been preheated for several hours in a solid-medium apparatus in the presence of water. The water was released by dehydration of the talc pressure medium. The same was observed in synthetic crystals containing relatively high concentrations of water (~0.1 wt%) (Griggs and Blacic, 1965). The weakness of the crystals was
only evident above a certain temperature, called the critical weakening temperature $T_c$, which was found to depend on the total OH content of the crystal (Fig. 3.9).

![Graph showing flow shear stress versus temperature for dry and hydrolytically weakened natural quartz crystals at several strain rates and synthetic crystal at $10^{-5}$ s$^{-1}$ strain rate. Confining pressure is 1500 MPa for all data except those of Balderman (1972) which are at 200-500 MPa. Note the strong decrease in flow stress of synthetic quartz at temperatures above a critical weakening temperature. The strength of dry natural crystals is rather insensitive to temperature up to 1273 K, depending on strain rate, and drops significantly at higher temperatures. The difference in flow behavior of natural and synthetic quartz can be attributed to different amounts and specification of water species. From Blacic and Christie (1984).](image)

Griggs and Blacic (1965) attributed the large reduction in strength at „wet“ conditions to the hydrolysis of the strong Si-O-Si bridges near advancing dislocations by water. This would lead to much weaker bonds between the hydrolysed silanol groups (hydrolytic weakening; Griggs and Blacic, 1964; see also Griggs, 1967; Blacic, 1975).

Significant progress in understanding intracrystalline plasticity of quartz was achieved by studying the relationship between rheology and specification of the hydrogen present in the samples by infrared spectroscopy. In the following, the behavior of quartz single crystals will be reviewed, then the behavior of polycrystalline quartz will be discussed.

Attempts by Kekulawala et al. (1978), Paterson and Kekulawala (1979) and Mackwell and Paterson (1985) failed to repeat the results of Griggs and Blacic (1964) in natural single crystals.
of Brazilian-type quartz in a hydrous environment, but using a gas medium apparatus at 300 to 500 MPa confining pressure: The samples remained strong and no measurable amount of water diffused into dry natural quartz even after many hours of heat-treatment. It was suggested that this difference was mainly due to the dependence of the diffusion coefficient of the water species on pressure (Paterson and Kekulawala, 1979; Mackwell and Paterson, 1985). However, it appears now that most of the weakening effect observed in earlier studies in solid medium apparatus was associated with the introduction of water through microcracking and subsequent crack healing (Kirby and Kronenberg, 1984; Kronenberg et al., 1986; Rovetta et al., 1986; see also paragraph 2.2.3.2). On the other hand, Kekulawala et al. (1978) found in a gas medium apparatus a relatively low strength for natural amethyst and wet synthetic quartz crystals which both have similar water contents and infrared absorption spectra (Fig. 3.10 and 3.11a). The authors distinguished three types of hydroxyl absorption in quartz: (1) Sharp bands attributed to OH in well-defined structural sites at various wavenumbers (“structurally-bound hydroxyl”), (2) absorption by molecular water, recognizable as ice bands around 320 mm\(^{-1}\) at low T (freezable fluid inclusions, “water-bound hydroxyl”), and (3) broad absorption around 340 mm\(^{-1}\) which did not sharpen into ice bands at low T (non-freezable molecular fluid inclusions, “gel-bound hydroxyl”). Amethyst crystals and wet synthetic quartz showed higher strength if they were annealed before deformation at conditions that favour the replacement of gel-bound hydroxyl by freezable fluid inclusions (Kekulawala et al., 1978, 1981; Paterson and Kekulawala, 1979). Dry Brazilian quartz crystals exhibited mainly sharp bands (structurally-bound hydroxyl) and were mechanically strong. On the other hand, milky vein quartz containing \(\sim 2000 \text{ H/10}^6 \text{ Si}\), which was incorporated mainly as freezable fluid inclusions (Aines and Rossman, 1984), yielded at smaller stresses compared to those required to deform dry natural and wet synthetic crystals (Kekulawala et al., 1978). Furthermore, Kekulawala and Paterson (1979) found a direct correlation between yield strength measured in constant strain rate experiments and integral absorbance of the gel-bound hydroxyl in wet synthetic quartz (see fig. 3.11b, c). Thus Kekulawala et al. (1978) suggested that weakening of quartz is only affected by the gel-bound hydroxyl. Aines et al. (1984) and Gerretsen et al. (1989) showed that the gel-bound hydroxyl absorption band is due to high-pressure clusters of molecular water, which in contrast to H\(_2\)O fluid inclusions, are non-freezable. They also pointed out that most of the water in wet synthetic quartz is present as non-freezable molecular water clusters.
Fig. 3.10  IR absorption spectra for different samples of quartz. a) Spectra from quartz single crystals used in experimental rock deformation. Wet synthetic quartz crystals exhibit broad absorption attributed to molecular water, dry Brazilian quartz crystals are characterized only by small absorption bands due to hydrogen interstitials. Milky quartz shows a wide absorption band associated with liquid water within fluid inclusions. b) Spectra of quartz within naturally deformed aplite. Broad bands are characteristic of freezable, fine-scale water inclusions. c) Spectra of quartz within undeformed aplite. The small, sharp absorption bands 320.5, 330.5, 337.8 and 342.5 mm\(^{-1}\) are due to hydrogen interstitials. After Kronenberg et al. (1990).

Fig. 3.11  a) Stress-strain curves of quartz single crystals at 300 MPa confining pressure, 1073 K and 10\(^{-5}\) s\(^{-1}\) strain rate in triaxial compression. The wet synthetic quartz and the amethyst were heated at 1173 K for 49 and 27 hours, respectively. b), c) Rheology of synthetic quartz single crystals with variable water contents in uniaxial compression at 783 K and constant stress (\(\sigma\) = 140 MPa). b) Strain-time data c) Maximum strain rates (prior to strain hardening). After Kekulawala et al. (1978) and Kronenberg (1994).
These clusters were trapped in the lattice during rapid growth of quartz and act as highly efficient sources of dislocation nucleation due to stress concentrations around them. High dislocation densities may explain the low yield strengths of synthetic quartz (McLaren et al., 1989, Gerretsen et al., 1989). Several observations indicated that the dislocation nucleation at the clusters tend to be inhibited by an increase in hydrostatic pressure. Furthermore, evidence exists that the rate of recovery is positively correlated with the bulk water content in wet synthetic quartz crystals, although the mechanism of water-enhanced climb of dislocations is not clear (McLaren, 1991). Since recovery is always associated with unstrained bubbles (at an atomic scale) on dislocations, McLaren et al. (1989) suggested that these bubbles promote climb by acting as sources and sinks for Si and O vacancies. It was found that natural polycrystalline quartz aggregates generally contain substantial amounts of water (Paterson, 1989) as well as high dislocation densities at the beginning of deformation (Kronenberg, 1994). In general, quartzites in the presence of water (6700 to 27'000 H/10^6 Si) are weak, while quartzites deformed without added water, but with their original intragranular water contents (ranging from 600 to 4000 H/10^6 Si) have intermediate strengths, and quartzites that were vacuum-dried at elevated temperatures before deformation are strong (Kronenberg, 1994). Dislocation substructures developed in dry quartzites are heterogeneously distributed and low rates of recovery are observed, whereas quartzites deformed with water added exhibit homogeneous dislocation densities and organized dislocation configurations. The latter ones result from climb and recovery (Kronenberg, 1994). IR spectra of fluid inclusions in quartzites are comparable to the spectra of milky quartz with freezable fluid inclusions of varying sizes (Mainprice and Paterson, 1984; Koch et al., 1989; Kronenberg, 1994). Mainprice and Paterson (1984) deformed quartzites (bulk water contents of around 1000 to 4000 H/10^6 Si) at 300 MPa and temperatures of 1000-1300 K. They yielded at slightly higher strength than wet synthetic single crystals with similar water contents.

Synthetic quartz aggregates made from crushed quartz sand with water present had similar strength as quartzites when tested at 300 MPa, 1273 K. On the other hand, aggregates of similar grain size crystallized from silica gel had much lower strengths, comparable with those of wet synthetic crystals (Paterson and Luan, 1990; Luan and Paterson, 1992). In the latter case, the quartz grains have grown rapidly in the presence of water during hot pressing, and Paterson (1989) suggested that water is incorporated in the same way as during growth of 'wet' synthetic single crystals.

Clearly, water has a significant influence on the strength of quartz. Several experiments on water-added quartzites suggested that the diffusion coefficient of water in quartz is very strongly pressure dependent (Paterson and Kekulawala, 1979; Mackwell and Paterson, 1985; see also Chapter 2.2.3.2). Therefore, quartz should be weaker at high confining pressures. However, other
studies showed that the pressure effect on the diffusion coefficient was due to microcracking and subsequent introduction of molecular water inclusions (Kirby and Kronenberg, 1984; Kronenberg et al., 1986; Rovetta et al., 1986; see also Chapter 2.2.3.2). In more recent studies, different opinions exist about the rate of water penetration into quartz and equilibration of the samples with respect to water (Gerretsen et al., 1989; Paterson and Luan, 1990; Kronenberg and Wolf, 1990; den Brok, 1992; Den Brok et al., 1994; Post and Tullis, 1998). Paterson and Luan (1990) discussed the difficulty to attain water equilibration, mainly in gas-medium experiments on natural coarse-grained quartzites. They calculated a mean diffusion length of 1 μm in 10 h at 1173 K, 300 MPa. They concluded that a homogeneous hydrogen defect distribution in equilibrium with intergranular fluids may only be achieved in fine-grained quartz aggregates. Therefore, fine-grained synthetic quartz aggregates, flints, and novaculites are probably best suited for studying the hydrolytic weakening effect of polycrystalline quartz aggregates because they are more likely to have equilibrium concentrations of hydrogen species (Mainprice, 1981; Kronenberg and Tullis, 1984). Similarly, den Brok et al. (1994) did not observe any diffusion of water into coarse quartz grains though the samples were maintained for 14-22 days under high P-T (1073 K, 1200 MPa) conditions. This was in agreement with results obtained by Kronenberg et al. (1986), Rovetta et al. (1986) and Gerretsen et al. (1989). A dependence of strength on grain size was observed in the experiments of Kronenberg and Tullis (1984) on natural quartz aggregates at temperatures between 973 K and 1373 K, 950-1600 MPa and strain rates of 10⁻⁶s⁻¹. They concluded that the dependence was caused by different amounts of structurally incorporated water: in fine-grained quartz aggregates, the grains are completely penetrated and weakened by water which was present as fluid films along grain boundaries. In coarse-grained samples, gradients in water concentration will persist from grain cores to rims. Therefore, coarse-grained samples will be stronger than fine-grained ones. However, fluid films may also assist solution transfer leading to an additional grain size effect on strength (Kronenberg, 1994).

The influence of the chemical environment for polycrystalline aggregates was investigated by Post et al. (1996). They performed experiments on natural quartzites under controlled chemical environment at 1173 K, 700 or 1700 MPa, and 10⁻⁶ s⁻¹ strain rate. The experiments indicated a strong dependence of creep strength on f[H₂O] and no dependence on f[H₂], f[O₂], or a[H⁺]. They concluded that f[H₂O] affects both dislocation climb and strain-induced grain boundary migration. Since f[H₂O] is pressure-dependent, they proposed that pressure should have an effect on the hydrolytic weakening of quartz, despite of the above mentioned results. Post and Tullis (1998) suspected that the creep strength depends on the concentration of a water related crystal defect, which is controlled by the water fugacity. However, the nature of this defect or the relationship
between the crystal defect and the water fugacity are not known. It is still under discussion, whether increasing pressure has a weakening effect on quartz.

In summary, intracrystalline plasticity in experimentally deformed quartz appears to be promoted in various ways by hydrogen defects, molecular water clusters and fluid inclusions (Paterson, 1989), but the processes at the atomic scale are not clearly understood. It appears that the mechanisms that weaken quartz single crystals are also responsible for the weakening of polycrystalline aggregates, even if one has to keep in mind that fluids at grain boundaries can promote recrystallization and solution transfer processes (den Brok, 1992; Kronenberg, 1994). Dislocations may be generated at fine-scale molecular water clusters and fluid inclusions (McLaren et al., 1983; Gerretsen et al., 1989) which serve as internal reservoirs of water, in communication with advancing dislocation kinks and jogs by pipe diffusion (Paterson, 1989). Furthermore, molecular water appears to facilitate dislocation glide and climb, processes of dislocation reorganization and recovery, and dynamic recrystallization (e.g. Hobbs, 1968). Recovery of dislocation substructures within grains by dislocation climb and annihilation may be assisted by hydrogen point defects, which accelerate rates of oxygen and silicon diffusion (Kronenberg, 1994). Reduction of dislocation density at grain margins due to dynamic recrystallization may be assisted by water at grain boundaries (Paterson, 1989; Kronenberg, 1994). Kronenberg (1994) summarized that up to now, no evidence for an influence of water on the pure glide of dislocations was reported. Mechanical properties of quartz could be correlated to hydrogen species present in the samples, but there is not a single mechanism of chemical weakening that would explain all of the experimental results. Thus, internal hydrogen species may play multiple roles in the experimental deformation of quartz.

### 3.2.2.2 Slip systems

Slip systems of quartz are summarized in Tab 3.4 and Fig. 3.12. Slip systems for α- and β-quartz are believed to be identical except some additional slip systems in β-quartz which are not definitely established (Blacic and Christie, 1984). In experimentally deformed natural α-quartz single crystals, variations in the active slip systems with temperature, strain rate and water content were observed (Blacic, 1971; Blacic, 1975). The preferred slip systems have Burgers vectors parallel to \( \langle 11\bar{2}0 \rangle \) and \( [0001] \) and slip on the \( (0001) \) and \( \{10\bar{1}0\} \) planes: the critical shear stresses for slip parallel to \( \langle 11\bar{2}0 \rangle \) and \( [0001] \) directions are approximately 3 times smaller as those for slip parallel to \( \langle 11\bar{2}3 \rangle \) (Bäeta and Ashbee, 1969b). In dry natural crystals at low temperatures up to about 973 K and a strain rate of \( 10^{-5} \) s\(^{-1} \), \( (0001)\langle 11\bar{2}0 \rangle \) is the dominant slip system. Above 973 K, \( \{10\bar{1}0\}[0001] \) slip becomes dominant. The transition temperature decreases with decreasing strain rate (Bäeta and Ashbee, 1969b, Blacic, 1971). For wet quartz at
temperatures above 500 K and a strain rate of $10^{-5}\text{s}^{-1}$, \{10\text{10}\}<00\text{01}> tended to be replaced by \{11\text{20}\}<00\text{01}>, and \{00\text{01}\}<11\text{20}> slip became important again. The transition temperature, which coincided with the critical weakening temperature, was dependent on the water content of the samples (Blacic, 1971; Nicolas and Poirier, 1976).

Linker and Kirby (1981, 1984) deformed wet synthetic quartz crystals at constant compressive stress and atmospheric pressure in the temperature range $T = 673 - 1073$ K and in 8 different crystallographic directions. They demonstrated a strong rheological anisotropy for synthetic quartz single crystals: When slip in the \{00\text{01}\} direction was promoted, the strain rate was highest. At 1023 K they observed \{11\text{23}\} slip but at much slower rates than \{11\text{20}\} slip. They concluded that this rheological anisotropy is similar to the anisotropic behavior of diffusivities of impurities in quartz. They suggested that a relationship between hydrolytic weakening and impurity diffusion exists. In their anisotropy model, deformation is fastest when the slip direction is parallel to \{00\text{01}\}, which is the high diffusivity direction for impurities in quartz.

The strain rate and temperature dependence of the critical shear stresses for the different slip systems is not yet sorted out. Also, it is not clear if slip on positive and negative rhombs is equivalent in $\alpha$-quartz, which is the case in $\beta$-quartz (Wenk, 1994).

<table>
<thead>
<tr>
<th>Plane</th>
<th>Direction</th>
<th>dry/wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>{00\text{01}}</td>
<td>{11\text{20}}</td>
<td>Low T, high $\varepsilon$</td>
</tr>
<tr>
<td>{10\text{10}}</td>
<td>{00\text{01}}</td>
<td>High T, low $\varepsilon$</td>
</tr>
<tr>
<td>{10\text{10}}</td>
<td>{12\text{10}}</td>
<td>High T, low $\varepsilon$</td>
</tr>
<tr>
<td>{10\text{10}}</td>
<td>{12\text{13}}</td>
<td>High T, low $\varepsilon$</td>
</tr>
<tr>
<td>{11\text{20}}</td>
<td>{00\text{01}}</td>
<td>High T, low $\varepsilon$</td>
</tr>
<tr>
<td>{11\text{22}}</td>
<td>{11\text{23}}</td>
<td>High T, low $\varepsilon$</td>
</tr>
</tbody>
</table>

### 3.2.2.3 Twinning

The most common twinning law reported in naturally and experimentally deformed quartz is Dauphiné twinning (definition see chapter 2.2.2). Dauphiné twinning does not contribute to the strain, but the two twin orientations do not equally occur. The poles to \{10\text{11}\} $r$-positive rhombohedron have a much stronger tendency to lie parallel to the compressive stress $\sigma_1$ than the poles of the corresponding \{01\text{11}\} $z$-negative rhombohedron (Tullis, 1970; Tullis and Tullis, 1972).
Brazil twinning (definition see chapter 2.2.2) was observed in dry natural crystals deformed at high confining pressure and stress at temperatures from 773 K to 973 K (McLaren et al., 1967). This twinning mechanism probably does not operate in natural deformation or under most experimental conditions (Blacic and Christie, 1984).

### 3.2.2.4 Constitutive flow laws

A number of experimentally determined flow laws for intracrystalline plasticity of quartz rocks have been published. Most often the flow stress data were fitted to a power law of the form

\[ \dot{\varepsilon} = A\sigma^n \exp\left(\frac{-H_L}{RT}\right) \]  

where \( A \) and \( n \), the stress exponent, are empirical constants and \( H_L \) is the activation enthalpy for power-law creep. A compilation of some of the experimentally derived quartz flow laws is given in Tab 3.5. The data show some scatter mainly because of the following difficulties:

1. The strength derived from experiments in solid-medium apparatus may be overestimated due to the significant strength of the solid-confining media (Gleason and Tullis, 1995). Some authors (Luan and Paterson, 1992; Brodie and Rutter, 2000; Hirth et al., 2001) suggested that only the flow laws from the highest stress resolution data should be used, especially those from experiments using a gas medium apparatus or liquid confining medium.
(2) Samples deformed in gas apparatus were in the $\beta$ stability field, while samples deformed in solid-medium or molten salt medium machines were in the $\alpha$ stability field. However, compared to the overall scatter of flow laws reported, the effect of the $\alpha$-$\beta$ transition is probably small (Brodie and Rutter, 2000).

(3) Flow laws for quartz were all determined in compression experiments where the amount of attainable strain is limited. Therefore steady-state flow was often not achieved. Gleason and Tullis (1995) argued that steady-state flow can be achieved at low strain in samples deformed by climb-accommodated dislocation creep (regimes 2 and 3 of Hirth and Tullis, 1992, see below), whereas for samples deformed by recrystallization-accommodated dislocation creep (regime 1 of Hirth and Tullis, 1992, see below) high strains are required until steady-state. If non-steady-state conditions were considered, the strength will be overestimated.

(4) There is a scatter in the stress exponent $n$ between 1 and 6.5 which is believed to be due to one of the following reasons. (i) Flow laws have been calculated from data involving more than one deformation mechanism (Paterson, 1989; Gleason and Tullis, 1995). Theoretically, pure dislocation creep should give a stress exponent $n$ of 3 or higher. Values of $n$ below 3 could be due to a contribution of grain size sensitive flow to the deformation. This would lead to a lower strength than for pure dislocation creep (Paterson and Luan, 1990). Especially at higher temperatures, the presence of melt has been reported in some studies (Jaoul et al., 1984; Kronenberg and Tullis; 1984; Luan and Paterson, 1992), which would enhance grain boundary sliding. (ii) Non-attainment of steady-state flow could give a lower stress exponent (Gleason and Tullis, 1995).

(5) As already discussed in paragraph 3.2.2.1, different opinions exist about the rate of water penetration into quartz and equilibration of the samples with respect to water. It is possible that most of the experimentally deformed quartz samples did not have an equilibrium concentration of hydrogen species, especially the coarse-grained ones.

(6) The water activity seems to play an important role in plastic flow of quartz. In many studies a stress exponent $n$ between 2 and 3 was obtained, and the values of the activation enthalpy $H_I$ were all quite similar (Tab. 3.5). This led to the suggestion that, if a minimum amount of water is present in the samples, the stress exponent and the activation enthalpy will be independent of the total amount or fugacity of water. Paterson (1989) proposed to describe the dislocation-creep flow law of quartzites and quartz-dominated rocks with a flow law of the form

$$
\dot{\varepsilon} = A \sigma^n j_{H_2O}^m \exp\left(\frac{-H_I}{RT}\right)
$$

(3.3)
where $A$ and $n$, the stress exponent, are empirical constants, $f_{H2O}$ is the water fugacity, $m$ is the water fugacity exponent and $H_L$ is the activation enthalpy for power-law creep. Theoretical considerations indicated that the equilibrium solubility of water in quartz will always be less than $100 \, H/10^6 \, Si$ (Paterson, 1989). A major problem in extrapolating a flow law of the form of (3.3) to natural conditions is therefore the possible influence of metastable uptake of water (Brodie and Rutter, 2000). Also, there is some discrepancy in the exact value of the water fugacity exponent $m$. Based on data for novaculite at pressures between 350 and 1590 MPa from Kronenberg and Tullis (1984), Kohlstedt et al. (1995) inferred a water fugacity exponent of $m=0.8$ (if $n=2.6$ was used) or $m=1.2$ (if $n=4.0$ was used). Gleason and Tullis (1995) obtained a value of $m \approx 1$ (if $n=4$) by using only the three highest pressure samples of Kronenberg and Tullis (1984). Based on the strengths of buffered samples at 1700 MPa and 700 MPa, Post et al. (1996) postulated a minimum value of $m=2$ using a stress exponent of 3.9. For the samples of Luan and Paterson (1992) a value of even $m=2.8$ was calculated (Post et al., 1996). Hirth et al. (2001) pointed out that the value of $m=2$ measured by Post et al. (1996) was due to a change in deformation mechanism with increasing differential stress, and they obtained a value of $m \approx 1$ if only samples with flow stresses less than $\sim 300$ MPa were analysed.

### 3.2.2.5 Textures and microstructures of experimentally deformed quartzites

Preferred orientation in experimentally deformed quartz aggregates can be produced by slip and recrystallization, selective grain growth and twinning.

A preferred orientation after almost no permanent strain was observed in flint and quartzite samples subjected to compression (Tullis, 1970; Tullis and Tullis, 1972). The authors attributed the preferred orientation to Dauphiné twinning. Dauphiné twins do not change the orientation of the c-axis, but they reverse positive and negative rhombs. The LPOs of deformed, but non-recrystallized grains (‘deformation texture’) consist of a small circle girdle around the compression axis with opening angle ranges from $\sim 25^\circ$ to $\sim 35^\circ$ (Tullis et al., 1973; Gleason et al., 1993; see Fig. 3.13b). It was suggested that these patterns are due to $\langle 0001 \rangle$ $\langle 1 \bar{1} 2 0 \rangle$ slip with variable amount of $\{10 \bar{1} 0\}$ $\langle 1 \bar{1} 2 10 \rangle$ slip (Tullis et al., 1973).
Table 3.5  Flow parameters for quartz

<table>
<thead>
<tr>
<th>Reference</th>
<th>Starting material</th>
<th>( \log A ) (MPa(^{-3})s(^{-1}))</th>
<th>( H_L ) (kJmol(^{-1}))</th>
<th>( n )</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brodie and Rutter (2000)</td>
<td>Hot-pressed Brazilian quartz</td>
<td>-3.3</td>
<td>220</td>
<td>3.0</td>
<td>wet</td>
</tr>
<tr>
<td>Gleason and Tullis (1995)</td>
<td>Black Hills</td>
<td>-3.96</td>
<td>223</td>
<td>4.0</td>
<td>wet, no melt</td>
</tr>
<tr>
<td>Gleason and Tullis (1995)</td>
<td>Black Hills</td>
<td>-7.74</td>
<td>137</td>
<td>4.0</td>
<td>wet, melt</td>
</tr>
<tr>
<td>Luan and Paterson (1992)</td>
<td>Grown from silicic acid</td>
<td>-9.4</td>
<td>150</td>
<td>3.9</td>
<td>wet</td>
</tr>
<tr>
<td>Paterson and Luan (1990)</td>
<td>Average wet quartzite</td>
<td>-7.2</td>
<td>135</td>
<td>3.1</td>
<td>wet</td>
</tr>
<tr>
<td>Koch et al. (1989)</td>
<td>Simpson</td>
<td>-5.94</td>
<td>134</td>
<td>2.7</td>
<td>wet</td>
</tr>
<tr>
<td>Jaoul et al. (1984)</td>
<td>Heavitree</td>
<td>-2.28</td>
<td>146</td>
<td>1.4</td>
<td>wet</td>
</tr>
<tr>
<td>Jaoul et al. (1984)</td>
<td>Heavitree</td>
<td>-2.54</td>
<td>151</td>
<td>1.8</td>
<td>wet</td>
</tr>
<tr>
<td>Kronenberg and Tullis (1984)</td>
<td>Heavitree</td>
<td>-5.66</td>
<td>120</td>
<td>2.7</td>
<td>wet</td>
</tr>
<tr>
<td>Jaoul et al. (1984)</td>
<td>Heavitree</td>
<td>-5.0</td>
<td>163</td>
<td>2.4</td>
<td>dry</td>
</tr>
<tr>
<td>Jaoul et al. (1984)</td>
<td>Heavitree</td>
<td>-5.46</td>
<td>184</td>
<td>2.8</td>
<td>dry</td>
</tr>
<tr>
<td>Kronenberg and Tullis (1984)</td>
<td>Heavitree</td>
<td>-5.30</td>
<td>170</td>
<td>2.9</td>
<td>dry</td>
</tr>
<tr>
<td>Hansen and Carter (1982)</td>
<td>Heavitree</td>
<td>-4.5</td>
<td>123</td>
<td>1.9</td>
<td>dry</td>
</tr>
<tr>
<td>Shelton and Tullis (1981)</td>
<td>Heavitree</td>
<td>-2.90</td>
<td>168</td>
<td>2.0</td>
<td>dry</td>
</tr>
<tr>
<td>Parrish et al. (1976)</td>
<td>Simpson</td>
<td>-11.17</td>
<td>266</td>
<td>6.5</td>
<td>dry</td>
</tr>
</tbody>
</table>

The development of preferred orientation during recrystallization in quartz was first systematically studied by Green et al. (1970) in experimentally deformed flint. Recrystallization during axial compression yielded two different preferred orientations in the \( \alpha \)-quartz field: at lower temperatures or faster strain rates a maximum of c-axes developed parallel to the compression direction (‘c-maximum fabric’, Fig. 3.13a), and at higher temperatures or slower strain rates a maximum developed near \( r \{10\overline{1}1\} \) (small circle girdle pattern, ‘r-maximum fabric’). At intermediate temperatures and strain rates, aspects of both fabric types developed (‘composite fabric’). In the \( \beta \)-quartz field, a strong concentration of c-axes parallel to the compression direction and a weaker concentration normal to the compression direction developed (Green et al., 1970). However, the studies of Tullis et al. (1973) and Gleason et al. (1993) did not show a change in the LPO corresponding to the \( \alpha - \beta \) transition. In contrast, Gleason et al. (1993) showed that the LPOs of dynamically recrystallized quartz aggregates depend on the dominant mechanism of recrystallization, which itself depends strongly on the dominant mechanism of recovery (grain boundary migration recrystallization or dislocation climb) (Fig. 3.13).

Hirth and Tullis (1992) used microstructures to identify three different recrystallization mechanisms with increasing temperature, increasing water content or decreasing strain rate, and thus decreasing flow stress: (1) strain-induced grain boundary migration recrystallization with no
or little dislocation climb (regime 1), (2) progressive subgrain rotation recrystallization with easy dislocation climb (regime 2), and (3) progressive subgrain rotation with easy dislocation climb and rapid grain boundary migration (regime 3). These regimes depend on the relative rates of dislocation production, dislocation climb and grain boundary migration. When grain boundary migration dominated (regime 1), c-axes in recrystallized grains were oriented parallel to the compression direction (Fig. 3.13c). The c-axes of the non-recrystallized grains showed a small circle girdle (Fig. 3.13b). When subgrain rotation was important (regime 2), the texture for recrystallized grains was similar to the non-recrystallized ones. In both cases a small circle girdle of c-axes developed (Fig. 3.13d). At temperatures and strain rates corresponding to regime 3, the LPO was similar to that of non-recrystallized grains (small circle girdle of c-axes with an opening angle around 45°, Fig. 3.13e) (Gleason et al., 1993). The authors suggested that the strong c-axis maximum parallel to the compression direction (‘c-maximum fabric’) in fine-grained quartz aggregates observed by Green et al. (1970) was produced by grain growth. Gleason et al. (1993) postulated that grains oriented with c-axes parallel to σ₁ would be favored for growth. With increasing strain, grain growth stopped and the texture evolved towards a small circle girdle (r-maximum fabric) which is characteristic of intracrystalline slip (regime 2).

Annealing can have a profound effect on the texture of experimentally deformed quartz aggregates (Green et al., 1970; Tullis and Heilbronner, 1999). Green et al. (1970) observed a strengthening of the preferred orientation in experimentally deformed Dover flint (42% shortening) when it was annealed for 3 days at 973 K, 1600 MPa. Tullis and Heilbronner (1999) performed deformation and subsequent annealing experiments in the three regimes defined by Hirth and Tullis (1992). Annealing temperature was left at the deformation temperature (973 K - 1473 K) or raised 100 K for 1 to 10 days. In regime 1, annealing replaced the work-hardened original grains with polygonal strain-free grains with a weaker LPO. Deformed fine-grained aggregates (novaculites) showed a complete change in pattern with annealing: the strong c-axis maximum parallel to σ₁ in the deformed samples was replaced by a c-axis great circle girdle normal to σ₁. In regime 2 and 3, annealing did not substantially change the LPO.

Only few studies investigated the effect of second phases on texture development. The addition of 25% mica strongly reduced the degree of preferred orientation of quartz (Tullis and Wenk, 1994).
Fig. 3.13 Textures in dynamically recrystallized quartzites represented as c-axis profiles from parallel ($\phi = 0$) to perpendicular ($\phi = 90$) to the compression direction (top) and inverse pole figures (bottom). a) Selective grain growth. Novaculite shortened 57% at 1173 K, $10^{-6}$ s$^{-1}$. b) Non-recrystallized quartzite of regime 1. Quadrant quartzite shortened 60% at 973 K, $10^{-6}$ s$^{-1}$. c) Recrystallized quartzite of regime 1. Novaculite shortened 45% at 973 K, $10^{-6}$ s$^{-1}$. d) 60 vol.% recrystallized quartzite of regime 2. Black Hills quartzite shortened 75% at 1173 K, $10^{-6}$ s$^{-1}$. e) Fully recrystallized quartzite of regime 3. Black Hills quartzite shortened 76% at 1273 K, $10^{-7}$ s$^{-1}$. After Gleason et al. (1993).

All experiments described above were performed using axial compression. However, general deformation is more relevant to geological conditions. There are only a few experiments described in the literature for pure shear (Tullis, 1977) and simple shear, those with substantial shortening normal to the shear zone boundary (Dell’Angelo and Tullis, 1989; Raiser, 1990; Tullis and Heilbronner, 2001). The latter studies showed the importance of noncoaxial experiments to develop textures which are similar to those in naturally deformed rocks, but different to those in axially compressed samples. In the experiments of Dell’Angelo and Tullis (1989), the lowest strain sample ($\gamma = 1.3$) exhibited a type-1 crossed girdle, symmetrically disposed about the pole to
the foliation (Fig. 3.14a). The intensities of c-axes on both sides of the girdle were equal, i.e., the pole figure has orthorhombic symmetry with respect to the foliation. A slightly higher strain sample \((\gamma = 1.7)\) showed a similar rhombic symmetry, but the maxima were not symmetric to the foliation, but inclined opposite to the sense of shear (Fig. 3.14b). At the highest strains reached \((\gamma = 2.1 \text{ and } 2.9)\), there was a broad single maximum and inclined with the sense of shear (Fig. 3.14c). For a sample deformed under plane strain conditions up to a shear strain of \(\gamma = 2.8\) an asymmetric girdle with a point maximum approximately normal to the SZB and oblique to the flattening plane was observed (Fig. 3.14d). However, a substantial part of c-axes tended to form a second maximum at the periphery of the pole figure and opposite to the sense of shear displaced from the main maximum. This was also observed in low strain experiments on ice (Schmid, 1994). The results suggest that a symmetric pattern does not exclude simple shear deformation, but may simply indicate low shear strain (Dell’Angelo and Tullis, 1989).

The experiments seem to indicate that the c-axis asymmetry with respect to the SZB can be used as a shear sense criteria (Schmid, 1994). The maxima are displaced from a symmetric position with the sense of shear.

\[\text{Fig. 3.14} \quad \text{c-axis pole figures of experimentally sheared quartzite. All samples deformed at 1073 K, } 10^6 \text{ s}^{-1}, \text{ and } 1500 \text{ MPa. Equal area, lower hemisphere projections. The foliation is horizontal. Shear zone boundary is marked by a dashed line when not coincident with the foliation; sense of shear is sinistral. a)-c) Samples deformed in combined shear and axial compression. d) Sample deformed in shear and plane strain. After Dell’Angelo and Tullis (1989).}\]
4 Techniques and methods used in this study

4.1 Introduction

This chapter describes (1) the instrumentation and technique used for specimen fabrication and deformation; (2) microstructural observation methods; (3) texture measurements methods; (4) the instrumentation and technique for water content estimations and (5) chemical composition and secondary phase determinations.

4.2 Paterson gas medium apparatus

All experiments were performed in an internally heated Paterson gas medium apparatus with torsion capabilities (Paterson and Olgaard, 2000). The apparatus is made for reaching pressures up to 500 MPa and temperatures up to 1600 K. The basic design of the system is shown in Fig. 4.1. The apparatus has five main components: housing, pressure vessel and pumping system; high temperature furnace; deformation equipment (axial deformation and torsional part) and pore-fluid part.

The housing serves as the framework for the complete machine and as a protective shielding. The pressure vessel A is composed of duplex steel and has a working space of 65 mm diameter and 360 mm length. With the furnace and internal load cell E mounted, the free volume is about 200 ml. It is mounted with its axis vertical. Chemically inert argon is used as a pressure medium. The pumping system consists of two parts: an argon gas booster pump is used to bring the vessel up to 120 MPa, while the second stage of pumping, up to the desired working pressure, is done with a 10:1 intensifier. Overpressuring of the vessel and tubes is prevented by rupture disks (20, 80, 200, and 700 MPa). A bubbler system helps detecting leaks at the different O-ring seals. Under typical conditions of this study, the pressure was very stable, dropping less than 2 MPa h\(^{-1}\) at 300 MPa confining pressure. At 350 MPa confining pressure, leaks were more common and drops in pressure of 3 MPa h\(^{-1}\) were typically observed.

The high temperature furnace is contained in a stainless-steel tube. It has three molybdenum windings that produce a constant high temperature zone of typically 50 mm length. A control thermocouple is located adjacent to each winding and a specimen thermocouple is installed in the bore of the specimen assembly 3 mm away from the top end of the specimen. A Eurotherm\textsuperscript{TM} self-tuning programming controller permits control through the signal from the specimen
thermocouple, while another temperature indicator independently records all thermocouples. A stable thermal profile is calibrated by adjusting the currents in the three windings.

![Schematic drawing of the Paterson gas medium apparatus with torsion actuator. Black dots are O-ring seals. From Paterson and Olgaard (2000).](image)

The deformation equipment consists of an axial deformation part and a torsional part.

An internal load cell E permits to measure both torque and axial load simultaneously without any friction effects. An estimation of the friction effect is obtained by an external load cell. With the axial deformation part mechanical tests can be carried out in compression and extension under constant strain rate. A pressure-compensated loading piston D at the bottom closure plug C of the pressure vessel can apply an axial load of up to 100 kN to the sample. The piston is moved by a servo-controlled electromechanical actuator. The axial displacement rate ranges between 0.5 mm s\(^{-1}\) and <0.01 mm s\(^{-1}\). The axial piston displacement is recorded with an internal displacement transducer (LVDT).

The torsional part applies torque to samples. In theory, the amount of twist that can be applied and therefore the strain are not limited. In practice, it is limited by the ductility of the specimen jacket.
and the winding up of the cable of the rotary displacement transducer H. The latter one is mounted on top of the torsion driver handle G to record directly the twist of the specimen. The servo-controlled electromechanical torsion actuator is mounted at the top of the pressure vessel. The maximum torque is 1000 Nm and the rates of twist can be varied over a range corresponding to strain rates from around $10^{-3}$ to $10^{-7}$ s$^{-1}$.

Strain gauges are mounted on the boss of the torsion driver G, which fits into the top steel anvil piston F. They also provide external torque measurement for an estimation of the friction occurring at the upper closure B.

The main part of the pore fluid system is a servo-controlled electromechanically driven volumometer (piston diameter 7 mm, stroke 50 mm) of 2000 mm$^3$ capacity. It is made for argon or water at pressures up to 500 MPa and contains pressure and displacement transducers, and down- and upstream pore pressure connections. The following two experimental arrangements are possible: (1) Experiments under constant fluid volume with recording changes in pore fluid pressure or (2) experiments under constant pore fluid pressure with recording changes in pore fluid volume. The first arrangement was used for this work.

### 4.3 Furnace calibrations

The behavior of a furnace changes with age due to various effects (degradation or shifting of the alumina insulation in the stainless steel, abrasion of the molybdenum windings, microcracks in the furnace ceramics etc.). In order to keep a stable thermal profile, furnace calibrations have to be performed frequently. For calibrating the furnace at different temperatures and confining pressures, a calibration assembly similar to the specimen assembly (Fig. 4.2) was used, except that the diameter of the column was everywhere 15 mm, an alumina piston replaced the sample and all the alumina pistons and spacers had a central hole. With this assembly the temperature could be measured with a travelling thermocouple across the whole assembly. Once the desired pressure and temperature were reached, the power settings for each of the three windings were varied until variations in the temperature gradient were smaller than $\pm 2$ K along 30 mm parallel to the column axis (so-called hot-zone). For a deformation experiment, the length of the alumina pistons and spacers were such that the sample was located within the central part of the hot-zone. During a calibration run, the voltage, current and temperature were recorded for each of the three windings. These settings allowed reproducing the thermal profile when the calibration assembly was replaced by a deformation assembly.
Both furnaces used in this study behave stable for a temperature of 1400 K and calibration was only repeated after 10-30 experiments. However, the thermal profile for one of them was very unstable for a temperature of 1300 K and calibration was required after every second experiment.

4.4 Sample assembly

Fig. 4.2 shows the standard piston and sample assembly.

![Diagram of sample assembly](image)

Fig. 4.2 Standard sample (left) and piston (right) assembly for samples with 10 mm diameter and connected pore pressure system. A central hole through the alumina, zirconia and steel pistons ensured the connection to the pore fluid system. Undrained conditions should be attained using non-porous spacers, drained conditions using porous spacers and opened pore pressure valves. A Ni and/or Pt or Au foil (thickness 0.025 mm) was wrapped around the sample in order to prevent a reaction with the Fe jacket.

Samples of the natural quartz aggregates (Dover flint, novaculite) were cylindrical with a diameter of 10 mm and a length of 8-19 mm. An alumina (Al₂O₃) spacer of the same diameter was at each end of the sample. These spacers were either porous or non-porous and prevented the specimen being extruded up the thermocouple hole. A 50 mm long alumina piston with a diameter of 15 mm and a 30 mm long partially stabilized zirconia (PSZ) piston was next to them. PSZ is very tough and has high strength and low thermal conductivity, but is not stable at high temperatures, in contrast to Al₂O₃.
The zirconia and alumina pistons had a 1.5 mm central hole, allowing a thermocouple to measure the temperature close to the sample and ensuring the connection to a pore fluid system. If the pore fluid system was opened, this hole remained at ambient pressure during an experiment.

All the assembly was jacketed in the simplest case in a 0.25 mm thick Fe jacket of 15 mm internal diameter, which had been turned down to 10 mm over the specimen and adjacent spacers. The jacket isolated the sample from the confining argon gas medium, thus preventing the build-up of high pore pressures within the sample by argon. However, quartz samples reacted with the Fe to form fayalite. Therefore, in most of the runs, an inner jacket (consisting of 0.025 mm thick foils of Au, Ni and/or Pt) was wrapped around the specimen in order to avoid any reaction. Finally, the bottom and top steel anvil pistons were inserted into the jacket ends. The jacket and the specimen assembly were sealed against the top and bottom steel pistons with O-rings.

Three main technical problems were encountered during the experimental deformation of quartz aggregates: (1) high strength of quartz aggregates under the conditions studied, (2) the difficulty associated with water in the samples and (3) the embrittlement of the specimen jacket. The first problem is especially critical in torsion experiments, since the maximum torque available is limited to that which would cause slip at any of the interfaces between specimen and pistons (about 60 Nm). Different sample assemblies were tested with the aim of reaching higher torque values before slip (see Chapter 7). Also, the assembly preparation had to be elaborated. Higher torques could be achieved if the interfaces of the different parts of the sample assembly were carefully cleaned with ethanol and dried with gaseous N₂ before mounting them together. Any dust particles were removed by this procedure ensuring a higher resistance to slip. Quartz strength is strongly reduced in the presence of water by different mechanisms (see Chapter 3). Several different starting materials with various water content were therefore tested. Ideally, water remains within the sample during deformation if the samples are sealed. This was done by using non-porous spacers on each side of the sample (undrained conditions). However, this setup prevented to reach torque values higher than 10 Nm (corresponding to a shear stress of about 45 MPa for a sample with 10 mm diameter) due to slip at the sample-spacer interface. This can be explained by the increase in pore pressure reducing the effective pressure and therefore the friction at the sample-spacer interface. In torsion, the specimen is loaded by the friction on its end as function of the effective pressure. If the latter is low, high torque values are prevented by slip along the sample-spacer interface. Therefore, a setup was required which allowed some drainage of the sample. For this purpose porous spacers (porosity 20-30%) were placed at each extremity of the sample. With this assembly and the pore pressure valves opened (drained conditions), torque values as high as 60 Nm (corresponding to a shear stress of about 280 MPa for a sample with 10 mm diameter) could be reached.
The embrittlement of the jacket was probably also related to water in quartz: it was found that at shear strains of $\gamma \approx 1.5$, the Fe jacket failed by development of a leak in an area in contact with the sample. It is well known in metallurgy that hydrogen can substantially reduce the mechanical stability of transition metals under tensile stress (‘hydrogen embrittlement’, Beachem, 1977). Therefore, dehydration of the water-rich specimens probably led to diffusion of hydrogen into the Fe jacket, causing embrittlement of the jacket. To solve this problem, different metals for inner jackets (Pt, Ni, Au) were tested. They all are chemically inert and did not react with quartz. Pt has a melting point of 2042 K. In the presence of Fe the melting temperature can be lowered to a minimum of 1246 K. Leak development occurred only at $\gamma = 4$, but it was found that at 1400 K, Pt flowed into cracks and opened grain boundaries within the sample. Therefore, an inner Ni jacket was inserted between the Pt and Fe jackets. Pure Ni has a melting point of 1726 K which is lowered to 1713 K and 1693 K by the addition of Fe and Pt, respectively. By using Pt and Ni jackets, embrittlement was delayed significantly and leakage occurred only at shear strains of about $\gamma \approx 3.5$. For three runs, an Au foil was used as inner jacket. The melting point of pure Au is at 1336 K, in the Au-Fe system the melting point can be lowered to a minimum of 1303 K depending on the amount of Fe present. Leakage of the jacket already occurred at a shear strain of $\gamma \approx 1.2$.

For the fabrication of the synthetic quartz aggregates, the isostatic hot-pressing process was used (see Kingery et al., 1976). The powders (silicic acid, 100 mesh particle size) was first uniaxially cold-pressed. For this purpose, a small amount of powder was inserted in an Fe jacket of 15 mm diameter. The jacket was sealed at the bottom with a steel piston. Cold-pressing was then performed at 200 MPa in a piston-cylinder device producing a pellet of about 20 to 35 mm length and 15 mm diameter. For the hot-pressing procedure, a slightly different sample assembly than the standard one in Fig. 4.2 was used: The sample pellets and the adjacent alumina spacers had a diameter of 15 mm instead of 10 mm. Porous as well as non-porous spacers were used for hot-pressing (see Chap. 7). After hot-pressing, the experiment was either continued as a deformation test or terminated by cooling down and depressurizing. For one of the samples, the Fe jacket was mechanically peeled off after hot-pressing. Afterwards the planar end surfaces of the sample were machined parallel to each other (within ± 5 μm) and oriented exactly perpendicular to the cylinder axis (± 1°) by diamond polishing on a lathe. Then the sample was inserted in a standard sample assembly and used for subsequent deformation experiments.
4.5 Heat-treatment and deformation experiments

After being assembled, the sample column was inserted into the furnace through the top of and within the main pressure vessel. After closing the pressure vessel, the axial deformation piston was advanced until it touched the sample column. The touchpoint could be recognized by a sudden increase in the internal axial load. A maximum load of 0.5 kN was applied. This ensured sealing at the bottom piston at low confining pressures and that there was no gap between the different pieces of the sample assembly. After determination of the touchpoint, the piston was retracted again. The remaining air in the vessel was flushed in order to minimize water condensation and oxidation of the furnace windings.

Pressure was raised to about 250 MPa at room temperature. Then, the furnace was switched on and the temperature was increased automatically at a rate of 20 Kmin\(^{-1}\). The pressure was increased gradually so that the desired temperature and pressure were reached simultaneously. Again the touchpoint for axial load was determined and afterwards the axial deformation piston was retracted at least 0.5 mm from the touchpoint position. This ensured that no load was accidentally applied during twisting of the sample because of potential non-parallelism in the sample assembly.

For a deformation experiment, the sample was left for at least 15 min at the desired temperature and pressure in order to obtain a stable temperature profile. Deformation tests were all performed under constant twist rates.

In some experiments, the torque was released from the samples to correct for any possible drift in the background torque. A maximum drift was 3 Nm h\(^{-1}\).

Before cooling, the touchpoint was often determined again. In theory, this would allow to determine any sample expansion or contraction during preheating and deformation, respectively. In practice, the porous alumina spacers also changed length in a non-reproducible way, probably due to varying microstructural characteristics. Furthermore deformation experiments normally ended with catastrophic failure (leak) making the determination of the touchpoint impossible.

 Cooling from run temperature to room temperature was performed by reducing the currents in the three windings. Room temperature was attained for all of the runs in about 20 min, corresponding to a cooling rate of about 60 Kmin\(^{-1}\). The first increment of cooling was performed at a faster rate (about 100 Kmin\(^{-1}\)) in order to freeze the microstructure of the sample.

A typical PT path of two samples is shown in Fig. 4.3. Also indicated are the isochores of water for 1 g cm\(^{-3}\), 0.5 g cm\(^{-3}\) and 0.3 g cm\(^{-3}\) as a function of pressure and temperature. One of the samples
(P312) was heat-treated at 350 MPa, the other one (P357) at 150 MPa. For most of the experiment, the sample P-T path is well below the water isochore of 1 g cm$^{-3}$. Therefore, in contrast to experiments conducted in solid-medium apparatus, the PT path of the samples in a gas medium apparatus cannot follow the water isochore of 1 g cm$^{-3}$ due to the low pressures used. This had major implications for the porosity evolution of wet polycrystalline quartz aggregates (like Dover flint) as will be discussed in Chapter 5.

After the experiment, the jacket was dissolved in aqua regia (50% hydrochloric acid + 50% nitric acid) or mechanically peeled off. The samples were very fragile requiring immediate impregnation with epoxy. Then they were cut, polished, and analysed using optical microscopy, scanning electron microscopy, and transmission electron microscopy.

![Fig. 4.3 Experimental P-T paths for heating and cooling. The samples were heat-treated at 350 MPa (run P312, solid circle) or 150 MPa (run P357, open circle) prior to deformation at 350 MPa. Cooling path is the same for both runs. The dashed lines are the isochores of water for 1000, 500 and 300 kg/m$^3$ as a function of PT (after Burnham et al., 1969).](image)

### 4.6 Experiments under controlled pore pressure

A few experiments with the pore pressure system mounted were conducted on Dover flint. In order to reach a high resolution, the stroke of the volumometer was reduced to 1.5 mm. The error of the pore pressure gauge was estimated to be around 0.2 MPa. A slight leaking rate in the pore pressure system could never be avoided except in one run (P257). The leaking rate was determined by introducing some argon in the pore pressure system (max. 8 MPa) and measuring the decrease in pore pressure with time.
By recording the pore pressure, the quantity of gaseous fluid released from the sample can be estimated as followed: First, the working volumes of the pore pressure system and volumometer as well as the pores of the spacers at each extremity of the sample have to be estimated (Tab. 4.1).

According to the ideal gas law, the number of moles \( (n) \) at a given \( p, T \) for a gaseous fluid can be obtained from:

\[
n = \left( \frac{pV}{RT} \right)
\]  

(4.1)

where \( p \) is the pressure, \( T \) the temperature and \( R \) the universal gas constant.

The weight of the gaseous fluid is given by:

\[
w = Mn
\]

(4.2)

where \( M \) is the molar mass. If it is assumed that the gas phase is composed of pure water (H\(_2\)O), \( M \) is equal to 18.

By combining (4.1) and (4.2) one obtains

\[
w = \left( \frac{pV}{RT} \right) M
\]

(4.3)

Dover flint contains 1.7 wt.\% H\(_2\)O, corresponding to about 0.03 g for a cylindrical sample of 8 mm length and 4.95 mm radius. If all of the water is released during an experiment, the expected pore pressure can be calculated by rearranging Eq. 4.3 in the following way:

\[
p = \left( \frac{wRT}{VM} \right)
\]

(4.4)

Most of the pore pressure system (volume) is at room temperature. The temperature in the hot zone has a negligible effect on the calculations. Therefore, a temperature \( T \) of 300 K can be inserted in
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Eq. 4.4. The expected pore pressure would therefore be around 9 MPa. However, in all of the experiments the pore pressure never went above 0.8 MPa. This would correspond to only about 0.01 wt% released H$_2$O which is unrealistically low compared to water determinations on the samples obtained from FTIR and/or DTA measurements. The low value of the measured pore pressure can be explained by the following reasons: (1) Not all of the water was released during an experiment probably due to low permeability of the samples. This is confirmed by FTIR and TGA measurements (see chapter 5). (2) Water not only flowed out through the top and bottom of the sample, but also on the sample side through the jacket, probably leading to embrittlement of the jacket by hydrogen.

4.7 Analysis of mechanical data

A data acquisition program recorded during each experiment the radial and axial position, internal and external load and torque, sample temperature, confining pressure and pore pressure. Sampling rates of 30 s intervals were typically used, except during initial yielding of the specimen, where sampling rates of 10 s were used. The information was saved in files which were analysed with Microsoft EXCEL 2000.

The analysis of a sample deformed in torsion is based on the assumption that the deformation along the cylindrical specimen of diameter $d$ and length $l$ is homogeneous at any given radius $r$ and can locally be described as simple shear. The derivations of the calculations are discussed in Handin et al. (1960), Paterson and Olgaard (2000) and Pieri et al. (2001).

The shear strain $\gamma$ at any given radius $r$ is

$$\gamma = \left( \frac{r \theta}{l} \right)$$

(4.5)

where $\theta$ is the angular displacement.

Analogously the strain rate $\dot{\gamma}$ is obtained by

$$\dot{\gamma} = \left( \frac{r \theta}{l} \right)$$

(4.6)

where $\dot{\theta}$ is the twist rate in radians per second.

If it is assumed that the solid cylinder deforms everywhere under the same power law rheology, then the shear stress at maximum radius $R$ is:
\[ \tau_{\text{max}} = \left( \frac{3 + 1/n}{2\pi R^3} \right) M \]  

(4.7)

where \( n \) is the stress exponent and \( M \) the torque applied to the cylinder.

The stress exponent \( n \) can be determined from twist rate stepping tests as the slope of the line in a log-log diagram of \( \dot{\theta} \) versus \( M \) according to:

\[ \log \dot{\theta} = n \log M + \text{const} \]  

(4.8)

The measured torque in the experiments of this study was partitioned between the sample and the sample jackets. The strength of the inner Pt, Ni and Au jackets was negligible. Even if the Fe jacket was very weak, its strength had to be calculated in order to evaluate the true torque supported by the sample. Pure Fe shows two crystallographic phase transitions (\( \alpha \rightarrow \gamma \rightarrow \sigma \)) associated with a sharp discontinuity in flow strength (Frost and Ashby, 1982). For the conditions of this study, Fe is in the \( \gamma \) phase, and the torque supported by the jacket could be calculated using Fe flow laws derived from creep data from Frost and Ashby (1982). In general, jacket corrections at temperatures above 1200 K were less than 5% of the shear stresses calculated from the measured torque.

The stress state in a cylindrical sample subjected to torsion can easily be visualized by the graphical construction of the Mohr diagram (Mohr, 1900). According to Handin et al. (1960) a local Cartesian coordinate system is used in which the y axis is parallel to the cylindrical axis of the sample and the z and x axis are in the circular area with x in tangential and z in radial direction (Fig. 4.4).

![Fig. 4.4 Cartesian coordinate system for a sample subjected to torsion.](image)
The stress tensor is

\[
\begin{bmatrix}
\sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\
\sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\
\sigma_{zx} & \sigma_{zy} & \sigma_{zz}
\end{bmatrix}
\] (4.9)

The stresses \((\sigma_{xx}, \sigma_{yy}, \sigma_{zz})\) are normal stresses acting parallel to the \(x, y, z\) directions, respectively, and the shear stresses (which from now on are denoted with the symbol \(\tau\)) are

\[
\tau_{xy} = \sigma_{xy}; \quad \tau_{yz} = \sigma_{yz} = \sigma_{xz} = 0.
\]

The maximum principal stress \(\sigma_1\) is inclined at +45° to the cylinder axis, and the minimum principal stress \(\sigma_3\) is inclined at -45° to the cylinder axis (Handin et al., 1960). The intermediate principal stress \(\sigma_2\) is parallel to \(z\) direction. In triaxial torsion, \(\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = P \neq 0\). Then \(\sigma_n\) and \(\tau\) across a plane \(F\) can be calculated by (Handin et al., 1960):

\[
\sigma_n = \tau_{xy} \cos 2\theta + P
\] (4.10)

\[
\tau = \tau_{xy} \sin 2\theta
\] (4.11)

where \(\theta\) is the angle between \(\sigma_1\) and the normal to \(F\). In the Mohr circle the horizontal axis is the normal stress \(\sigma_n\), and the vertical axis is the shear stress \(\tau\) (Fig. 4.5A). The centre of the circle lies at \(\sigma_2 = P\). The maximum and minimum principal stresses \(\sigma_1\) and \(\sigma_3\) have values given by the intersection of the Mohr circle with the horizontal axis, the maximum shear stress by the intersection of the circle with the vertical axis. Each point on the circle represents the stress state on a different sample plane.
Fig. 4.5  Mohr diagrams for a cylindrical sample subjected to torsion. Angles are counted clockwise, compressive stresses are positive. A. Triaxial torsion. $\tau_{xy}$ is the shear stress at maximum sample radius; $\sigma_1$ and $\sigma_3$ are the maximum and minimum principal stresses inclined at 45° and 135° to the cylindrical axis, respectively; $\sigma_2$ is the intermediate principal stress in the circular area of the sample. In grey is shown a plane with its stress components $\sigma_n$ and $\tau$. B. Effect of pore pressure. The Mohr circle is shifted to the left without changing the magnitude of the shear stress.

If a pore pressure $p_{pore}$ is applied to the sample, the effective confining pressure is reduced to $p_{eff} = P - p_{pore}$. This shifts the Mohr circle to the left (Fig. 4.5B) without affecting the magnitude of $\tau_{xy}$.

### 4.8 Microstructural characterization

All of the samples were analysed using optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The latter was done by Dr. H. Stünitz (University of Basel). The aims were to determine the grain sizes, the grain size distributions, distribution of water bubbles (pores), the possible presence of other phases (like melt), and the nature of the deformation mechanisms in the deforming samples.

For microstructural analysis of specimens from torsion tests, three principal ways of cutting thin sections exist (Paterson and Olgaard, 2000; Pieri et al., 2001):

1. 'Transverse': Cut perpendicular to the cylinder axis. The shear displacement lies in the plane of the section, and the shear strain, strain rate and shear stress increase radially from the centre.

2. 'Axial': Cut parallel to the cylinder axis through the cylinder centre. The shear direction is normal to the section. Shear strain, strain rate and shear stress increase radially from the centre.

3. 'Tangential': Cut parallel to the cylinder axis close to the outer surface. The shear direction is approximately parallel to the section. Shear strain, strain rate and shear stress are nearly constant.
across such sections. In this study, most of the sections were cut in this way since it gives the standard reference frame used for observations of naturally deformed geological samples.

For optical microscopy, ultra-thin sections (<10 μm) were often required due to the fine grains of the samples. All of the thin sections were polished on both sides. Grain sizes were determined by using the public domain program NIH Image version 1.59 with the macro ‘Lazy grain boundaries’ (Heilbronner, 2000). The input consisted of a set of six polarization micrographs with different orientations of the polarizer-λ plate assembly.

Some SEM observations were performed on broken surfaces with a Hitachi S2300 using secondary electron imaging and on polished surfaces with a CamScan CS44LB using secondary electron images and backscattered electron images, respectively.

Broken surfaces were used for studying the shape of individual grains and pores. Polished surfaces on the other hand were more suitable for examining the presence of secondary phases and the distribution of Riedel shear bands. They could also be used for an estimation of the porosity. Estimated porosities were compared to densities measured by the method described in Pennings and Wolfgang (1989).

Thin sections for TEM were polished on both sides to a thickness of about 20 μm. The sections were examined optically in transmitted light. They were mounted by Dr. H. Stüni (University of Basel) on a TEM grid, ion-beam thinned, and examined using a Hitachi H8000 TEM at 200 KV accelerating voltage. The nature of the deformation mechanisms, the presence and distribution of micropores and the presence of melt were observed.

### 4.9 Texture measurements

Textures give information about the mechanisms by which the samples deformed. Texture determinations were performed by using X-ray texture goniometry, electron backscatter diffraction using a SEM and synchrotron experiments. The latter ones were performed by Dr. F. Heidelbach (University of Bayreuth) at the European Synchrotron Radiation Facility in Grenoble. Texture goniometry and synchrotron experiments provided information on the bulk texture of samples, while electron backscattered diffraction allowed local measurements of a sample texture.

For X-ray texture goniometry, bulk samples with a planar tangential cut were used in reflection geometry. Their dimensions were typically 8*10 mm². They were moulded in plexiglass of 25 mm diameter and mounted in a round sample holder. The measurements were performed on a SCINTAG XDS2000 goniometer with Cu-Kα radiation (0.154 nm), 0.5 mm collimator and a solid
state HPGe-Detector. The Kβ-lines are suppressed without any physical filtering by an energy
discrimination giving high counting rates.

Incomplete pole figures (maximum tilt angles of 60° to 80°) were measured in a 5° raster for 6
diffraction peaks (Tab. 4.2).

Table 4.2 Experimental details of x-ray texture goniometry for the 6 diffraction peaks used in this
study. Indicated are the diffraction angle 2θ, lattice plane indices (hkil) including overlaps, overlap weight, maximum tilt angles and position of the background measured left and right of the diffraction peaks.

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>Cu-Kα</th>
<th>Overlap weight (%)</th>
<th>Tilt stop</th>
<th>Background left</th>
<th>Background right</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.83</td>
<td>10-10</td>
<td>100</td>
<td>60°</td>
<td>18°</td>
<td>23°</td>
</tr>
<tr>
<td>26.64</td>
<td>10-11/01-11</td>
<td>70/30</td>
<td>65°</td>
<td>23°</td>
<td>69°</td>
</tr>
<tr>
<td>36.50</td>
<td>11-20</td>
<td>100</td>
<td>70°</td>
<td>33°</td>
<td>38.3°</td>
</tr>
<tr>
<td>39.43</td>
<td>10-12/01-12</td>
<td>17/83</td>
<td>70°</td>
<td>38.3°</td>
<td>41.5°</td>
</tr>
<tr>
<td>50.14</td>
<td>11-21</td>
<td>100</td>
<td>75°</td>
<td>48°</td>
<td>52.5°</td>
</tr>
<tr>
<td>59.95</td>
<td>21-31/12-31</td>
<td>53/47</td>
<td>80°</td>
<td>58°</td>
<td>62.5°</td>
</tr>
</tbody>
</table>

In texture goniometry, sample statistics are greatly improved by oscillating the samples. However,
due to the small size of the samples used in this study, no sample oscillation could be applied (see
Section 6.1). The measured incomplete pole figures were processed by ODF calculations using
the discrete WIMV procedure (Matthies and Vinel, 1982) and complete pole figures were
recalculated (software Beartex, UC Berkeley; Wenk et al., 1998). A smoothing width of 15° was
typically applied. The two main problems encountered in X-ray texture goniometry were (1) the
small rectangular sample size, and (2) the very weak texture in the samples (see Section 6.1).

For EBSD measurements, axial cuts were used for the heat-treated samples, and tangential cuts
for the deformed samples. For the latter ones, measurements were performed in the central part of
the section to have the shear direction as parallel as possible to the section. Samples were first
ground and polished with diamond-paste down to 0.5 μm. Damages produced during mechanical
polishing were removed by ultra-polishing the samples with SYTON colloidal silica solution
(particle size of 0.025 μm) for 15 hours. This relatively long ultra-polishing time is due to the high
strength of quartz and the very high porosity of the samples making it difficult to obtain a surface
free of damage. Samples were covered by a thin carbon coat and contacted using silver paint. SEM
work was performed with a CamScan CS44LB equipped with EBSD attachment. Samples were
tilted 70° to the incident beam for analysis. Automated as well as manual EBSD measurements
were performed with different scanning step sizes and areas covered. ODF and pole figures were
calculated through Gaussian convolution with a 15° smoothing width within the harmonic
expansion calculus to a maximum expansion degree of L=47 (algorithm HIOR, software Beartex,
UC Berkeley, Wenk et al., 1998).
For synchrotron experiments, thin slabs of about 100 μm thickness were prepared from longitudinal axial cuts. This allowed measuring the evolution of the texture with increasing strain from sample centre to sample edge. The sections were measured in transmission geometry with a monochromatic beam (λ = 0.78 Å) focused to a diameter of 30 μm. The samples were rotated around one axis up to +62.5° in 5° steps with the rotation axis being perpendicular to the axis of the sample cylinder as well as perpendicular to the shear direction. The reflections (Debye Scherrer rings) of up to eight lattice planes were recorded simultaneously with a two-dimensional CCD detector. From the measurements incomplete pole figures were constructed, which were then used to calculate the orientation distribution function (ODF) with the discrete WIMV procedure. Complete pole figures were then recalculated from the ODF, which was additionally smoothed with a Gaussian filter of 15° FWHM in order to reduce single grain effects. The computation of both the ODF and the complete pole figures was carried out with the software package Beartex (Wenk et al., 1998). A detailed description of the texture analysis by synchrotron experiments is given in Heidelbach et al. (1999).

4.10 Estimation of water content

The water content of the samples was determined by using Differential Thermal Analysis (DTA) and Fourier Transform Infrared Spectroscopy (FTIR). FTIR was performed in collaboration with Prof. S. Mackwell and Dr. I. Stretton (Geoinstitut Bayreuth, Germany). DTA was performed by Dr. H. Stünitz (University of Basel, Switzerland) and Dr. S. Köbel (ETH Zurich, Switzerland). FTIR and DTA of the polycrystalline quartz samples provided information about the loss of water during pre-heating and deformation. In addition, FTIR allowed the characterization of the water present in the samples and the comparison with other studies on polycrystalline quartz.

For FTIR, thin slabs of about 100-250 μm thickness were prepared from longitudinal axial cuts polished on both sides with sand paper and diamond paste down to 0.5 μm. Afterwards they were heated at 423 K for 15 min. to remove water introduced during sample preparation and water present in pores and along grain boundaries connected to the surface. The infrared transmission spectra were obtained using an IFS 120HR Bruker Fourier transform infrared spectrometer with attached IR microscope at the Geoinstitut Bayreuth. The IR microscope allowed to examine the sample optically before taking a measurement. All spectra were taken at room temperature at wavenumbers ranging from 4000 to 2000 cm⁻¹. The IR beam diameter was 140 μm wide thus allowing only bulk hydroxyl measurements. Correction of the sloping background was made by subtracting a baseline that was assumed to be linear (Kronenberg and Wolf, 1990).
Hydroxyl content was calculated using the integrated absorption coefficient from 3000 cm\(^{-1}\) to 3750 cm\(^{-1}\) assuming isotropic absorption (Paterson, 1982):

\[
c_{OH} = \frac{1}{I_p \gamma} \int K(\tilde{\nu}) d\tilde{\nu}
\]

where \(c_{OH}\) is hydrogen content in mol H/1, \(I_p\) is the molar extinction coefficient and commonly around 44'000 cm\(^2\) per mol H/1, \(\gamma\) is the orientation factor and can be taken as 1/3, and \(K(\tilde{\nu})\) is the absorption coefficient at wavenumber \(\tilde{\nu}\). For \(\alpha\)-quartz, 1 mol H/1 = 22'679 H/10\(^6\) Si. Therefore, Eq. 4.12 reduces to

\[
\frac{3750}{3000} \frac{cm}{cm^{-1}} \frac{H}{10^6 Si} = 1.546 \int \frac{K(\tilde{\nu}) d\tilde{\nu}}{3750 cm^{-1}}
\]

The results can be regarded as being semi-quantitative mainly due to two effects. First, samples deformed at 1300 K showed more cracking and higher porosity than samples deformed at 1400 K. If the results obtained from FTIR are compared with those of DTA, FTIR gave consistently lower water content, which can probably be attributed to water released from pores during heating. Second, the background in some measurements had a large curving slope due to scattering of the IR beam on grain boundaries and pores. The linear correction may only be regarded as approximation.

For differential thermal analysis, the samples were ground with an agate mortar to a uniform size. They were heated up within 15 min to a temperature of 1340 K and stayed there for 3 min before cooling.

### 4.11 Chemical composition and secondary phase determinations

The chemical composition of the samples was determined by using X-ray fluorescence. Samples were pulverized and analysed at University of Basel with a WD-XRF spectrometer (SRS-3000). Secondary phases were determined with X-ray diffraction and with SEM. For X-ray diffraction, the specimens were ground with an agate mortar to a uniform size and mixed with acetone until a homogeneous paste results. Some of this paste was put on a glass plate and dried. The measurements were performed on an X-ray diffractometer XDS2000 (Scintag, USA). For SEM, bulk samples were cut longitudinal axially and the sections were impregnated and polished. Secondary phases were then detected by scanning with BSE and SE over the section, and
eventually occurring secondary phases were analysed with X-ray energy dispersive spectroscopy (EDS). The measurements were performed with the EDAX Phoenix system on a CamScan CS44LB at ETH Zurich.
5 Heat-treatment and deformation of Dover flint

5.1 Granular flow and Riedel band formation in water-rich quartz aggregates experimentally deformed in torsion*


5.1.1 Abstract

We have investigated the influence of aqueous fluid on the deformation behavior of fine-grained quartz aggregates in the semi-brittle field by deforming wet Dover flint to high shear strains in torsion. Tests were carried out under drained conditions at temperatures of 1250 K and 1300 K, 350 MPa confining pressure and constant twist rate (corresponding to a maximum shear strain rate of $10^{-4}$ s$^{-1}$). Heat-treatment prior to deformation was performed at 1300 K for different amounts of time (1 h to 25 h) at confining pressures of 150 MPa or 350 MPa, resulting in an initial dilation with an isotropic distribution of water-filled pores followed by compaction with continuous reduction in porosity and grain growth. Deformation of the heat-treated samples reached steady-state behavior until a shear strain of $\gamma = 0.2$ followed by sudden hardening stages for shear strain up to $\gamma = 2.5$. Deformation was mainly accommodated within the samples by granular flow. During steady-state deformation, the pores redistributed anisotropically in planes oriented at $\pm 25^\circ$ to the maximum principal stress direction $\sigma_1$. Hardening was associated with the interconnection of pores to form continuous bands in a synthetic R1- Riedel orientation, with no discernible lateral offset along them. These R1 bands served as fluid pathways enhancing local drainage of their surrounding, thus causing hardening by loss of pore pressure. Two samples were unloaded at a shear strain of $\gamma = 1.3$ and 2.5, respectively, and reloaded after 0.5 h at the same deformation temperature and confining pressure. Subsequent deformation occurred primarily by displacement along the existing R1 bands.

Keywords: quartz, experimental deformation, torsion, granular flow, semi-brittle, Riedel structures.
5.1.2 Introduction

Aqueous fluids exert an important control on mechanical properties of rocks through a direct mechanical pressure effect (i.e. Terzaghi's concept of effective stress) and through chemical interactions. Both effects generally weaken the rock mechanically. The chemical effects are by (1) promoting diffusive mass transfer processes and crystal plasticity, and (2) acting as lubricating medium in granular flow [Carter et al., 1990; Kronenberg, 1994]. It is widely believed that fluid overpressure may occur in the Earth's crust [e.g. Fyfe et al., 1978; Etheridge et al., 1984; Hickman et al., 1995], which may trigger brittle failure along a fault plane (earthquake rupture) due to reduced effective normal stress on the fault plane [Byerlee, 1990]. Fault structures in brittle and semi-brittle shear zones may act as highly permeable zones giving rise to fluid release along them immediately after rupture. Fluid-assisted processes like pressure solution and precipitation tend to seal existing fluid pathways resulting again in high pore fluid pressure ('fault-valve behavior' of Sibson, 1990]. These processes are expected to be important especially near the brittle-ductile transition (BDT), when discontinuous brittle faulting and distributed ductile flow occur together (so-called semi-brittle flow; Carter and Kirby, 1978]. Complex interactions of cataclastic, crystal-plastic and mass transfer mechanisms have been observed in natural fault rocks interpreted to have deformed in the semi-brittle field [e.g. Evans et al., 1990; Rutter, 1993; Stöckhert et al., 1999; White, 2001]. Most moderate to large magnitude earthquakes are believed to nucleate in such a regime [Sibson, 1989]. The depth at which the BDT occurs, is probably a function of effective pressure [Sibson, 1990]. The interplay between fluids and deformation in the semi-brittle regime is therefore of great geological and geophysical interest.

The aim of this paper is to study the influence of an aqueous fluid on deformation of quartz aggregates under conditions favoring semi-brittle deformation. We used the torsion technique since it allows (1) non-coaxial deformation and (2) deformation to very high strain [Paterson and Olgaard, 2000]. The geometry of the principal stress directions and possible fracture planes in torsion are shown in Figure 5.1. Deformation anywhere in the sample can be regarded locally as simple shear with the sample-spacer interfaces representing the shear zone boundaries (SZB), and the shear direction is normal to the radius. At these conditions, the maximum and minimum principal stress directions ($\sigma_1$, $\sigma_3$) lie also normal to the radius and at $\pm 45^\circ$ to the cylinder axis and to the shear direction [Handin et al., 1960]. The intermediate principal stress direction ($\sigma_2$) is parallel to the cylinder radius and equal to the confining pressure. Because the kinematic and stress principal axes are not constant over the volume of the cylinder, a potential shear fracture will form a helical surface around the cylinder axis. The surfaces $R_1$ and $R_2$ are oriented at an angle of less than $45^\circ$ to the maximum principal stress (Figure 5.1b, c).
In the present study, we conducted heat-treatment and deformation experiments on microcrystalline quartz aggregates at 1250 K and 1300 K and confining pressures from 150 MPa to 350 MPa. As a starting material we used Dover flint, which is a very pure and homogeneous quartz aggregate with a high water content and no lattice preferred orientation.

![Triaxial torsion of a cylindrical sample](image)

**Fig. 5.1** Triaxial torsion of a cylindrical sample. a) Helical shape of RI Riedel shears in torsion sample. Shaded area represents a part of the section plane where deformation is nearly simple shear. b) Angular relationships of principal stresses and Riedel shear system. (Modified after Petit, 1987). c) Mohr stress circle. Compressive stresses are positive. Dots indicate states of stress for the planes shown in b). R1 = synthetic Riedel shear; R2 = antithetic Riedel shear; X, Y = additional shears; SZB = shear zone boundary; σ1, σ2, σ3 = maximum, intermediate, minimum principal stress; τ5 = shear stress at maximum sample radius; α = fracture plane angle between the trace of R1 and σ1.

### 5.1.3 Experimental and analytical methods

#### 5.1.3.1 Experimental Techniques

All experiments were conducted in an internally-heated Paterson gas-medium (argon) apparatus with torsion capabilities [Paterson and Olgaard, 2000]. The samples had a cylindrical shape with a diameter of 9.9 ± 0.1 mm and a length of 8 ± 0.5 mm. A porous alumina spacer (porosity 20-30%) with the same diameter and a length of 3 ± 0.5 mm was placed on each side allowing drainage of the sample. This assembly (Figure 5.2) was placed between alumina pistons with a 1.5 mm central hole, ensuring venting to the atmosphere and allowing a travelling K-type thermocouple to measure the temperature close to the sample.

Sample and pistons were first dried at 403 K (130 °C) and 1 atmosphere for 24 h. An inner sleeve (consisting of 25 μm thick foil of nickel) was wrapped around the specimen in order to avoid direct contact of iron with the flint and everything was inserted in an iron-jacket tube.
Seven heat-treatment experiments and ten deformation experiments were performed at temperatures of 1250 K and 1300 K (977 °C and 1027 °C) and confining pressures of 150 MPa and 350 MPa (1.5 and 3.5 kbar) (Table 5.1). Immediately after heat-treatment, a torque was applied and the samples were deformed in torsion. The experimental set-up was such that any fluid phase was free to escape from the samples during heat-treatment and deformation (drained conditions, Figure 5.2). The temperature gradient along the sample was estimated during furnace calibration runs to be less than ±2 K. Experiments were terminated by releasing the torque and immediately starting controlled cooling and depressurizing.

After each experiment, the jacket was dissolved in aqua regia (50% hydrochloric acid, 50% nitric acid) or was peeled off mechanically (for samples where water determination was required). Sample dimensions were measured again at room temperature and ambient pressure after the experiments. The torque was converted to shear stress assuming a constant flow law with a stress exponent $n = 1$ through the whole sample [Paterson and Olgaard, 2000]. The P-T path for all samples heat-treated at 350 MPa and at 150 MPa is well below the water isochore of 1000 kg/m³ during most of the experiment (Figure 5.3).
<table>
<thead>
<tr>
<th>Run</th>
<th>Heat-treatment conditions</th>
<th>Deformation conditions</th>
<th>Volume variation(^c)</th>
<th>Water content (^d)</th>
<th>(D_{eq})</th>
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<tr>
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<td>Duration (T)</td>
<td>(T)</td>
<td>(T)</td>
<td>(%)</td>
<td>(wt %)</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>350</td>
<td>1300</td>
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<tr>
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<td>1250</td>
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<tr>
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<tr>
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<td>0.5</td>
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<td>0.5</td>
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<td>6</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>1300</td>
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<td>1300</td>
<td>350</td>
<td>1300</td>
<td>3.5</td>
</tr>
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</table>

\(T\), temperature; \(P\), confining pressure; \(D_{eq}\), average equivalent grain diameter

\(^a\) compared to untreated samples. Positive numbers indicate volume increase

\(^b\) variability due to presence of Riedel bands (see text)

**Table 5.1** List of experiments for heat-treatment and deformation on Dover flint. Confining pressure during deformation was 350 MPa, shear strain rate was \(1 \times 10^{-4} \text{ s}^{-1}\) except during the stepping strain rate test (run P217). Water content, variation in sample volume and average equivalent grain diameter are indicated where available.

**Fig. 5.3** Experimental \(P-T\) paths for heating and cooling. The samples were heat-treated at 350 MPa (run P312, solid circle) or 150 MPa (run P357, open circle) prior to deformation at 350 MPa. Cooling path is the same for both runs. The dashed lines are the isochores of water for 1000, 500 and 300 kg/m\(^3\) as a function of \(PT\) (after Burnham et al., 1969).
5.1.3.2 Analytical methods

Microstructural observations were performed using light microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Thin sections were prepared parallel to the cylinder axis, about 1 mm from the outer surface of the cylinder. In this plane, deformation is nearly simple shear. The shear direction is approximately parallel to the section, and shear strain, strain rate and shear stress are approximately constant across the section. Grain sizes were determined using the public domain program NIH Image on polarized light images from ultra-thin sections. SEM observations were performed on broken surfaces using secondary electron (SE) imaging, and on polished surfaces using secondary electron (SE) and backscattered electron (BSE) images. Thin sections for TEM - foils were polished on both sides. The foils were prepared by ion milling and examined at 200 kV accelerating voltage.

Textures were determined using synchrotron radiation and conventional X-ray goniometry. For synchrotron measurements, thin slabs of about 100 μm thickness were prepared from cuts containing the cylindrical sample axis. Such samples allow the analysis of the texture as a function of shear strain (and shear strain rate) in a radial profile from the centre to the edge of the sample. The measurements were performed on the microfocus-beamline at the European Synchrotron Radiation Facility in Grenoble (France). Incomplete pole figures of eight reflections were extracted from Debye-Scherrer diffractograms taken for several sample orientations and processed by ODF calculations using the discrete WIMV procedure [Heidelbach et al., 1999]. Complete pole figures of c- and a-axes were recalculated using software Beartex [Wenk et al., 1998].

The water content of the samples after the experiments was determined by dry crushing the samples and measuring the weight loss on ignition at 1273 K (1000 °C) for 48 h at 1 atmosphere. An error of +0.02 wt.% may be due to exposure of the crushed samples to air before weighting.

In order to determine the type of water present in the samples, Fourier transform infrared spectroscopy (FTIR) was performed on heat-treated and deformed samples. All spectra were taken at room temperature for wavenumbers ranging from 4000 to 2000 cm⁻¹. The IR beam diameter was 140 μm wide thus allowing only bulk hydroxyl measurements (grain size was < 10 μm).

5.1.3.3 Starting Material

All experiments were performed on flint from the Upper-Cretaceous Chalks of Dover (England). Untreated Dover flint consists of 98.2 wt.% SiO₂ and has a remarkably low impurity content (Table 5.2). The average density is 2.58 g/cm³. Thermogravimetric analyses indicated an initial
water content of 1.3 wt.%. Carbon content was 0.06 wt.%. Accessory minerals including apatite, rutile, calcite, and illite were detected in negligible quantities by X-ray powder diffraction.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
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</tr>
<tr>
<td>Al₂O₃</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe₂O₃</td>
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<tr>
<td>CaO</td>
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<tr>
<td>Na₂O</td>
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</tr>
<tr>
<td>K₂O</td>
<td>0.04</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.06</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.01</td>
</tr>
<tr>
<td>Total</td>
<td>98.22</td>
</tr>
</tbody>
</table>

Table 5.2 Chemical composition of solid components (no volatiles) of untreated Dover flint, major elements determined by X-ray fluorescence. All Fe is recalculated as Fe⁵⁺.

Light microscopy on ultrathin sections and SEM analyses of broken surfaces of untreated Dover flint revealed that it is composed mainly of microcrystalline quartz with a grain size of less than 1 μm (Figure 5.4a). Occasional subeuhedral quartz grains of larger size (up to 30 μm) are dispersed in the matrix but do not account for more than 2 - 3% of the volume. They show no intragranular deformation features. Fibrous silica in the form of radiating bundles of a few microns in size occurs as a minor component. Small pores are abundant with a diameter of up to 1 μm. Texture analysis showed a random lattice preferred orientation of the crystals.

5.1.4 Experimental results

5.1.4.1 Heat-treated samples

Rheological behavior of Dover flint during the deformation experiments is affected by changes in grain size, water content and porosity. These changes were investigated by pure heat-treatment experiments under drained conditions at 1300 K for at least 1 h up to 25 h at confining pressures of 150 MPa or 350 MPa (Table 5.1). SiO₂-rich deposits were found in the pores of the alumina spacers adjacent to the sample indicating that silica rich pore fluid migrated out of the sample.

As in untreated flint, accessory minerals are very minor in the heat-treated samples. TEM observations did not show the presence of any amorphous material. The texture of the heat-treated samples is random.
Heat-treatment of Dover flint caused various microstructural changes (Figure 5.4). All fibrous silica has disappeared. Grains became more equiaxed and increased in size with increasing heat-treatment time (Figure 5.4). The microstructure evolved towards an equigranular structure with straight or slightly curved grain boundaries. Impingement of grains and contact truncations are widespread growth features. There is no evidence for intragranular deformation or grain crushing. For all samples, the grain size histograms (as area percentage) show unimodal distributions with an increase in mean diameter and progressive removal of the fine-grained fraction with duration of heat-treatment (Figure 5.5a). After 25 h, grains smaller than 2 μm no longer existed, and an average grain size of around 9 μm is established, compared to an average of < 3 μm after 1 h of heat-treatment (Table 5.1, Figure 5.4, 5.5).

After 1 h of heat-treatment, very few large (> 40 μm) subeuhedral grains appeared within the fine-grained matrix. With longer heat-treatment they increased in size and number and became euhedral. However, they always accounted for < 4% of the total area. They are referred to as porphyroblasts.
Fig. 5.5 Characterization of starting material after heat-treatment at 1300 K, 350 MPa. a) Grain size distribution of Dover flint, subjected to heat-treatment of 1 h (P247), 6 h (P310), 25 h (P271). b) IR absorption spectra of Dover flint, subjected to heat-treatment for 1 h (P247) and 6 h (P310) (spectras measured at room temperature). c) Changes in grain diameter, sample volume and water content with time during heating up (grey shaded) and subsequent heat-treatment.

In plane polarized light, microscopic opaque dots are visible, especially after long heat-treatment (Figure 5.6). The dots are mainly distributed along grain boundaries and at triple grain junctions. Using TEM, the opaque dots were identified as pores of a size of approx. 0.2 to 1 μm.

Volume changes of samples as a result of the heat-treatment are given in Table 5.1 and Figure 5.5c, together with water content. An increase in sample volume was observed during heating up and pressurizing. The barrelling of a sample heat-treated for 6 h at 350 MPa is shown in Figure 5.7a. When the samples were kept at 1300 K and 350 MPa for 25 h, the volume increase was reduced from around 5.6% (at 0.5 h) to around 0.5% (compared to volume of untreated samples). A decrease in water content occurred from about 1.3 wt.% in untreated flint to 0.18 wt.% in samples heat-treated for 25 h. Total volume increase and water content were higher for confining pressure maintained at 150 MPa than for 350 MPa.

In order to determine the type of hydrogen present in the samples, IR absorption spectra of heat-treated samples were measured at room temperature (Figure 5.5b). The spectra are characterized by a broad band (extending from around 3000 cm^{-1} through a peak at about 3400 cm^{-1}).
Fig. 5.6  Pore distribution in heat-treated and deformed samples after low strain. Samples were heat-treated for 6 h at 1300 K, 350 MPa. Black dots are mainly pores. All microphotos in plane polarized light. a), b) Heat-treated sample (P310). Isotropic pore distribution. c), d) Sample deformed to $\gamma = 0.15$ (P355), steady-state regime. No Riedel bands. Anisotropic pore distribution at $\pm 25^\circ$ to the maximum principal stress direction $\sigma_1$. e) Sample deformed to $\gamma = 0.5$ (P224), beginning of hardening regime. Few Riedel R1 bands (arrows). f) Sample deformed to $\gamma = 0.7$ (P312), hardening regime. Strong Riedel R1 + R2 bands (arrows).

cm$^{-1}$ to around 3700 cm$^{-1}$), which is attributed mainly to various forms of aggregated molecular water [Paterson, 1982] and some surface silanol (Si-OH) groups [Graetsch, 1994]. Most of this water corresponds to small inclusions of H$_2$O in untreated flint [Lange and Flörke, 1974]. The sharp peaks at 3380 cm$^{-1}$ and 3595 cm$^{-1}$ are due to intra-crystalline hydrogen point defects [Kronenberg, 1994]. The peak from 2820 cm$^{-1}$ to 3000 cm$^{-1}$ can be attributed to epoxy used during sample preparation. Most of the hydrogen is therefore present as aggregated molecular
water. The measurements suggest some heterogeneity in the water distribution, the sample rim containing about 10 - 20% less water than the inner sample core.

Most of the compaction and grain growth occurred during the first six hours of heat-treatment (Table 5.1, Figures 5.4, 5.5), and the water distribution appeared rather homogeneous after this time. Therefore most of the samples were deformed after a heat-treatment of 6 h.

![Fig. 5.7](image.png)

**Fig. 5.7** Samples of Dover flint within the iron jacket after torsion test. Spacers visible at top and bottom. Scratches or wrinkles on the jacket were originally parallel to the cylinder axis and serve as strain markers. Triangles and numbers indicate shear strain. Samples were heat-treated for 6 h at 1300 K, 350 MPa (a-e), 150 MPa (f). a) Heat-treated sample without torsion (P356). b) Sample deformed to \( \gamma = 0.15 \) (P355). Steady-state regime. No R1 bands. c) Sample deformed to \( \gamma = 0.5 \) (P224). Beginning of hardening regime. Few R1 bands (arrows). d) Sample deformed to \( \gamma = 0.7 \) (P312). Hardening regime after first steady-state. Well developed R1 bands (arrow). A profile (white line) shows volume decrease across an R1 band. e) Sample deformed to \( \gamma = 3.1 \) (P217). Failure plane developed with lateral offset (arrow). f) Sample deformed to \( \gamma = 1.3 \) at 350 MPa, after a heat-treatment for 6 h at 150 MPa (P357). Steady state regime. Very poorly developed R1 bands.

### 5.1.4.2 Deformed samples: Mechanical behavior

Most of the deformation experiments were performed under drained conditions at temperatures of 1300 K and confining pressures of 350 MPa (in the \( \beta \)-stability field of quartz) at a constant twist rate corresponding to a shear strain rate of \( 1 \times 10^{-4} \text{s}^{-1} \) (Table 5.1). A maximum shear strain of \( \gamma = 3.5 \) was reached in one experiment (P218). The sample P238 heat-treated for 25 h at 1300 K and 350 MPa was too strong, so that deformation was stopped during elastic loading. Sample P357 was heat-treated at 150 MPa and 1300 K for 6 h and immediately deformed thereafter at 350 MPa in order to evaluate the effect of a different porosity on the rheology.
5.1.4.2.1 Low finite strain

Samples deformed to low shear strain ($\gamma = 0.7$) established an apparent steady-state plateau around 100 MPa at $\gamma = 0.2$ followed by a marked strain hardening (Figure 5.8a). The hardening either continued up to the end of the experiment (P220, P312), or it ended with a second peak stress, and subsequent strain weakening of up to 15 MPa to a plateau at higher stress than before hardening (P353, P354).

![Fig. 5.8 Shear stress versus shear strain for (a) low strain and (b) high strain experiments performed at 1300 K, 350 MPa, after 6 h heat-treatment (unless indicated). Shear strain rate was $1\times10^{-4}$ s$^{-1}$. Shear stress-torque conversion assuming stress exponent $n = 1$.](image)

Most samples were at least slightly barrelled after the experiments (Figure 5.7b-f). Scratches on the jacket, originally parallel to the cylinder axis, served as strain markers displaying the amount of shear deformation. No displacement was detected along sample-spacer interfaces, hence all of the deformation was accommodated within the samples. Sample P355 where deformation was stopped during the first stress plateau showed a homogeneous distribution of strain (Figure 5.7b). In contrast, all of the strain-hardened samples exhibited surface relief on the iron-jacket suggesting bands in a synthetic Riedel geometry (Figure 5.7c-e). All of the bands extended up to the sample-spacer interface. Minor shear localization along the bands could be recognized from stronger deflection of the strain marking scratches (Figure 5.7d). The samples shrunk locally along the bands producing grooves along them (Figure 5.7d). The bands were more pronounced and more numerous in samples that underwent continuous hardening (P220, P312) than in those with a second stress plateau. Typically one prominent band was present with "en échelon" sets of less prominent bands around it. In samples where hardening was followed by a second plateau, bands were formed only on one side of the sample (e.g. P353, P354).

A stepping strain rate test was performed in experiment P217 after deformation to $\gamma = 1.3$ (Figure 5.8b). The stress exponent $n$ was derived directly from the slope of the best fitting line in a
log(torque) vs. log(twist rate) diagram (Figure 5.9). The stress exponent (n) is ~2.3 at high stress, and ~1 at low stress.

![Diagram showing log-log plot of twist rate versus internally measured torque M (shear stress conversion assuming stress exponent n = 1 or 3). The slope of the curve gives the stress exponent n.](image)

Fig. 5.9 Stepping strain rate test run P217. Log-log plot of twist rate versus internally measured torque M (shear stress conversion assuming stress exponent n = 1 or 3). The slope of the curve gives the stress exponent n.

One deformation experiment was performed at similar conditions as above, but after a heat-treatment of 6 h at 150 MPa instead of 350 MPa (P357). The heat-treatment at lower confining pressure resulted in a less compacted sample with a higher water content and higher porosity prior to deformation (Table 5.1). During deformation, we measured a peak stress at a shear strain of γ = 0.1, followed by about 20% weakening up to γ = 0.2 (Figure 5.8a). Afterwards, flow stress was steady up to a shear strain of γ = 1.3, with only minor subsequent hardening. Scratches on the jacket indicated that deformation was rather homogeneous, and only very poorly developed bands could be observed macroscopically on the iron-jacket (Figure 5.7f).

A sample deformed at 1250 K after heat-treatment for 6 h at 1300 K and 350 MPa reached a first apparent steady-state at about 130 MPa followed by a strong and continuous strain hardening up to 300 MPa at a shear strain of γ = 0.6 (Figure 5.8a). Shear stresses were therefore considerably higher than in samples deformed at 1300 K.

5.1.4.2.1 High finite strain

Samples P217 and P218 were deformed to shear strains 3 < γ < 3.5 (Figure 5.8b), until the experiments were terminated by jacket failure and loss of the confining medium. In both cases, the samples were temporarily unloaded at intermediate shear strains (γ = 1.7, resp. γ = 2.5) for 10 min (P217) or 30 min (P218). Before unloading, both samples exhibited continuous strain...
hardening. After reloading, the sample P217 showed continuous weakening and sample P218
deformed under a steady state stress.

An inspection of the iron-jacketed samples showed macroscopic failure planes with lateral
displacements along them, which were responsible for the sudden leak (Figure 5.7e). The failure
planes are inclined at about 17° clockwise to the shear zone boundary (sample-spacer interface).
As revealed by the offset of the scratches, a relative displacement (maximum about 0.8 mm) took
place along a main failure plane corresponding to an "equivalent" shear strain of about \( \gamma = 0.1 \) if
this displacement had been accommodated across the whole sample length. Microscopically, we
observed numerous smaller failure planes in the same orientation and with smaller displacements.

5.1.4.3  Deformed samples: Microstructures and texture

5.1.4.3.1  Low finite strain

Distribution of pores

The changes in rheology noticed with increasing strain correlate with a redistribution of pores in
the samples. During the initial apparent steady state deformation (\( \gamma < 0.2 \)), the pores reorganized
from an isotropic distribution after heat-treatment (Figure 5.6a, b) into an anisotropic alignment
along two planar orientations at ±25° off the maximum principal stress direction \( \sigma_1 \) (Figure 5.6c,
d). They make an angle of about 20° respectively 70° clockwise to the SZB and correspond to R1
and R2 orientations in Figure 5.1. Each individual porous region extends in length over a few
grain diameters. Concomitant with the redistribution of pores, the decrease in sample volume
accelerated (Table 5.1).

In all samples where strain hardening started, some of the porous regions interconnected locally
to form prominent bands at low angle (15-20° clockwise, R1-geometry) to the SZB (Figure 5.6e).
These bands correspond to those observed from the outside on the iron-jacketed samples (Figure
5.7). They are widely spaced, and extend over a length of about 1.5 mm inside the samples. The
matrix adjacent to the bands is depleted in pores. From a macroscopic inspection of scratches on
the iron-jacket (Figure 5.7), the sense of displacement is synthetic to the bulk shear. Hence the
orientation and kinematics of the bands is comparable to R1 Riedel structures [Tchalenko, 1970;
Logan et al., 1979] and the bands are called R1, even if there is no noticeable offset along them.
A second set of weaker developed bands is occasionally present at high angles (70° - 80°
clockwise) to the SZB oriented like R2 Riedel shears. Both sets are more numerous and better
developed in samples with a higher hardening rate (e.g. P220, P312) (Figure 5.6f). No bands or
shears developed parallel to the SZB (Y-shears, Figure 5.1). TEM observations confirm that the
R1 bands are zones of higher porosity and grain refinement compared to the matrix (Figure 5.10, 5.11).

Grain size inside the R1 bands is about 1 to 2 \( \mu \text{m} \) (Figure 5.10). The intragranular microstructures are heterogeneous. Very high dislocation densities are observed near grain boundaries in contact with other grains while in other regions the density is very low. No angular fragments, fault gouge with highly variable grain size, or microstructures indicating recovery (subgrains) or recrystallization (new grains) were found.

**Matrix and porphyroblasts**

In all of the samples deformed to shear strains up to \( \gamma = 0.7 \), microstructures in the matrix look similar to those of only heat-treated samples. Grain boundaries of matrix grains tend to be less straight in deformed samples (compare Figure 5.11a with Figure 5.4c). Matrix grains are equiaxed and often exhibit a tabular grain-structure. Their shape anisotropy is lower than the calculated anisotropy, which corresponds to the imposed bulk shear strain. Typically, grain impingement and truncation occur (Figure 5.11a). Some intracrystalline deformation features like deformation lamellae and deformation bands are visible in the larger grains. No evidence of grain comminution was found in the light microscope. Apparently no grain growth occurred during deformation (Table 5.1). On the TEM-scale intragranular cracks are quite common but no displacement could be detected along them, thus excluding fracturing and frictional sliding as the primary strain accommodating mechanism. Dislocation density is strongly variable within and between grains. High densities of tangled dislocations are often observed in conjunction with microcracks and along grain boundaries (Figure 5.11b). Porosity of small size (micropores) is high and in part appears to have formed during the healing of microcracks. No evidence for subgrain boundaries was found (Figure 5.11b, c).

None of the porphyroblasts grown during heat-treatment is cut by a Riedel band, and the formation of Riedel bands is not related to the location of larger porphyroblasts.
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Fig. 5.10  Riedel band microstructure after low strain. TEM bright field micrograph of a R1 band. Sample deformed to $\gamma = 0.5$ (P220). Notice high porosity, small grain size and localized high dislocation density at grain contacts. Inner parts of grains show low dislocation densities.

Fig. 5.11  Matrix microstructure after low strain. a) Microphoto in crossed polarized light. Sample deformed to $\gamma = 0.7$ (P312). Notice equiaxed grains with truncations and grain impingement. The fine-grained pockets are remnants from the starting material. b), c) TEM BF micrographs. b) Sample deformed to $\gamma = 0.5$ (P224). Notice high dislocation density especially at grain contacts and porosity. c) Sample deformed to $\gamma = 0.6$ (P354). Notice high porosity of small pore size (arrows) and tangled dislocations. Micropores occur often along microfractures.
5.1.4.3.1 High finite strain

Riedel structures

The two high-strain samples P217 and P218 show a more complex pattern of Riedel structures than the low-strain samples (Figure 5.12). Once again, the structures are composed of zones of higher porosity. From a macroscopic inspection, there is clear displacement along R1 structures (Figure 5.7e), and these high-strain R1 structures are called R1 shears rather than bands. R1 shears form a pervasive and closely spaced pattern throughout the thin section (Figure 5.12a). They are longer and more discrete than those at low shear strain. They do not have a planar but an anastomosing geometry (Figure 5.12b). Occasionally, curvilinear bands in angles of 40 to 70° clockwise to the SZB crosscut R1 shears. They end with asymptotic deflections into the R1 shears and are comparable to S splay faults (Figure 5.12c). R2 bands with the same appearance as in the low strain samples are present as well. X-cracks also occur occasionally. Both samples P217 and P218 show axial shortening by ~1%. The general appearance of the microstructure is rather similar at different scales (Figure 5.12a-c), suggesting that the deformation processes are not of any characteristic length scale.

Fig. 5.12 Riedel structures after high strain. Black features are mainly pores or cracks. Microphotos in plane polarized light. (a)-(b) Sample deformed to $\gamma = 3.5$ (P218). a) Overview of Riedel array. b) Anastomosing R1 shears. c) Sample deformed to $\gamma = 3.1$ (P217). Notice S splay shear in central part of image.
In the TEM the R1 shears are identical as the R1 bands of the low strain samples. They are zones of high porosity and with smaller grain size of around 1 - 2 μm with a narrow spread in the grain size distribution. No fault gouge or recovery microstructures were observed.

**Matrix and porphyroblasts**

In both high strain samples P217 and P218, matrix grains show a weak shape preferred orientation (SPO) with elongation towards the minimum principal stress $\sigma_3$ (Figure 5.13). The grain shape is far more isotropic than the aspect ratio of the finite strain ellipse derived from the imposed shear strain. Grain boundaries are lobate. Grain sizes are larger than in low shear strain samples with an average around 9 μm. TEM observations showed numerous tangled dislocations along grain boundaries. Dislocation density is more homogeneous than in the matrix of low shear strain samples.

The same amount of porphyroblasts is present as in the low strain samples. EBSD measurements of the large grain size fraction (>20 μm) did not show any lattice preferred orientation in the porphyroblasts.

![Matrix microstructure after high strain](image.jpg)

**Fig. 5.13 Matrix microstructure after high strain. Microphoto in crossed polarized light. Sample deformed to $\gamma = 3.5$ (P218). Notice spurious grain elongation towards $\sigma_3$. Grain shape is much more equiaxed than the strain ellipse of this sample.**

**5.1.4.3.1 Texture development**

The lattice-preferred orientation (LPO) of a heat-treated sample and a sample deformed to high shear strain are shown in Figure 5.14. At a shear strain of $\gamma = 0$, the texture is very close to random. At a shear strain of $\gamma = 0.2$, an oblique c-axis girdle opposite to the sense of shear starts to develop, and remains in the same position during deformation to larger strain. The c-axes maximum is oriented at about 25° to $\sigma_1$ and 70° clockwise to the SZB. The a-axes [11-20] (and also prism m-poles (10-10)) form girdles perpendicular to the c-axis maximum, i.e. ∼20° oblique to the SZB
(Figure 5.14). With increasing shear strain, the texture becomes a little more pronounced but remains weak (texture index $J = 1.06$ for $\gamma = 3.3$). Several texture measurements on other samples using small collimator X-ray texture goniometry verified the general trend in the LPO development. The quantitative details vary somewhat, but are very difficult to define for such weak textures.

![Polefigures of heat-treated sample and sample deformed to high strain. Orientation densities in multiples of random distribution (m.r.d.) in logarithmic scale, upper hemisphere, equal area projections with smoothing width 15°. Texture index $J$ is indicated for the overall textures (based on ODF). Minima and maxima of density are indicated at the bottom of each pole figure. Horizontal line in pole figures represents trace of shear direction and shear zone boundary.](image)

5.1.5 Discussion

5.1.5.1 Compaction during heat-treatment

Heat-treatment of Dover flint samples at high temperatures and pressures resulted in (1) a continuous decrease in water content, (2) an initial increase in volume during heating up (under pressure) followed by a continuous volume decrease during heat-treatment (nearly to the original volume), and (3) substantial grain growth.

After 6 h at high temperature and pressure, water content decreased to less than a quarter of that in untreated flint. Nevertheless, even after 25 h of heat-treatment, a considerable amount of water was still present in the samples (Table 5.1). Percolation tests after the experiments showed that porous spacers placed next to the samples retained their permeability. Therefore, the rate at which water leaves the assembly is probably determined only by the permeability of the sample itself and the rate of grain growth. The observation that water content is more reduced at the sample rim than
in the inner core suggests that permeability within the sample is low and that fluids can migrate faster along the sample-sleeve interface. This has major implications for the porosity evolution within the samples: The increase in volume of the samples during heating up under pressure is related to the build-up of a high pore pressure. As the PT-path was mostly below the water isochore of 1000 kg/m$^3$ during heating up under pressure (Figure 5.3), molecular water in the pores expanded. If pores are completely filled with water and drainage is slow due to low connectivity of pore space, a fluid overpressure occurs, resulting in loosening of grain boundaries and sample dilatancy. At lower confining pressures (150 MPa) the specific volume of water is even higher and a more pronounced increase of the sample volume occurred than at 350 MPa. The expansion stops as soon as the experimental conditions are reached. Pore pressure is then controlled by the balance between porosity reduction by compaction and finite drainage rate. We believe that the aggregated molecular water observed in IR spectra is mainly stored within the microscopic pores visible as black dots along grain boundaries in transmitted light (Figure 5.6a, b). Our assumption that the pores are filled with water is supported by the fact that the pores did not collapse during heat-treatment under confining pressure. The observed sample dilation must be caused by a pore pressure exceeding the confining pressure. The porosity of the samples at the experimental conditions was estimated using a specific volume of water of 0.002 m$^3$/kg [Burnham et al., 1969] at the PT conditions applied here yielding a porosity of about 3% (0.9%) after 1 h (25 h) of heat-treatment at 1300 K and 350 MPa.

Porosity reduction in diagenetic and tectonic settings may occur through mechanical compaction associated with brittle processes and/or plastic deformation of grains, or through dissolution-precipitation processes [De Boer et al., 1977, David et al., 1994]. In this study, no evidence for cataclastic processes like angular grain shapes or large grain size ranges was found. Also, intracrystalline deformation features are rare. Instead, grain coarsening by removal of the finest grain size fractions as well as interpenetration of grains and contact truncations suggest that diffusive mass transfer processes were dominant (Figure 5.4b-d). This interpretation is consistent with several studies that showed that compaction creep involving dissolution-precipitation processes in quartz aggregates are enhanced at high temperature in the presence of water [Cox and Paterson 1991; Schutjens, 1991; Lockner and Evans, 1995]. In fact, using equation (2) of Fournier and Potter [1982], the solubility of quartz in water at the temperature used in this study was calculated to be as high as 4 wt.%. In summary, compaction creep in our samples occurs mostly by diffusive mass transfer processes during the heat-treatment, accompanied by water loss and grain growth.
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5.1.5.2 Deformation mechanisms in deformed samples

5.1.5.2.1 Low finite strain

In samples deformed up to $\gamma = 0.7$, shear strain was homogeneously accommodated in the matrix. Compaction still continued, indicated by a further decrease in sample volume. In the following, we discuss several pieces of evidence suggesting that deformation occurred primarily by granular flow. Granular flow involves mainly the relative movement of rather rigid grains. Important deformation accommodating mechanisms are diffusive mass transfer and grain boundary sliding, and to a lesser extent intracrystalline deformation [Ashby and Verrall, 1973; Paterson, 1995]. Fracturing of grains is another accommodation mechanism [Milliken, 1994].

Microstructures in our samples show that cataclasis and intracrystalline plasticity can be excluded as dominant deformation mechanisms here. We observed no evidence for any of the typical features produced by cataclastic deformation [Stünitz and Fitz Gerald, 1993], such as crushing of grains and displacements at fractures (Figure 5.11b, c). The narrow grain size distributions are very similar in deformed and in only heat-treated samples, suggesting that cataclasis was negligible. Similarly, only very few features document intracrystalline slip. The heterogeneous dislocation density and the absence of recovery features indicate little dislocation glide but no creep. Thus, dislocation creep is not the dominant strain accommodating mechanism. In addition, grains have equant shapes and show an aspect ratio close to 1.0, a value that does not match the imposed high bulk strain. The development of a non-random LPO is typically used as an indication for dislocation glide and creep. However, the textures in our samples are close to random even at high strains. The low texture index corresponds to only 2-4% of the grains having a preferred orientation, and 96 - 98% of the sample volume occupy random orientations. Deformation experiments of flint in the dislocation creep field (at 1173 K, 1.0 - 1.2 GPa and $10^{-5}$ s$^{-1}$), indeed produced a strong texture at 48% shortening (corresponding to a shear strain of $\gamma = 1$; Gleason et al., 1993). On the other hand, granular flow should not produce any lattice preferred orientation [e.g. Padmanabhan and Davies, 1980]. We therefore attribute the weak but clearly developed textures to either a very minor component of intracrystalline plasticity in the bulk rock or to fluid-enhanced oriented growth. It is also possible that some grains were passively reoriented due to a grain shape weakly correlated with the crystallographic lattice, with a habitus of preferably low-index crystallographic planes.

While cataclastic deformation and intracrystalline plasticity may be excluded, the following observations point to granular flow accommodated by diffusive mass transfer and grain boundary sliding as the dominant deformation mechanism.
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Sliding of grains relative to each other is facilitated by the relatively high porosity of our samples, and the high water content, which may form a lubricating film along grain boundaries thus enhancing sliding. The tabular grain structure with grain boundary bulges is characteristic for a cooperation of grain boundary sliding and migration [Urai et al., 1986; Drury and Humphreys, 1988]. We emphasize that we did not observe any amorphous material or any other evidence for melt.

Diffusive mass transfer is promoted by the small grain size in our samples and the high temperatures of the experiments. It is documented by grain impingement and truncation as well as by equiaxed grains up to high shear strain.

The measured values of shear stresses do not fit with existing flow laws for intracrystalline plasticity [e.g. Luan and Paterson, 1992; Gleason and Tullis, 1995] and diffusive mass transfer [den Brok, 1992]. Instead, the stress data are consistent with estimates given by the model of Paterson [1995] for granular flow (theoretical stress exponent \( n = 1 \)) where the dissolution or precipitation of material takes place at grain interfaces and pores. The derived stress exponent at high stress (\( n \approx 2.3 \)) is ambiguous: we do not know how strongly the shear stress was affected by the formation of R1 and R2 bands. As will be discussed in the following, we believe that R1 bands and the regions adjacent to them represent mechanically stronger volumes than the rest of the samples. Thus, strain heterogeneity may imply that the stress exponent for the matrix is lower than 2.3.

5.1.5.2.2 High finite strain

In the high shear strain samples after un- and reloading, strain was primarily accommodated along the R1 shears. In the matrix, the weak SPO with elongation at 45° anticlockwise to the SZB is qualitatively consistent with but quantitatively does not correspond to the imposed bulk shear strain. Furthermore, both high strain samples show the same SPO although they were not deformed to the same shear strain. In addition, there was a substantial increase in grain size compared to low shear strain samples. We conclude that this SPO is due to preferred growth along the minimum principal stress \( \sigma_3 \) [Karato and Masuda, 1989].

5.1.5.3 Development of "Riedel" structures and shear strain accommodation

Microstructures of the deformed samples show a distinct evolution with shear strain. The most striking feature is the spatial distribution of pores, which are believed to be filled with water.

We interpret the formation of R1 and R2 bands at low shear strain to be due to migration and interconnection of the water-filled pores while the total pore volume slightly decreased. After
heat-treatment, water distribution was isotropic and water resided within isolated pores mostly along grain boundaries and at triple junctions. With the onset of deformation, water flows towards dilatant grain boundaries in R1 and R2 orientations while other pores become more compressed and close. After some deformation pores interconnect to form continuous porous bands in R1 orientation extending all the way from the bottom to the top of the sample. With increasing shear strain, new R1 bands develop and grow until they become pervasive. In a similar way, R2 bands form by coalescence of pores at high angle (70 - 80° clockwise) to the SZB. They did not become as pervasive as R1 bands, maybe due to geometrical constraints imposed by rigid boundary conditions. At shear strain of $\gamma = 0.7$, numerous throughgoing R1 bands and fewer R2 bands are present. It is important to note that very little or virtually no displacement occurred along the R1 bands at low strains.

An anisotropic redistribution of water has been described in studies on quartz aggregates [den Brok et al., 1994], partially-molten granite [van der Molen and Paterson, 1979], fine-grained quartz aggregates [Karato and Masuda, 1989], fine-grained feldspar aggregates [Tullis et al., 1996] and analogue materials [norcamphor, Bauer et al., 2000]. Except for the feldspar aggregates, where all of the grain boundaries dilated, fluid always aligned along planes oriented parallel to the principal stress direction $\sigma_1$. In contrast to these studies, we observe an alignment of pores at $\pm 25^\circ$ off the principal stress direction $\sigma_1$ in a R1 and R2 geometry.

Unloading and short annealing of the samples have a profound effect on their subsequent deformation behavior. After reloading, existing R1 shears, which formed in the low shear strain regime, are reactivated and develop into shear zones with discernible displacement along them. However, the rigid boundaries (spacers) of the experimental set-up and the torsion geometry restrict large displacements along them. As a result, displacement is not concentrated along one single shear but along multiple ones.

In frictional sliding experiments on quartz gouges, the formation of boundary-parallel shear surfaces (Y-shears) is typically observed after large strains [e.g. Logan et al., 1992; Gu and Wong, 1994]. Mandl et al. [1977] argued that in experiments in a ring shear apparatus, displacement along R1 shears stop after some amount of strain and Y-shears form because of the rigid boundaries. Despite the relatively high shear strains attained in the frictional regime (up to $\gamma = 1.3$ after reloading) in our study, no Y-shears were observed even though such a boundary-parallel plane may be predestined to accommodate displacement in a torsion geometry. Instead, R1 shears become anastomosing. A possible explanation is the space available for shear surfaces to develop [Logan et al., 1992]. Typical shear experiments are conducted on a few millimetres thick gouges. As a consequence, only a limited number of R1 shears can form. In our experiments, samples are
about 8 mm long with more space available for shear surfaces to form. In the high shear strain samples (P217, P218) we estimate the total number of R1 shears to be in the order of several hundred. Accommodation of displacement by reorientation of R1 shears can therefore occur on numerous planes. The reorientation is achieved by an anticlockwise external rotation (about 15°) of the shears towards the SZB. Since R1 shears penetrate right to the sample-spacer interface and no displacement between spacers and sample has been observed (Figure 5.7), the displacement on R1 shears stops at this interface and must result in an external rotation of the R1 shears. Laboratory studies suggest that boundary-parallel Y-shears are the dominant movement planes only after larger displacements forming a steady-state fracture array [Logan et al., 1992]. Due to jacket failure, we could not test whether the externally rotated R1 shears would develop into Y-shears with increasing strain. It is possible that deformation in our experiments was not large enough for Y shears to develop and that the microstructure does not represent a steady-state condition.

5.1.5.4 Mechanical behavior

The rheological behavior of our samples can be closely related to the microstructural changes during deformation. During incipient steady-state flow, deformation is distributed throughout the aggregate matrix. Strain hardening is correlated with the formation of highly porous R1 bands and a depletion of pores in the matrix adjacent to the bands. Samples exhibiting continuous strain hardening developed numerous R1 bands visible everywhere in the sample. In contrast, samples exhibiting a second steady-state plateau show prominent R1 bands only on one sample side. Most of the strain is accommodated in the matrix by granular flow.

We explain strain hardening as follows: permeability strongly increases with the coalescence of pores along highly porous water-filled R1 bands (Figure 5.15a). This provides fast pathways for water to escape into the spacers (Figure 5.15b). Water drainage from the matrix adjacent to the R1 bands, due to pore fluid pressure gradients, leads to local water depletion in narrow volumes adjacent to each R1 band [Rosenberg and Handy, 2000; Bauer et al., 2000]. The water depletion is accompanied by reduction in volume along the R1 bands. Since granular flow is strongly dependent on effective pressure [Paterson, 1995], the decrease in pore fluid pressure and increase in effective pressure in the drained volume leads to overall strengthening of the material. Concomitant with drainage, pore pressure within the R1 bands drops resulting in a higher effective normal stress on the R1 surfaces, which prevents any displacement along them. It is speculated that some of the observed jumps in sample strength are correlated with the formation of the more pronounced R1 bands. R1 bands therefore serve as highly permeable fluid channels that allow drainage of the adjacent matrix, but do not localize deformation. As deformation continues, new
R1 bands develop away from existing ones. This continuous process results in progressive strain hardening. It is also likely that R1 bands and their surrounding with lower porosity represent obstacles for granular flow. By contrast, in samples exhibiting a second apparent steady-state flow stress, only a limited number of R1 bands develop during hardening. Deformation in the matrix continues by granular flow but at a higher stress level resulting from material hardening due to a decreased water content.

Fig. 5.15  Schematic drawing of fluid drainage along an R1 band. a) Water-filled pores (black) interconnect to form an R1 band. b) The highly permeable R1 band serves as a pathway for fast water drainage, and the region adjacent to the R1 band becomes rapidly depleted of water and compacted. Inserted microphoto (from sample P312) in plane polarized light (black dots are mainly pores).

After heat-treatment at 150 MPa porosity was higher than at 350 MPa. Sample P357, heat-treated at 150 MPa and deformed to $\gamma = 1.3$, did not show strain hardening and nearly no Riedel bands formed. Therefore, we speculate that coalescence of pores into R1 bands is related to a specific value of sample porosity as proposed by Lambe and Whitman [1968], Marone and Scholz [1989], Wong [1990] and Kanagawa et al. [2000]. The orientation of R1 bands in our samples is in accordance with the Coulomb criterion for shear fractures forming along planes containing the intermediate principal stress axis $\sigma_2$ and at fracture angles of $\pm 20^\circ < \alpha < \pm 30^\circ$. This suggests that pore pressure during formation of the R1 bands was higher than the minimum principal stress direction $\sigma_3$ [Sibson, 1996]. However, we believe that pore pressure gradients may be present in the deforming samples due to low permeability and closed pores. Compaction may lead to overpressurization of the pore fluid with respect to $\sigma_3$ in some parts of the sample with subsequent microcracking in a Riedel orientation. The sample heat-treated at 150 MPa did not compact enough for pore fluid overpressurization and consequently no R1 bands formed.

Kanagawa et al. [2000] performed experiments on porous synthetic quartz gouges at 1200 K, 300 MPa confining pressure and 200 MPa pore water pressure. They observed two different types of
mechanical and microstructural behavior: slip hardening with distributed deformation along numerous R1 bands and slip softening with localization of deformation along the gouge-forcing block interface. In slip-hardened samples, compaction and granular flow led to an increase in number of grain-to-grain contacts and in the load-bearing contact area, resulting in continuous increase in gouge strength. The slip-softened samples became overcompacted and too strong to accommodate distributed shear strain and slip localization with concomitant softening occurred. Both types of behavior were rate-controlled by cataclasis. The fabric produced by the R1 bands in our samples is comparable to the one in the slip-hardened samples of Kanagawa et al. [2000], but we believe that hardening in our experiments is due to rapid fluid escape. In our study pore pressure was not kept constant and formation of R1 bands led to rapid drainage resulting in a hardened matrix adjacent to R1 bands. In contrast, Kanagawa et al [2000] maintained a constant pore pressure in the samples, and their rheology should therefore not be affected by varying pore pressure. In addition, our study was conducted at higher temperatures where diffusive mass transfer processes rather than cataclastic processes were probably rate-controlling in the matrix.

We do not fully understand why unloading and reloading of high strain samples trigger strain localization along existing R1 bands. One explanation may be that microcracks may open along the R1 bands due to stress relaxation with unloading. However, crack healing may also be active and prevent or slow down fluid drainage along R1 bands. Fluid redistribution may lead to increased pore pressure in some parts of the R1 bands and therefore to reduced effective normal stress on the R1 surfaces. Hence, the R1 bands may then represent zones of weakness, and may be activated as soon as the shear stress acting on their surfaces reaches the condition for frictional sliding according to Byerlee's law.

5.1.6 Summary and conclusions

Major changes in water-filled pore distribution and permeability occur during deformation of heat-treated Dover flint in torsion (Figure 5.16). After heat-treatment, water-filled pores are distributed homogeneously and isotropically (stage 0). With the onset of deformation, the pores redistribute along dilatant grain boundaries aligned at ± 25° to the maximum principal stress direction σ₁, i.e. at about 20° and 70° clockwise to the SZB (stage I). The material temporarily exhibits a steady-state behavior and bulk rock permeability is low. The Mohr stress circle (representing the stresses of the bulk sample) represents a reduced effective stress because of pore pressure. When pores interconnect to form throughgoing R1 bands or less numerously R2 bands (stage II), they serve as highly permeable fluid channels. Water adjacent to the R1 bands quickly drains along them, which results in local water depletion in a narrow volume around each R1 band.
The decrease in pore pressure and increase in effective pressure leads to local strengthening around the R1 bands, and following of the overall material. Deformation does not localize along the R1 bands due to a higher effective normal stress in the drained R1 bands. Instead, strain continues to be accommodated within the matrix by granular flow with diffusive mass transfer and grain boundary sliding. The sample strain hardens as more R1 bands develop and more matrix volume gets drained, which is illustrated by the growing Mohr stress circle shifting towards higher effective pressures.

Unloading and subsequent deformation of the samples induced localized slip along existing R1 band, as soon as the growing Mohr stress circle touches the friction envelope (stage III). Due to geometrical constraints by the rigid boundaries of the experimental set-up, displacement occurs with external rotation of the R1 shears, producing an anastomosing geometry of Riedel surfaces. The concomitant occurrence of a brittle (interconnection of pores into Riedel bands by microcracking) and a ductile deformation mechanism (granular flow) indicates that deformation in our samples occurred in the semi-brittle field according to the terminology of Rutter [1986].

Our results on wet polycrystalline quartz samples are in agreement with recent laboratory studies on analogue materials that showed the importance of overpressurized fluids for the development of interconnected fluid pathways with high permeability along them [Bauer et al., 2000; Streit and Cox, 2002]. It was shown that the changes in pore fluid distribution with increasing strain have major implications for the permeability and strength of rocks deformed in the semi-brittle regime.
Fig. 5.16  Idealized schematics of porosity evolution and mechanical behavior with increasing shear strain. Six boxes (top) show strain-dependent change in microscopic pore distribution (pores are represented as black dots and lines). Typical stress-strain curve (middle) as obtained from run P218. Four Mohr stress circles (bottom) indicate the sample strength with changing pore pressure. See text for further explanation. $P = \text{confining pressure}$, $P_{\text{eff}} = \text{effective pressure}$, $p_{\text{pore}} = \text{pore pressure}$ (in $M = \text{Matrix}$ and $R = \text{Riedel band}$), $D = \text{immediately after heating up under pressure (dilation)}$, $C = \text{later during heat-treatment (compaction)}$, $S = \text{slip along R1 shears}$. 
5.2 Further experiments on Dover flint performed at 1300 K

5.2.1 Introduction

Here are described four torsion experiments (three of them performed with an inner sleeve of gold and one under undrained conditions) performed on Dover flint at 1300 K with slightly different sample assemblies than previously. They have not been included in the previous section (paragraph 5.1), because one believes that their rheological behaviour was strongly influenced by the experimental set-up.

5.2.2 Experiments performed with an inner sleeve of gold.

For most of the experiments at 1300 K, an inner sleeve consisting of 25 μm thick foil of nickel was wrapped around the specimen in order to avoid any direct contact of iron with quartz where fayalite would form (see paragraph 5.1). At shear strains of $\gamma \sim 3.5$, the jacket failed near the sample. Hydrogen can substantially reduce the mechanical stability of transition metals under tensile stress ('hydrogen embrittlement', Beachem, 1977). Therefore, we believe that dehydration of the water-rich flint specimens led to diffusion of hydrogen into the sleeve and jacket, causing embrittlement of both.

To solve this problem, experiments were performed with an inner sleeve of gold. The gold sleeve consisted of a 100 μm thick foil, which was wrapped around the sample. The melting point of pure gold is at 1336 K, in the gold-iron system the melting point can be lowered to a minimum of 1303 K depending on the amount of iron present. The gold was assumed to be so viscous at the deformation conditions used in this study that it might diffuse into microcracks of the iron jacket and delay therefore leakage during deformation.

Three experiments were conducted under drained conditions using a gold sleeve after 6 h of heat-treatment at 1300 K, 350 MPa (Tab. 5.3). One of them (P269) was terminated by a leak before the deformation conditions were reached, the other two samples (P270, P279) were deformed under drained conditions at 1300 K, 350 MPa and a strain rate of $1 \times 10^{-4}$ s$^{-1}$.

In contrast to the samples with a nickel sleeve, those with a gold sleeve did not exhibit any longer apparent steady-state plateaus at low shear strain but rather continuous hardening (Fig. 5.17). P279 showed sudden weakening by 10% at about $\gamma = 1.3$ followed by a steady-state plateau up to $\gamma = 1.9$, where the experiment was terminated by jacket failure at the sample-spacer interface.
Table 5.3  List of torsion experiments on Dover flint using an inner sleeve of gold. Confining pressure was 350 MPa, strain rate was $1 \times 10^{-4}$ s$^{-1}$.

<table>
<thead>
<tr>
<th>Run</th>
<th>Heat-treatment time (h), T (K)</th>
<th>Deformation-T (K)</th>
<th>$\gamma$</th>
<th>Volume increase$^a$ (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P269</td>
<td>1280</td>
<td>-</td>
<td>-</td>
<td>5.2</td>
<td>leak</td>
</tr>
<tr>
<td>P270</td>
<td>6, 1300</td>
<td>1300</td>
<td>0.6</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>P279</td>
<td>6, 1300</td>
<td>1300</td>
<td>1.9</td>
<td>?</td>
<td>slip at sample-spacer interface</td>
</tr>
</tbody>
</table>

$^a$ compared to untreated samples  ? – not available

Fig. 5.17  Shear stress versus shear strain for experiments with a gold sleeve performed at 1300 K, 350 MPa, 6 h heat-treated. Shear strain rate was $1 \times 10^{-4}$ s$^{-1}$. Shear stress was calculated from the measured torque assuming a power law creep with stress exponent of $n = 1$.

A macroscopic examination of the iron-jacketed samples showed that they were slightly barrelled, but no synthetic shear bands of a Riedel geometry were detected (Fig. 5.18). P279 revealed a displacement (slip) of the strain marking scratches at the top sample-spacer interface, indicating that not all of the deformation was taken up by the sample. In fact, the deflection angle of the strain marking scratch on the sample indicates a shear strain of $\gamma \approx 1.3$ (Fig. 5.18b). The microstructure of P270 and P279 shows a similar pore distribution like in the low strain samples with a nickel sleeve (e.g. P220, P312): R1 as well as R2 bands are very well developed (Fig. 5.19). R1 bands occur at 15 - 20°, R2 bands at 70 - 80° clockwise to the SZB. Additionally, in P279 X cracks at high angle (110 to 140°) to the SZB exist (Fig. 5.19b), just like in the two other high strain samples P217 and P218.
Fig. 5.18  Samples of Dover flint after torsion test within the iron jacket. Scratches or wrinkles on the jacket were originally parallel to the cylinder axis and serve as strain markers. Triangles and numbers indicate shear strain. Samples were heat-treated for 6 h at 1300 K, 350 MPa. a) Sample deformed to $\gamma = 0.6$ (P270). b) Sample deformed to $\gamma = 1.9$ (P279). Sample-spacer interface at top with large frictional displacement. The strain marking scratch indicates that the sample accommodated a shear strain of $\gamma \approx 1.3$.

The matrix microstructure of P270 and P279 is very similar to that observed in low strain samples with a nickel sleeve. Despite similarities between the two different sample assemblies (gold vs. nickel sleeve), there is one main difference in the resulting microstructures between them: the two experiments with a gold sleeve (P270, P279) show an about 400 $\mu$m wide rim depleted in pores (Fig. 5.20).

Fig. 5.19  Pore distribution in samples after low strain in torsion at $1 \times 10^4 \text{s}^{-1}$. Samples were heat-treated for 6 h at 1300 K, 350 MPa. Black dots are mainly pores. a) Sample deformed to $\gamma = 0.6$ (P270). b) Sample deformed to $\gamma = 1.9$ (P279).
Discussion

The rheology and microstructure for both types of sample assemblies (gold vs. nickel sleeve) are comparable. Therefore the same mechanisms were probably active in both: the sudden hardening stages are associated with the development of R1 bands and concomitant fluid loss along them. There was no displacement along the R1 bands, but deformation was mainly accommodated in the matrix by granular flow. The fact that the R1 bands visible in thin sections (Fig. 5.19) are hardly visible macroscopically on the iron-jacketed samples (Fig. 5.18) can be explained by the thicker and more viscous gold foil, which was probably filling out the relief of the R1 bands on the sample surface. It is likely that the steady-state stress from \( \gamma = 1.3 \) to 1.9 in P279 is due to slippage on the sample-spacer interface since the amount of shear strain during the steady-state corresponds to the macroscopically visible amount of displacement along the interface. The main striking difference is therefore the absence of pronounced steady-state stress plateaus at low shear strain and the general high flow-stress level in samples with a gold sleeve.

One has to keep in mind that at 1300 K gold was close to melting (see paragraph 5.2.2), therefore many crystal defects were probably present in its lattice allowing fast diffusion pathways for the fluid to escape the sample. This may explain the presence of a zone depleted in pores adjacent to the sample rim (Fig. 5.20). The progressive depletion in fluid adjacent to the rim may explain the absence of pronounced steady-state stress plateaus at low shear strain: since most of the torque in torsion is supported by an outer fraction of the sample radius, progressive loss of fluid may lead to increasing sample strength. This may have masked the steady-state stress plateaus before the sudden hardening stages related to the formation of R1 bands.

Fig. 5.20  Pore distribution in P270. Note depletion in pores in a zone adjacent to the sample rim. Sample section parallel to cylinder axis and to radius.
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In summary, there were two main disadvantages by using an inner sleeve of gold: (1) fluid distribution was probably more heterogeneous than in samples with an inner sleeve of nickel. (2) With the early development of R1 bands and drainage of the samples, the shear stresses at a shear strain of $\gamma = 1.3$ were already so high, that slip occurred at the sample-spacer interface. Therefore, no testing was possible if leakage due to embrittlement of the iron jacket at high shear strain could be prevented by using gold as a sleeve material.

### 5.2.3 Undrained experiment

In order to test the influence of water content on the deformation behaviour of Dover flint at 1300 K, one experiment was performed under undrained conditions, i.e., by using non-porous spacers (see Chap. 4). Deformation was at 1300 K, 350 MPa and a strain rate of $1 \times 10^{-4}$ s$^{-1}$ (Tab. 5.4) after a heat-treatment (again undrained) of 1 h at the same conditions.

#### Table 5.4

<table>
<thead>
<tr>
<th>Run</th>
<th>Heat-treatment time (h), T (K)</th>
<th>Deformation-T (K)</th>
<th>$\gamma$</th>
<th>Volume increase$^a$ (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P239</td>
<td>1, 1300</td>
<td>1300</td>
<td>&lt;0.1</td>
<td>10.1</td>
<td>slip at top sample-spacer interface</td>
</tr>
</tbody>
</table>

$^a$ compared to untreated samples

Due to slipping at the top sample-spacer interface, the experiment was terminated at $\gamma < 0.3$ without any macroscopical deformation of the sample. The microstructure did not show any deformation features like cracks. All of the strain was probably accommodated along the sliding interface.
5.3 Heat-treatment and deformation of Dover flint at 1400 K

5.3.1 Motivation

The motivation to perform experiments on Dover flint at very high temperatures (1400 K) was twofold:

(1) Attainment of plastic flow by intracrystalline plasticity and/or diffusive mass transfer processes. In general, a solid is more likely to deform plastic at high effective pressures, high temperatures, and at low strain-rates (Murrell, 1990). In order to reach large strains in a reasonable amount of time, the shear strain rate in torsion experiments cannot be much lower than $1 \times 10^{-4}$ s$^{-1}$ for samples with a diameter of 10 mm ($\gamma = 3$ in about 9h). In the Paterson gas-medium apparatus used in this study, the maximum confining pressure routinely used is 500 MPa, and the risk for leaks is quite high at such pressures. The only feasible way in this experimental setup to enhance plastic flow is to raise the temperature even higher than 1300 K.

(2) Influence of different parameters on rheology and microstructure. In order to learn more about the deformation of quartz in torsion, groups of experiments were performed in which only one parameter at a time was varied. As parameters, we tested (a) sample assemblies, (b) water content, (c) heat-treatment time, (d) amount of shear strain, and (e) strain rates (as stepping strain rate test), and (f) temperature (in this chapter).

5.3.2 Experimental conditions

The deformation apparatus as well as sample and piston assembly are described in Chap. 4. Drained as well as undrained conditions were tested. Tests under drained conditions were conducted by using porous spacers at each sample end. For the experiment performed under undrained conditions (P191), a non-porous spacer was inserted at the sample bottom, but a porous one at the sample top. Further above, a non-porous spacer was added. It was thought that the porous spacer would act as a pore fluid buffer, (1) allowing to reduce the pore pressure at the sample-spacer interface, but (2) preventing that all of the water leaves the assembly.

A summary of the experiments is given in Tab. 5.5. Before deformation, all samples were heat-treated for 0.5 h or 6 h at 350 MPa and 1400 K. In order to study the effect of heat-treatment on the microstructure, two samples (P248 and P250) were only heat-treated under drained conditions and then quenched. After heat-treatment, experiments at constant twist rate corresponding to a shear strain rate of $1 \times 10^{-4}$ s$^{-1}$ (except for strain rate stepping test in P202) were conducted at 1400 K, 350 MPa in the $\beta$-stability field of quartz (Fig. 5.22). In one of the
experiments (P202) a stepping strain rate test was performed after a shear strain of $\gamma = 1.1$ in order to evaluate the relationship of strain rate and shear stress and to determine the stress exponent $n$. The experiments were generally terminated by jacket failure at a shear strain $\gamma \leq 4$ (see Fig. 5.24f). Jacket failure was always due to development of a leak in an area in contact with the sample. As in the case for the 1300 K experiments, the torque was converted to shear stress assuming a constant flow law with a stress exponent $n = 1$ (see Paterson and Olgaard, 2000 and Pieri et al., 2001). Grain sizes were determined with the line intercept method from microphotos in crossed polarized light.

Table 5.5  List of experiments on Dover flint. Temperature was 1400 K, confining pressure 350 MPa, strain rate $10^{-4}$ s$^{-1}$.

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample length (mm)</th>
<th>Sleeve metal</th>
<th>Heat-treatment time (h), T (K)</th>
<th>$\gamma$</th>
<th>Volume increase$^a$ (%)</th>
<th>Water content (wt.%)</th>
<th>Average equivalent grain diameter ($\mu$m)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P189</td>
<td>17.9</td>
<td>none</td>
<td>0.5, 1400</td>
<td>-</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>leak</td>
</tr>
<tr>
<td>P190</td>
<td>19.4</td>
<td>none</td>
<td>0.5, 1400</td>
<td>1.3</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>leak</td>
</tr>
<tr>
<td>P191</td>
<td>15.1</td>
<td>none</td>
<td>0.5, 1400</td>
<td>0.2</td>
<td>11$^a$</td>
<td>?</td>
<td>?</td>
<td>undrained, slip</td>
</tr>
<tr>
<td>P198</td>
<td>10.4</td>
<td>Pt</td>
<td>0.5, 1400</td>
<td>0.5</td>
<td>4.2$^a$</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>P199</td>
<td>10.7</td>
<td>Pt</td>
<td>0.5, 1400</td>
<td>2.4</td>
<td>?</td>
<td>0.03</td>
<td>3.8</td>
<td>leak</td>
</tr>
<tr>
<td>P202</td>
<td>10.8</td>
<td>Pt</td>
<td>0.5, 1400</td>
<td>3.4</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>leak</td>
</tr>
<tr>
<td>P204</td>
<td>10.8</td>
<td>Pt</td>
<td>6, 1400</td>
<td>2.5</td>
<td>?</td>
<td>&lt;0.01</td>
<td>3.2</td>
<td>leak</td>
</tr>
<tr>
<td>P216</td>
<td>8.1</td>
<td>Ni</td>
<td>0.5, 1400</td>
<td>4.0</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>leak</td>
</tr>
<tr>
<td>P248</td>
<td>10.4</td>
<td>Pt</td>
<td>0.5, 1400</td>
<td>-</td>
<td>5.4</td>
<td>0.15</td>
<td>3.4</td>
<td>Heat-treatment</td>
</tr>
<tr>
<td>P249</td>
<td>10.8</td>
<td>Pt</td>
<td>-</td>
<td>-</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>Thermocouple broken</td>
</tr>
<tr>
<td>P250</td>
<td>10.8</td>
<td>Pt</td>
<td>6, 1400</td>
<td>-</td>
<td>2.6</td>
<td>0.1</td>
<td>5.3</td>
<td>Heat-treatment</td>
</tr>
</tbody>
</table>

$^a$ compared to untreated samples, ? = not available

5.3.3  Characterization of samples only heat-treated

The results from the heat-treatment experiments are very comparable to those obtained at 1300 K. Again, an increase in volume occurred during heating up under pressure that was followed during heat-treatment by a volume decrease not below the initial one (Tab. 5.5).

Texture measurements by synchrotron experiments showed that the texture is random. The microstructure consists of equiaxed grains, which increase in size with increasing heat-treatment time (Fig. 5.21). Some few large ($> 40 \mu$m) subhedral grains are present within the fine-grained matrix. They account for less than 4% of the total area. In plane polarized light, microscopic opaque dots with a homogeneous distribution, which are interpreted as fluid-filled pores like in
the 1300 K experiments, were observed. FTIR measurements indicate a strong decrease in water content with increasing heat-treatment time (see Tab. 5.5).

It is suggested that the same mechanisms were active as in samples of 1300 K heat-treatment experiments (see paragraph 5.1), that means:

1. During pressurization and heating, water expansion in the samples lead to an overall increase in sample volume.

2. As soon as the experimental conditions are reached, compaction creep mostly involving diffusive mass transfer processes and grain growth are the main deformation mechanisms resulting in sample compaction.

![Fig. 5.21](image) Microstructure of Dover flint heat-treated at 1400 K, 350 MPa for 0.5 h (a) (P248) and 6 h (b) (P250). Microphotos in crossed polarized light.

5.3.4 Experimental results: Deformation

a) Effect of different sample assemblies

In the first attempts to deform flint only an iron jacket was used without an inner nobel metal sleeve (P190, P191, Fig. 5.22). Sample P190 reached a plateau of 45 MPa at $\gamma = 0.1$ which was followed by marked strain hardening leading to a peak torque of about 57 MPa at $\gamma = 0.3$. This was followed by strong weakening and then by fluctuating stress-strain behaviour. The experiment was terminated at $\gamma = 1.3$ due to jacket failure. After removal of the jacket a dark thin rim was observed around the specimen, which displayed a set of parallel cracks (Fig. 5.23a) nearly normal to $\sigma_3$. Another minor set of cracks oriented normal to $\sigma_1$ was linking the main crack system. Below this dark rim the flint was white and clean. The thickness of the rim varied between 30 and 80 $\mu$m (Fig. 5.23b), and it penetrated dendritically into the quartz aggregate. After inspection with X-ray diffraction and X-ray mapping on a SEM, it was found that the dark layer was composed of fayalite. The rim is interpreted to be due to a reaction between the iron jacket...
and the quartz during heat-treatment. In order to test this hypothesis a platinum sleeve was inserted in run P198 between the iron jacket and the specimen. P198 was then deformed under the same conditions as P190 (Fig. 5.22). P198 deformed at a much lower stress (14 MPa) than P190 and did not display significant weakening or hardening.

![Graph showing shear stress versus shear strain for experiments performed at 1400 K, 350 MPa, 0.5 h heat-treated and with noble metal sleeve under drained conditions (unless indicated). Shear strain rate was $1 \times 10^{-4}$ s$^{-1}$. Shear stress was calculated from the measured torque assuming a power law creep with stress exponent of $n = 1$.]

![Image showing sample deformed with direct contact between quartz and the iron jacket. (a) Bulk sample with a fayalite mantle (P190). Note the set of cracks indicated with black arrows. (b) Microphoto in plane polarized light of P190. Section cut near the sample rim. The nearly horizontal crack perpendicular to the rim is filled with fayalite.]

Fig. 5.22: Shear stress versus shear strain for experiments performed at 1400 K, 350 MPa, 0.5 h heat-treated and with noble metal sleeve under drained conditions (unless indicated). Shear strain rate was $1 \times 10^{-4}$ s$^{-1}$. Shear stress was calculated from the measured torque assuming a power law creep with stress exponent of $n = 1$.

Fig. 5.23: Sample deformed with direct contact between quartz and the iron jacket. (a) Bulk sample with a fayalite mantle (P190). Note the set of cracks indicated with black arrows. (b) Microphoto in plane polarized light of P190. Section cut near the sample rim. The nearly horizontal crack perpendicular to the rim is filled with fayalite.
After deformation no fayalite rim was observed. Therefore, all the following experiments were conducted with an inner sleeve of nobel metal.

The leak development in P190 at $\gamma = 1.3$ was probably due to embrittlement of the jacket which is caused by water present in quartz. To solve this problem, different metals for inner sleeves (platinum, nickel) were tested. The formation of fayalite was no more observed. However, embrittlement of the jacket could not be prevented, but strongly retarded to shear strains of $\gamma > 2$ by using an inner sleeve of platinum or nickel.

\textit{b) Drained vs. undrained conditions}

Sample P191 was deformed under undrained conditions. The experiment was interrupted at $\gamma < 0.2$ because of loss of torque, which was caused by slip at the top interface between porous and non-porous spacer (Fig. 5.24a). In the drained experiments, slip at the sample-spacer interface did not occur, therefore, in order to reach larger strains, drained conditions were used for subsequent runs.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.24.png}
\caption{Samples of Dover flint after torsion test within the iron jacket. Scratches or wrinkles on the jacket were originally parallel to the cylinder axis and serve as strain markers. Triangles and numbers indicate shear strain, scale bar at bottom is always 10 mm, \(p\) = porous spacer; \(np\) = non-porous spacer. Samples were heat-treated for 0.5 h (a-f) or 6 h (g) at 1400 K, 350 MPa under drained conditions (porous spacers) except (a). All samples had an inner nobel metal sleeve except a)-b). a) P191, undrained. b) P190. c) P198. d) P199. e) P216. f) P202. g) P204.}
\end{figure}

The rheology of the undrained experiment P191 was compared to the one of the drained experiment P190 (Fig. 5.22). Assembly and heat-treatment factors were kept constant. Note that both samples P190 and P191 were only in an iron jacket, which led to the formation of a fayalite
Fig. 5.25 Microphotos in plane polarized light (a,b,g), crossed polarized light (c-f) and reflected light (h) of Dover flint deformed in torsion at 1400 K, 350 MPa. All samples heat-treated for 0.5 h except c)-d). a) P191, undrained, $\gamma = 0.2$. b) P190, drained, $\gamma = 1.3$. c)-d) P204, 6 h heat-treated, $\gamma = 2.5$. e)-f) P198, no hardening and no cracking, $\gamma = 0.5$. g)-h) P202, with hardening and cracking, $\gamma = 3.4$. 
rim. The drained sample P190 was about twice as strong than the undrained sample P191. After removal of the jacket and the pistons, some white and clean material was observed at the interface between the porous spacer and the bore hole of the pistons, which suggests that during fluid escape some material was deposited in the drained experiment.

Comparison of the microstructures of the drained and undrained samples shows major differences (Fig. 5.25a,b). In the undrained sample P191 throughgoing en échelon cracks are present normal to $\sigma_3$. Some cracks are healed and show fluid inclusions. The drained sample P190 displays a coarser network of randomly oriented and irregularly shaped cracks with no displacement along them.

c) Effect of different heat-treatment times

To attempt a quantification of the effect of water and grain growth on flow stress, a sample heat-treated for 6 h was compared to those of 0.5 h heat-treatment:

**6 h heat-treated.** P204 (heat-treated for 6 h) was five times stronger than samples heat-treated for 0.5 h (Fig. 5.22). P204 showed a steady-state stress at about 200 MPa, which was followed by strong weakening after a shear strain of about $\gamma = 1.8$. A leak at the end of the experiment led to a rapid drop in confining pressure while the temperature was still 1400 K. A macroscopic inspection of the sample assembly revealed a slight deformation of the porous spacers. This indicates that the maximum possible shear stress was reached, that can be tested at these conditions. Deformation of the spacers also implies that the strain rate was slightly lower than $1 \times 10^{-4}$ s$^{-1}$. The sample itself did not deform homogeneously (Fig. 5.24g): The strain marking scratches on the jacketed sample showed different deflection angles. By measuring these angles from sample bottom to top, the variation of shear strain was evaluated (Fig. 5.26). A maximum local shear strain of $\gamma = 3.5$ was attained towards the sample bottom.

After the experiment, cristobalite was detected using X-ray diffraction. The microstructure consists of fibrous grains showing a SPO with a preferred orientation at 120° clockwise to the SZB (Fig. 5.25c,d). In between there are bands (up to 100 $\mu$m wide) of sub-micron sizes grains. The bands are better developed next to the sample rim and less developed towards the sample centre. FTIR measurements indicate a water content of <0.1 wt.% throughout the sample.

Texture measurements were performed on P204 using synchrotron experiments (Fig. 5.27a). At a strain of $\gamma = 0.2$, an oblique c-axis girdle inclined with the sense of shear starts to develop. The c-axis maximum is oriented at about $130^\circ \pm 5$ clockwise to the SZB and $5^\circ \pm 5$ to $\sigma_3$. The texture becomes more pronounced with increasing shear strain.
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Fig. 5.26 Variation of shear strain from sample bottom to top. Strain vs. sample length curves, normalized to bulk strain and total sample length. All experiments were performed after 0.5 h heat-treatment except P204 which was heat-treated for 6 h. Run numbers and sample lengths as indicated.

0.5 h heat-treated. Strain weakening was not observed in the samples heat-treated for 0.5 h (Fig. 5.22). Instead, the samples either flowed at constant stress until the end of experiment (P198) or showed strain hardening after a large strain ($\gamma \leq 3$) at constant flow stress (P199, P202, P216). All of the experiments were terminated by jacket failure. Deformation was strongly heterogeneous (Fig. 5.24d-f): A macroscopic inspection of the iron-jacketed samples showed the occurrence of strong necking or bulging. The strain marking scratches were more deflected in the necked regions suggesting that strain was localized there. This was confirmed by measurements of the strain variation using the angle of the strain marking scratches (Fig. 5.26). A maximum local shear strain of $\gamma = 6.6$ was attained in sample P202. The strain distribution was more heterogeneous in longer samples.

After the experiments, the samples were exclusively composed of quartz, as revealed by X-ray diffraction. Two types of microstructure were observed: In the experiment with no strain hardening (P198) the microstructure is rather homogeneous (Fig. 5.25e-f). No cracks are present, but some very weakly developed R1 bands occur, which are composed of pores like in the 1300 K experiments. The grains are fine-grained (< 4 µm) and do not show an SPO. In the experiments with strain hardening (P199, P202, P216), the microstructure is heterogeneous (Fig. 5.25g-h). Next to the sample rim, there is a cracked zone extending up to several hundreds of micrometers inside the sample. In contrast to the 1300 K experiments, the cracks do not show a Riedel orientation, but they are nearly parallel to the SZB. Most of them are filled with metal from the
inner nobel metal sleeve or from the jacket (Fig. 5.25h). Towards the sample centre, the cracks disappear and the microstructure looks similarly homogeneous like to the one of P198. FTIR measurements indicate a water content of about 0.03 wt.% after deformation to $\gamma = 2.5$ (P199).

Strain-resolved local texture measurements by synchrotron radiation were performed on the high strain sample P199 (Fig. 5.27b). Texture is random up to a shear strain of about $\gamma = 0.3$. Then an oblique c-axis girdle starts to develop inclined opposite to the sense of shear. The c-axis maximum is oriented at about $60^\circ \pm 5$ clockwise to the SZB and at $15^\circ \pm 5$ to $\sigma_1$. Even at the highest shear strain, the texture remains very weak with a texture index $J$ of less than 1.1.

![Fig. 5.27](insert)

### d) Stepping strain rate test

According to Paterson and Olgaard (2000), it is possible to obtain a flow law (at least in the power law creep regime) during torsion testing by stepping strain rate tests, provided the rheology across the specimen is constant. The test was performed in experiment P202 in the following way (Fig. 5.28a):

a) The specimen was twisted at a displacement rate of $2 \times 10^{-4}$ rad s$^{-1}$, until an approximately constant torque was reached.
b) The twist rate was decreased by an order of magnitude (to $2 \times 10^{-5}$ rad s$^{-1}$) and kept constant until the torque had reached a new equilibrium.

c) The twist rate was increased in small steps up to a twist rate of $2 \times 10^{-3}$ rad s$^{-1}$ where the torque was recorded at each step.

No correction for the iron jacket was applied, but the jacket strength (see Chap. 4) was taken into account in the error estimation. The stress exponent $n$ can be derived directly from the slope of the best fitted line in a log(torque) vs. log(strain rate) diagram (Fig. 5.28b). The stress exponent $n$ increased monotonously with torque (and shear strain rate), from 1 at the lower values to 2 at the higher values, leading to a curve with upward concavity in the log-log diagram (Fig. 5.28b). It has to be pointed out that the resolution of the load cell is of the order of 1 Nm, therefore the results at low stresses can only serve as a qualitative indication.

![Graphs](image)

*Fig. 5.28 Stepping strain rate test P202. (a) Torque vs. shear strain curve. Twist rate steps are indicated. (b) Log-log plot of twist rate versus internally measured torque (shear stress is also given calculated from the measured torque assuming a power law creep with stress exponent of $n = 1$).*

### 5.3.5 Discussion

a) Effect of different sample assemblies

In torsion experiments most of the torque is supported by the external part of the cylindrical specimen (Paterson & Olgaard, 2000). Based on flow laws for polycrystalline olivine (Karato et al., 1986), the rim of fayalite in P190 was supporting a significant part of the torque. Therefore, it is concluded that the higher strength of the sample P190 with no inner sleeve compared to P198 with a platinum sleeve was mainly due to the presence of a fayalite rim in P190. The abrupt weakening events are interpreted to be due to micro-cracking of this rim, whereas the continuous weakening by 30% at $\gamma = 0.3\ldots0.5$ could be related to a temporary pore pressure build-up.
b) Drained vs. undrained conditions

The undrained sample assembly (non-porous spacers) prevented reaching torque values higher than 10 Nm (corresponding to a shear stress of about 53 MPa for a sample with 10 mm diameter and assuming a stress exponent of \( n = 1 \)) due to slippage at the interface between porous and non-porous spacer. This can be explained by filling up of the porous spacer with fluid released from the sample. The resulting increase in fluid pressure within the spacer reduces the effective pressure and therefore the friction at the spacer-spacer or sample-spacer interface. In torsion, the specimen loading relies on the friction at these interfaces as a function of the effective pressure. If the latter is low, high torque values are inaccessible due to slip along one of these interfaces.

The orientation of the cracks in the undrained sample P191 with their normal parallel to \( \sigma_3 \) suggests that they are tensile fractures (Mandl, 2000). Tensile fractures occur when the minimum principal (effective) stress \( \sigma_3 \) is negative (tensional) and equal to the uniaxial tensile strength. In Fig. 5.29, various fracture envelopes for different quartz-rich rocks are shown together with the Mohr circles of the stresses in some of the flint experiments. For all of the experiments, the confining pressure was 350 MPa. Tensile fractures can only form if the Mohr circle of P191 is shifted from 350 MPa towards the left until the least principal stress \( \sigma_3 \) touches one of the fracture envelopes in the field of tensile fracturing (grey shaded area in Fig. 5.29). The resulting effective pressure is almost zero in the case of P191. Therefore, pore pressure must have been similar to the confining one (i.e., around 350 MPa). In contrast, tensile fracturing in the drained samples (e.g. P190) was not observed. Instead, the irregular cracks in the drained samples (Fig. 5.25b) probably formed very late in the experiment during cooling. The suppression of tensile fracturing can be explained by an increased effective confining pressure and therefore a reduced pore pressure (Handin, 1966), but the exact value of the latter for drained experiments is unknown.
c) Effect of different heat-treatment times

**6 h heat-treated.** Under the stationary conditions of the experiment (1400 K, 350 MPa) quartz is the only stable phase in the phase diagram (Fig. 5.30). Cristobalite should develop only at temperatures exceeding 1700 K. There are two possible explanations for the presence of cristobalite in P204: (1) it precipitated from a fluid phase consisting of water, melt or a combination of both during sudden pressure release when the jacket failed; (2) it formed by polymorphic phase transformation. The first explanation can be ruled out: samples heat-treated for 0.5 h did not show cristobalite, even if they were also terminated by sudden pressure release due to jacket failure. Also, it would be expected that amorphous silica rather than cristobalite would precipitate from a fluid phase (pers. comm. M. Paterson, 2000). On the other hand, transformation of quartz to mixed tridymite/cristobalite reaction products was observed in extension experiments on synthetic quartz aggregates at 1473 K and 300 or 350 MPa confining pressure (Brodie and Rutter, 2000b), where a rapid stress release after initial plastic yielding was interpreted to result from the polymorphic transformation. Polymorphic transformation could take place because the axial stress in extension took the specimens across the phase boundary between β-quartz and tridymite, even if the mean stress was still well within the β-quartz stability field. Brodie and Rutter (2000b) reported fibres of quartz, tridymite and cristobalite with their length and c-axes.
parallel to the extension direction (i.e., the least principal stress $\sigma_3$). The authors suggested that tridymite and cristobalite developed simultaneously due to a metastable epitaxial relationship, even though the experimental conditions were well away from the cristobalite stability field.

The results of this study are consistent with the observations of Brodie and Rutter (2000b): Fig. 5.30 shows the phase diagram for the low-pressure silica polymorphs together with the minimum principal stress $\sigma_3$ for P202 (heat-treated for 0.5 h) and P204 (heat-treated for 6 h). The minimum principal stress for the sample heat-treated for 0.5 h lies well within the stability field of $\beta$-quartz, whereas for the sample heat-treated for 6 h it is on the boundary between $\beta$-quartz and tridymite. It is speculated that weakening in P204 is related to the growth of a low density silica phase (tridymite and/or cristobalite). We do not have a good explanation for the absence of tridymite in P204. It could be that only metastable cristobalite was formed during deformation or that tridymite reverted to quartz when the shear stress lowered and finally vanished.

![Phase diagram for the low-pressure silica polymorphs with excess water](image)

**Fig. 5.30** Phase diagram for the low-pressure silica polymorphs with excess water (modified after Kennedy et al., 1962). The symbols show $\sigma_1$ and $\sigma_3$ at $\gamma = 4$ (P202, heat-treated for 0.5 h) and $\gamma = 1.3$ (P204, heat-treated for 6 h), $P_c$ is confining pressure. Note that in torsion, $\sigma_1$ ($\sigma_3$) is calculated as the sum (difference) between confining pressure $P_c$ and shear stress $\tau$.

**0.5 h heat-treated.** Samples heat-treated for 0.5 h showed a very low flow strength and strongly heterogeneous deformation. Due to the high water content at the beginning of deformation and the high temperature used in this study, it is believed that melt was present along grain boundaries. This is consistent with the phase relationships in the system SiO2-H2O (Fig. 5.30): at 1400 K, quartz can be expected to occur together with melt and vapour. Melt distribution within the samples might have been heterogeneous (due to heterogeneous fluid distribution), so that deformation probably localized where melt was present. The matrix microstructure of the
experiments at 1400 K is very similar to the one observed in the low-strain experiments at 1300 K. Together with the low stress exponent (n < 2), it is proposed that the main deformation mechanism at 1400 K was granular flow, like in the experiments at 300 K. However, in contrast to the latter ones, granular flow was maybe more enabled at 1400 K by melt along grain boundaries.

The samples heat-treated for 0.5 h had a smaller grain size and higher water content than the sample heat-treated for 6 h. This may be an explanation for the large strength difference between the two types of experiments since flow stress of granular flow is directly correlated to grain size and inversely to water content (Paterson, 1995). Furthermore, a low water content in the 6 h heat-treated sample probably also resulted in a lower melt content. Melt can have a profound effect on the rheological behaviour of a sample: Dell'Angelo et al. (1987) observed a switch in deformation mechanism in experiments on fine-grained granitic aggregates from dislocation creep in samples with <1% melt to melt-enhanced diffusion creep in samples with 3-5% melt. In fine-grained olivine aggregates undergoing diffusion creep, the addition of a few percent of basaltic melt enhanced the creep rate by a factor of 2-5 at high temperature (Cooper and Kohlstedt, 1984).

Strain hardening observed at high strain in the three experiments P199, P202 and P216 was always associated with marginal cracking of the samples. Therefore it is possible that hardening is a consequence of crack development: once the cracks opened, they might provide fast pathways for water to escape from the sample. The fluid drainage is probably coupled with a continuously decreasing amount of melt, thus enhancing friction along grain boundaries. The reason for the development of the marginal cracks remains unclear. Since metal was flowing into the cracks, it cannot be ruled out that crack growth was influenced by the metals of the sleeve and/or the jacket: at 1400 K, they are so viscous that they may act like a pore fluid.

5.3.6 Conclusions

Section 5.3 has described the search for an optimal set-up of torsion experiments on Dover flint at 1400 K, which did only partially succeed. The accumulated data do not allow to draw strong conclusions about the deformation mechanisms. The following arguments should be taken into account in further attempt on similar experiments:

1. The formation of a fayalite rim in experiments with no inner noble metal sleeve had a strong influence on the observed rheology with higher measured flow stress and discontinuous hardening events. In the experiments with an inner noble metal sleeve, metal was found to diffuse into cracks at high shear strains. Therefore, the optimized sample assembly was not yet found. Furthermore,
hydrogen embrittlement of the iron jacket could not be avoided in any of the tested assemblies leading to leak development at $\gamma < 4$.

2. Deformation of wet Dover flint in torsion to high shear strains could only be achieved by using drained conditions (porous spacers) in order to avoid slip at low strain at the sample-spacer interface.

3. A sample deformed under undrained conditions failed by tensile fracturing suggesting that the pore pressure exceeded the confining pressure.

4. In the drained samples, deformation occurred by granular flow. Melt was probably present along grain boundaries leading to a strongly heterogeneous deformation. Deformation was less heterogeneous in shorter samples.

5. In general, deformation properties for Dover flint at 1400 K are very sensitive to history of the sample with respect to (1) heat-treatment time and (2) capability of water to flow out of the sample.
6 Determination of lattice preferred orientation

6.1 X-ray texture goniometry of weak textures in fine-grained quartz aggregates

6.1.1 Introduction

X-ray texture goniometry is a technique often used to measure the lattice preferred orientation (texture) in fine-grained (<200 μm), monomineralic rocks (Wenk, 1985). It has proven to be robust for determination of strongly developed textures in reasonably homogeneous, large samples. However, accurate determination of weak textures depends strongly on appropriate instrumental setup and tilt correction procedures. Especially for small and rectangular samples, careful defocusing corrections are required (Wenk, 1985).

The aim of the present study was to optimize the setup on a SCINTAG XDS2000 goniometer for texture determination of fine-grained Dover flint, both as-is (not heat-treated, undeformed) and samples experimentally deformed in torsion. Due to the very small grain size (often <1 μm), most samples were not accessible to EBSD analysis. The measurement of preferred orientation by texture goniometry of samples deformed in torsion is complicated because of heterogeneous deformation within the sample cylinder. The shear direction, which is perpendicular to the radius of the cylindrical samples, varies continuously around the cylindrical sample and shear strain varies with radius. The problem can be minimized by measuring an area which is as small as possible in the tangential direction (Casey et al., 1998). Therefore, all the samples in the present study had a small and rectangular size (8*10 mm²). A further problem were the weakly developed textures which make the measurements very sensitive to defocusing effects. Appropriate tilt correction curves for different sample sizes and shapes were empirically obtained by making reflection scans on slabs of as-is Dover flint, which was tested to have no preferred orientation. These tilt correction curves were subsequently used to correct texture measurements from experimentally deformed samples.

6.1.2 Principles of texture goniometry

The principles of texture goniometry were explained in detail by Wenk (1985), Bunge (1986) and Wenk (1998).
X-ray texture goniometry is based on diffraction according to Bragg’s law for monochromatic radiation. Lattice planes with a spacing $d_{hkl}$ will only diffract if the following condition is satisfied:

$$2d_{hkl} \sin \theta = n\lambda,$$

where $\theta$ is the angle between incident and diffracted beam, $n$ is an integer number defining the order of diffraction, and $\lambda$ is the X-ray wavelength ($\lambda = 1.54$ Å for Cu-Kα used here).

Two methods of analysis can be used: X-rays are reflected on a thick sample slab with a planar surface (reflection geometry) or X-rays penetrate a thin slab (<50 μm; transmission geometry). In this study, only the reflection geometry was applied.

In order to determine the orientation of a lattice plane (hkil) in reflection geometry, the goniometer positions the detector with respect to the X-ray beam to the appropriate diffraction angle $2\theta_{hkl}$. With an Eulerian cradle, the sample is rotated relative to the fixed detector-source-geometry (diffraction vector) about two axes around angles $\phi$ and $\chi$ (see definitions in Fig. 6.1), so that any sample direction can be placed parallel to the diffraction vector. Then the detected count rate is a measure for the volume fraction of crystals with planes (hkil) that are normal to that respective sample direction. The rotation axis $\phi$ is normal to the sample slab and rotates it in its own plane. The sample and rotation axis $\phi$ are both tilted about an angle $\chi$. In a pole figure, $\phi$ corresponds to the azimuth of a pole, and the pole distance is $90^\circ - \chi$. A pole figure is usually scanned stepwise by measuring the diffracted intensity at different discrete $\phi$-$\chi$ positions. Counting statistics can be improved (1) by oscillating the sample parallel to the surface, (2) by choosing a large collimator (typically 1 mm diameter for the incident beam) and (3) by using a slow scan rate. In general, the scan rates are chosen faster for strong reflections and slower for weak reflections.

![Fig. 6.1 Schematic design of texture goniometry in reflection geometry showing two different tilt angles $\chi$ with corresponding view of irradiated surface on the sample through the detector slits. Parts of the beam do not hit the sample especially at high tilt angle $\chi$.](image-url)
6.1.3 Texture corrections

The measured intensities in reflection geometry are subject to two main errors, which have to be corrected: (1) the background correction and (2) the defocusing corrections.

The first step in the data processing is to subtract the background from the measured intensity. Background intensity is caused by various effects (e.g., incoherent scattering and fluorescence in the sample, electronic noise). It is necessary to measure this background and subtract it from the total measured intensity. The background intensity is typically evaluated by calculating the average of the intensities measured a few degrees to the left and right of the diffraction peak.

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![Figure 6.2: Shape and orientation of the irradiated area on the sample surface as a function of tilt angle \( \chi \) and Bragg angle \( 2\theta \) for a circular incident beam. After Wenk (1998).](image)

Texture measurements in reflection geometry are strongly influenced by two defocusing effects: (1) For samples with small and non-circular size parts of the beam diameter do not reach the specimen especially for small Bragg angles \( 2\theta \) (geometric defocusing, Fig. 6.1). This leads to a decrease in diffracted and thus recorded peak intensity which is used to infer the amount of preferred orientation. Geometric defocusing is reduced with decreasing the collimator size, but the accompanying decrease in peak intensity leads to an increase of noise effects. (2) At zero sample tilt angle \( \chi \), the intersection of the beam with the sample surface is elliptical, which increasingly elongates and rotates with increasing sample tilt. Fig. 6.2 shows the change in shape and orientation of the irradiated area on the sample surface for different sample inclinations and Bragg angles \( 2\theta \). The spread in area leads to a peak broadening and therefore to a reduction of the recorded peak intensity (Fig. 6.3) (tilt defocusing). In any case, the intensity loss with increasing \( \chi \) due to both effects is severe and must be corrected. The magnitude of the corrections depends strongly on the experimental setup.
Correction of the defocusing effect is generally determined empirically by measuring a standard sample of the same material with the same specimen size and shape but with no preferred orientation (Wenk, 1985). The correction factor \( C(\chi) \) is obtained by (Bunge, 1986):

\[
C(\chi) = \frac{I_m(0)}{I_m(\chi)}
\]

(6.2)

where \( I_m(0) \) is the measured intensity at \( \chi = 0^\circ \) and \( I_m(\chi) \) the measured intensity at tilt angle \( \chi \).

---

Fig. 6.3 20 scans for as-is flint using Cu-K\( \alpha \) for two tilt angles \( \chi \) with normal (left) and small (right) collimator. Indicated are the reflections of quartz used in this study for pole figure determinations. Note peak broadening and slight peak shifts with increasing \( \chi \) and intensity loss but less peak broadening with smaller collimator.

---

### 6.1.4 Optimization of experimental setup

In this study, samples of as-is Dover flint were used for optimization of the experimental setup and determination of the defocusing corrections. As-is Dover flint shows a grain size of <1 \( \mu m \). It had to be tested to possess no LPO itself. Different sample shapes and sizes as well as different instrumental setups were tested in order to evaluate the effect of defocusing and find the optimized instrumental setup. All of the measurements were performed in reflection. Details on the sample preparation and measurement technique are given in Chap. 4.9.

The optimization was performed in four chronological steps which are described in the following.

**Step 0:** large rectangular sample (8*14 mm\(^2\)), normal collimator (1 mm diameter), 5 mm sample oscillation and fast scan rates (standard conditions):
As a first step, the lack of preferred orientation in as-is Dover flint had to be established. This was attempted first by measuring a rectangular sample (8*14 mm²) under standard conditions. The raw data (eight incomplete (hkl) pole figures after on-line background correction) show a suspicious orthorhombic symmetry parallel to the goniometer axis. Furthermore, some of the incomplete pole figures reveal a rotationally symmetric decrease of the measured intensity towards higher tilt angles \( \chi \) (Fig. 6.4 column 1 and 3). ODF (orientation distribution function) calculation by WIMV (software Beartex, UC Berkeley; Wenk et al., 1998) show incompatibilities to input pole figures (Fig. 6.4 column 2 and 4). The question therefore arose, if the anisotropy in the pole figures was due to geometric defocusing and reflected the sample shape and oscillation direction or if it was due to a preferred orientation in as-is Dover flint.

**Fig. 6.4** Step 0: large rectangular sample (8*14 mm²), normal collimator (1 mm diameter), 5 mm sample oscillation (standard conditions). Corrected incomplete pole figures (left) and corresponding complete ones recalculated from ODF (right), not smoothed. Contour intervals in logarithmic scale at 0.93, 0.96, 1.00, 1.04, 1.08, 1.12, 1.16, 1.20 m.r.d. ODF calculation shows incompatibilities to input pole figures. A suspicious anisotropy with orthorhombic symmetry parallel to the goniometer axis is visible.

**Step 1:** round sample (25 mm diameter), normal collimator (1 mm diameter), 5 mm sample oscillation, fast scan rates (60-120°/min. for different \( \phi-\chi \) positions) (standard conditions):

The lack of preferred orientation in as-is Dover flint still had to be established, but in this step, a circular sample was used in order to exclude any effect due to a sample shape. This was done by measuring a circular sample of 25 mm diameter under standard conditions. The raw data (eight incomplete (hkl) pole figures after on-line background correction) show all rotationally symmetric intensities, which decrease monotonously with increasing tilt angle \( \chi \) due to
defocusing effects (Fig. 6.5). However, the rotationally symmetric intensities imply that no anisotropy due to texture or sample shape is present.

![Fig. 6.5](image)

**Fig. 6.5** Step 1: Large round sample, normal collimator, sample oscillation (standard conditions). Uncorrected incomplete pole figures. Contour intervals in logarithmic scale at 0.89, 0.92, 1.00, 1.08, 1.28, 1.38, 1.50 m.r.d. Note rotationally symmetric intensities which are monotonously decreasing due to defocusing effects. No anisotropy due to texture or sample shape is visible.

---

Tilt correction curves were obtained from the raw intensities by azimuth averages and subsequently used to correct the measured pole figures themselves. The variation of intensity \( I_y(\chi) = I_m(\chi)/I_m(0) \) with increasing tilt angle \( \chi \) for the diffraction planes are shown in Fig. 6.6b. The measurements show decreasing peak intensity with increasing tilt angle \( \chi \). The effect is less pronounced with increasing Bragg angle \( 2\theta \). ODF (orientation distribution function) calculation by WIMV (software Beartex, UC Berkeley; Wenk et al., 1998) based on the corrected
incomplete pole figures gave an ODF texture index of $J=1.002$ with very satisfying fit parameters $(R_0=5.25, R_1=3.89)$, for explanation of the RP values see Wenk et al., 1998). The corrected incomplete pole figures and the corresponding recalculated complete ones are shown in Fig. 6.6a.

The two sets of pole figures are very consistent and no anisotropy due to texture or sample shape is visible. As-is Dover flint was also analysed with neutron diffraction by Prof. H. Siemes at the Research Center Jülich (Germany). Again no preferred orientation was detected (personal communication Prof. H. Siemes, 2001). Therefore as-is Dover flint does not possess any measurable texture, which makes it perfectly suitable as an isotropic standard for texture correction.

After having found a good isotropic standard sample, the measurements were performed on samples of the same material, but with a rectangular shape and small size $(8\times10 \text{ mm}^2)$. In a first approach, the same instrumental setup as in step 1 was used:

**Step 2:** Small rectangular sample $(8\times10 \text{ mm}^2)$, normal collimator (1 mm diameter), 5 mm sample oscillation, fast scan rates $(60-120^\circ/\text{min})$:

The raw data pole figures were corrected by using tilt correction curves determined with the round standard sample (see step 1). The corrected incomplete pole figures show an orthorhombic symmetry parallel to the goniometer axis. Furthermore some of the incomplete pole figures (e.g. $(10\overline{1}0), (21\overline{1}1)$) reveal a rotationally symmetric decrease of the measured intensity towards higher tilt angles $\chi$ (Fig. 6.7a).

ODF calculation by WIMV gave a texture index of $J=1.01$ with less satisfying fit parameters $R_0=8.82$ and $R_1=7.42$. The recalculated pole figures yield the orthorhombic symmetry again and show no consistency to the incomplete ones. The small inset in Fig. 6.6b. shows the change in shape and orientation of the irradiated area on the rectangular and the round sample surface for two different values of $\chi$. For the round sample the beam leaves the sample only at very high tilt angle $\chi$ whereas for the rectangular sample beam loss occurs already at lower tilt angle $\chi$, more parallel to the rectangle side than along the sample diagonals. Therefore the orthorhombic anisotropy can be entirely attributed to geometric defocusing and reflects the shape of the sample and the oscillation. The rotationally symmetric decrease of the measured intensity in some pole figures suspects that the tilt intensity correction determined on the round sample is not appropriate for the smaller rectangular sample.
Fig. 6.7  Step 2 and 3: Corrected incomplete pole figures (left) and corresponding complete ones recalculated from ODF (right), not smoothed. Contour intervals in logarithmic scale at 0.93, 0.96, 1.00, 1.04, 1.08, 1.12, 1.16, 1.20 m.r.d.. a) Step 2: Small rectangular sample, normal collimator, sample oscillation. Tilt correction of experimental pole figures taken from step 1. ODF calculation shows incompatibilities to input pole figures. Anisotropy is entirely due to geometric defocusing and reflects the shape of the sample and oscillation direction. b) Step 3: Small rectangular sample, normal collimator, no sample oscillation. Tilt correction curves obtained from the raw intensities by azimuth averages. Incompatible input pole figures. The maxima along the diagonals of the sample of some pole figures still reflect an effect due to the sample shape.

**Step 3**: Small rectangular sample (8*10 mm²), normal collimator (1 mm diameter), no sample oscillation, fast scan rates (60-120°/min):

Raw data pole figures were corrected by using tilt correction curves obtained from the raw intensities by azimuth averages. The orthorhombic symmetry in the corrected incomplete pole figures is less pronounced than on the setup with sample oscillation (step 2) but still visible (Fig. 6.7b).

On the other hand, the decrease in intensity with increasing tilt angle $\chi$ is satisfyingly corrected. The texture index after the ODF calculation was $J = 1.01$ with the average fit parameters $R(0) = 4.10$ and $R(1) = 3.53$. The consistency between the corrected incomplete pole figures and the recalculated complete ones is not yet satisfactory: the least consistent pole figures are the ones of the $(2021)$- and $(10\bar{1}4)$-reflections. This can be explained by a very low peak intensity leading to a strong contribution of background noise. Subsequently these two peaks were no more analysed. The strong maxima along the diagonals of some pole figures still reflect an effect due to sample shape.
Obviously in step 2 and 3 the area of the incident beam was too large compared to the sample area leading to a strong geometric defocusing effect. Therefore, the incident beam size was decreased in the following step by choosing a small collimator (0.5 mm diameter). Slower scan rates (30-60°/min.) must be used in order to attain usable counting statistics:

**Step 4:** Small rectangular sample (8 * 10 mm²), small collimator (0.5 mm diameter), no sample oscillation, long scan rates (30-60°/min.):

The (2021) - and (1014) -reflections were no more analysed due to the very low peak intensity. The raw data are very similar to the ones obtained on the round sample (step 1) with rotationally symmetric intensities. The tilt correction curves obtained from the raw intensities by azimuth averages reveal an intensity decrease which is less pronounced compared to the intensity decrease with normal collimator (Fig. 6.8b). The small inset in Fig. 6.8b shows the change in shape and orientation of the irradiated area on the sample surface for two different values of \( \chi \). The difference in beam size compared to normal collimator measurements is striking (compared to small inset in Fig. 6.6b). The tilt correction curves were subsequently used to correct the raw data pole figures. The corrected incomplete pole figures and the corresponding complete ones are shown in Fig. 6.8a.

The texture index was \( J = 1.06 \) with the fit parameters \( R_P^0 = 5.10 \) and \( R_P^1 = 4.88 \). The consistency between the two sets of pole figures is very good as they do not show any consistent trends to anisotropic intensity distributions, neither due to sample shapes nor to texture. Therefore any anisotropy due to geometric defocusing was suppressed with a small collimator causing a smaller incident beam size. Due to the much lower counting statistics, the pole figures and total intensities are more noisy than the ones obtained with a normal collimator.

In summary, intensity corrections for small rectangular samples were strongly affected by the size of the collimator and the sample oscillation. The instrumental setup could be optimized when a small collimator (0.5 mm diameter) and no sample oscillation were used.
6.1.5 Application

The tilt correction curves obtained from step 4 were tested by applying them to samples of as-is and experimentally deformed Dover flint of similar dimensions as the standard one. The measured incomplete pole figures were processed by ODF calculation using the discrete WIMV procedure. The complete pole figures were then recalculated after smoothing the WIMV generated ODF with a 15° smoothing width. For the as-is flint, the texture index was J=1.06/1.01 (before/after smoothing) with the fit parameters RP0=5.10 and RP1=4.88. No anisotropy can be detected (Fig. 6.9 left).

Another Dover flint sample, which was deformed in simple shear by torsion experiments to a shear strain of $\gamma = 3.3$, was measured. The texture index was J=1.13/1.06 (before/after smoothing) with the fit parameters RP0=6.37 and RP1=4.94. The pole figures show a weak but clearly developed preferred orientation with an oblique c-axis girdle opposite to the sense of shear and overall monoclinic sample symmetry about the pole figure center (Fig. 6.9 right).

Textures obtained by texture goniometry with the optimized setup of step 4 compare well with data from other experimental techniques (EBSD measurements, synchrotron experiments).
Fig. 6.9  Recalculated pole figures from optimally corrected measurements of as-is (left) and experimentally deformed (right) Dover flint: The measured incomplete pole figures were processed by ODF calculation using the discrete WIMV procedure and complete pole figures were recalculated after smoothing the WIMV generated ODF with a 15° smoothing width.

### 6.1.6 Conclusions

1. Texture measurements by X-ray goniometry require careful defocusing corrections. Tilt correction curves are strongly affected by the size of the collimator: Intensity corrections were found to be smallest with a small collimator (0.5 mm diameter), but at much lower total count rates.

2. The instrumental setup could be optimized for small and fine-grained samples (<1 μm) which are not accessible to EBSD analysis. The optimized setup for small and rectangular samples consists in using a small collimator (diameter 0.5 mm) and no sample oscillation.

3. Dover flint provides an excellent isotropic standard to determine texture corrections for quartz.

4. Weak and oblique textures were reliably measured on fine-grained flint samples experimentally deformed in torsion.
6.2 Quantitative comparison of random, weak and strong textures in quartz aggregates measured by X-ray goniometry, EBSD and synchrotron diffraction


Abstract

This contribution reports on textures (or lattice preferred orientations, LPO) measured by three different techniques (X-ray goniometry, EBSD, synchrotron diffraction) in natural and experimental quartz samples. The concept of texture index is employed to quantitatively compare the degree of preferred orientation by taking into account the different and always finite sizes of the respective analyzed grain populations. Our data stems from measurements of weak and random textures in samples of Dover flint after heat-treatment and deformation experiments and of strong textures in natural quartz mylonites from the Late Cretaceous Pejo fault (Italian central-eastern Alps).

Orientation data sets of different sizes were compared after appropriate normalization to an infinite number of data. The necessary number of independent data increases with decreasing strength of the texture itself and with increasing angular resolution (decreasing smoothing width) requested for the derived distributions.

Weak and random textures in flint can be reliably measured by EBSD, goniometry as well as synchrotron experiments and distinguished based on the evaluation of texture index with respect to the sampling number. Crystallographic fabrics of quartz mylonites were successfully analyzed using both X-ray goniometry and automated EBSD and the results compare well for data sets representing similar numbers of independent grains.

Statistical relevance of EBSD data can be evaluated by the analysis of texture index and its asymptotic extrapolation behavior versus number of measurements. The stationary value of the asymptotic extrapolation (if any) is a useful characteristic to compare texture strength of data sets obtained from different samples.

Keywords:
Lattice preferred orientation, texture index, X-ray goniometry, electron backscatter diffraction, synchrotron, quartz, random distribution.
6.2.1 Introduction

Lattice preferred orientations (LPO) in naturally and experimentally deformed rocks are studied to provide better constraints on the microscopic mechanisms which drive deformation and recrystallization of geologically significant materials (for quartz e.g. Tullis et al. 1973, Lister and Paterson 1979, Mancktelow 1987, Gleason et al. 1993) as well as on the possible deformation path and kinematics (e.g. Schmid 1982, Schmid and Casey 1986, Law 1990; also see Wenk 1985, 1998 for overviews).

Several techniques are available for fabric analysis in quartz. The optical polarization microscope equipped with a universal stage has been a widely used instrument to study fabrics, and can be adapted to fully automated analysis of c-axis orientations (Heilbrunner-Panozzo and Pauli, 1993). Automated X-ray and neutron goniometry provides a statistically reliable approach to analyze the complete crystal orientations (e.g. Bunge and Wenk 1977, Bouchez et al. 1979, Schmid et al. 1981, Casey 1981). The study of fabric and microstructural characteristics of geological materials has been greatly improved and given new impetus by electron channeling (Lloyd 1987) and by electron backscatter diffraction (EBSD) (for quartz e.g. Kunze et al. 1994, Trimby et al. 1998, Van Daalen et al. 1999, Heidelbach et al. 2000, Neumann 2000) in the scanning electron microscope (SEM). These techniques allow local measurements of complete crystal orientations with high spatial resolution, maintaining the link between the microstructural appearance and the crystallographic orientation of grains. Fully automated analysis of EBSD patterns provides the tool for orientation mapping, also known as orientation imaging microscopy (OIM, Adams et al. 1993).

The analysis of finite sets of real orientation data must be performed carefully, acknowledging the presence of errors in the data from several sources, but also taking into account principal statistical considerations. Factors to be mentioned are sample grain size, sampling volume, counting statistics, sample alignment, data normalization and number and choice of pole figures. Hence, the question arises, how far the results of LPO measurements, obtained through different experimental procedures on different instruments by different operators, are comparable and independent of the specific experimental conditions. To which extent can different data sets be reasonably compared? How should the texture strength that is derived from differently large data sets be evaluated? Perhaps even more relevant for utilizing EBSD to address geological problems is the following point: Given the high spatial resolution of the EBSD measurements and therefore the great detail achievable at the microscale, how many individual orientations have to be measured in a single sample in order to obtain a figure which is representative of the bulk sample texture and not exclusively of that local domain?
Trying to address these points in this contribution we employ the concept of texture index to quantitatively compare the ODF calculated from incomplete pole figures measured with an automated X-ray texture goniometer as well as using synchrotron or neutron radiation with ODF derived from local orientation measurements performed through automated EBSD. This approach will enable us to propose some general conclusions and recommendations for comparison of datasets based on differently sized (but always finite) datasets and obtained by different techniques. Our data stems from measurements of weak and random textures in flint (Dover flint) and of strong textures in natural quartz mylonites from the Late Cretaceous Pejo fault in the Italian central-eastern Alps. Most of these samples would not be accessible to conventional U-stage analysis because of small and very small grain sizes.

6.2.2 Theoretical considerations

6.2.2.1 Texture strength of finite data sets

Preferred orientations in a polycrystalline aggregate are quantitatively characterized by the orientation distribution function (ODF) \( f(g) \) defined by

\[
f(g)dg = \frac{dV}{V}
\]

with

\[
\int dg = 1 \rightarrow \int f(g)dg = 1
\]

which describes the volume fraction \( dV/V \) of grains in the aggregate that possess an orientation \( g \) within an orientation element \( dg \). It compares the sample texture with a random distribution of orientations \( (f(g) = 1) \) and is measured in multiples of a random distribution (m.r.d.). The strength of a texture is often characterized by the ODF intensity at its maximum, while the ODF minimum is sometimes used as estimate of the volume fraction with no preferred orientation. The weight of texture components can be identified by the integral over the ODF within a certain angular tolerance around problem-specific orientations. As an integral measure of the overall strength of a texture, the texture index \( J \)

\[
J = \int f^2(g)dg
\]

has been introduced, which gives 1 for a random ODF, but diverges to infinite positive numbers as the texture approaches the case of a single orientation covering the whole sample volume.

These considerations imply the assumption, that any orientation \( g \) is actually present in the sample with a frequency (or more precisely in a volume fraction) corresponding to the value of the ODF
for that \( g \). This would require an infinite number of grains in the sample volume, i.e. of elementary crystallites with a size infinitely smaller than the total volume \( V \).

The estimation of a (continuous) ODF from a (discrete) number of orientations is usually based on a convolution procedure

\[
    f(g; b) = \frac{1}{N} \sum_{n=1}^{N} f_G(g; g_n, b)
\]

where each individual measurement \( g_n \) is represented by a smooth distribution with peak at \( g_n \) and some finite width \( b \). This may be done by stepwise constant functions on a raster in orientation space with say 5 degrees spacing. Here we use bell-shaped distributions (so-called standard Gaussians), where the width \( b \) is the full width at half maximum.

It is clear, that the resulting ODF depends to a large amount on the choice of \( b \) for a given data set of \( N \) orientations. If \( b \) is chosen much smaller than the average orientation distance between the measurements, then the estimated ODF is composed of \( N \) individual peaks at the measured orientations with negligible overlap. On the other hand, if \( b \) is chosen very wide, then these peaks overlap significantly and the angular resolution of the ODF estimate is delimited, which hides further details in the data set.

Any ODF calculated from a finite data set contains some uncertainty, and will deviate from the one expected for an infinite number of data. The more data can be added, the closer the estimate should approach the latter. Matthies (1996) and Wagner et al. (1998) showed, that the texture index \( J_N \) for a finite number \( N \) of (independent) orientation measurements can be estimated by

\[
    J_N(b) = J_\infty(b) + \frac{1}{N} \left( J_1(b) - J_\infty(b) \right)
\]

where \( J_1(b) \) and \( J_\infty(b) \) are the texture indices for a single orientation and of the (unknown) distribution with infinite number of data, respectively. As illustrated in Fig. 6.10, this can be used to extrapolate the measured series of indices for finite \( N \) to the limit of infinitely large data sets, and thus to find a common basis to compare textures from measured data sets of different sizes. The extrapolated number is called the asymptotic texture index \( J_\infty(b) \), which still depends on the finite number \( N \) of available data, where the extrapolation is based on. However, the asymptotic index approaches much faster the limit of \( J_\infty(b) \) than the index \( J_N(b) \) itself. The texture index for a finite data set always overestimates the value expected for infinite \( N \). Even if the texture is truly random, the estimated texture index is always larger than 1 for any finite \( N \) and approaches 1 asymptotically with \( N \) towards infinity.
6.2.2.2 Texture index for weak and random textures

It is obvious, that the estimation of weak textures requires a larger number of data than for a sharp texture. In particular, the texture index J becomes less and less of a reliable tool to distinguish a weak texture from a random one as the texture gets weaker and the number of data reduces. This behavior will be illustrated by a simplified model calculation.

Let an aggregate be composed of two parts, a volume fraction $w$ ($0 < w < 1$) occupied by an arbitrary orientation $g_0$, and the remaining volume fraction $(1-w)$ containing random orientations. The corresponding model ODF calculated for a certain Gaussian width $b$ reads

$$f(g, g_0, b, w) = w \times f_G(g, g_0, b) + 1 - w$$

(6.8)

The ODF is equal to 1 for all $g$, if $w=0$ (random, 0% LPO). For $w=1$ it is equal to a Gaussian distribution with width $b$ around $g_0$ (single crystal, 100% LPO). Thus we will call $w \times 100\%$ the 'Percentage LPO' in this model (% LPO).

Such model textures have been simulated by finite data sets containing a certain number of random orientations plus a defined percentage of an arbitrary single orientation. Few model textures are shown in Fig. 6.11, where differently large data sets are processed and displayed as contour plots. For 100 data entries, it is impossible to distinguish visually the figures for a random texture from those for 2% LPO, and even for 1'000 measurements this difference appears spurious. It takes probably over 10'000 measurements, before a random data set will be immediately recognized as such. Vise versa, the sharp maxima in the pole figures for 10% LPO are clearly
visible in the set of 100 data, even though the choice of contour lines diminishes the absolute height of the c-axis maximum.

\[ J \approx (b, w) = 1 + w^2 \times (J_1(b) - 1) \] (6.9)

It is a quadratic function in \( w \), which is equal to 1 for \( w=0 \) (random LPO) and equal to the texture index of a single crystal \( J_1(b) \) for \( w=1 \). This expression inserted in Eq. (6.7) results in

\[ J_N(b, w) = 1 + (J_1(b) - 1) \times \left[ \frac{1}{N} + w^2 \times \left( 1 - \frac{1}{N} \right) \right] \] (6.10)

which is illustrated in Fig. 6.12. The texture index of a single crystal is obtained, if the last factor (in square brackets) is 1, which is the case either for \( N=1 \) (one measurement) or for \( w=1 \) (single crystal LPO). In any other case, the texture index falls below that of a single crystal. It reaches the random value of 1, only if the expression in brackets is zero, which requires \( w=0 \) as well as \( N=\infty \).

For a small \( N \), the texture index can be significantly above 1 even for very weak textures. For example, using \( b=15^\circ \), any data set with \( N=100 \) gives a similar texture index of 3, if the texture...
contains between 0% and 3% LPO. Therefore the texture index would not allow to distinguish whether such a data set corresponds to a weak or a random texture. Eq. (6.10) is applicable to orientation data like the ODF as well as to directional data like pole figures, if the appropriate values for $J_1(b)$ are applied.

Fig. 6.12 Texture index $J_N(b,w)$ vs. % LPO for $N = 100, 300, 1'000, 3'000, 10'000, \infty$ and smoothing width of 10°, 15°, 30° (double log scale). Pole figures (inset) of c- and a-axes for random (left) and 2% preferred orientation (right) using smoothing width of 10° (top), 15° (middle) and 30° (bottom) and number of measurements $N = 10'000$. Contour intervals in logarithmic scale at 0.85, 0.92, 1.0, 1.08, 1.18, 1.28, 1.38, 1.50, upper hemisphere, equal area projections.
6.2.3 Methods for texture measurements

6.2.3.1 Sample preparation

Flint

The analysed samples of Dover flint were heat-treated and deformed in torsion experiments. They had a diameter of $9.9 \pm 0.1 \text{ mm}$ and a length of $8 \pm 0.5 \text{ mm}$. Due to the geometry of torsion testing, a strain (and strain rate) gradient along the radius of the samples exists, with zero strain along the cylinder axis, and maximum at the outer radius (Paterson and Olgaard, 2000). For texture analysis of torsion samples, two different ways of cutting were chosen in this study:

1. For EBSD and texture goniometry, cylindrical bulk samples were cut perpendicular to the cylinder radius and about $300 \mu\text{m}$ away from the outer edge. This resulted in a planar surface with typical dimensions of $8 \times 10 \text{ mm}^2$. In such sections, shear direction is approximately parallel to the section. Shear strain, strain rate and shear stress are nearly constant across such section. The samples were mounted in Plexiglas discs of 25 mm diameter. The polishing and coating procedures of the samples for the EBSD analysis were the same as for the natural mylonites (see below). No further preparation was needed for X-ray goniometry.

2. For synchrotron experiments, thin slabs of about $100 \mu\text{m}$ thickness were prepared from central cuts containing the cylinder axis. Such sections allow to investigate the texture as a function of shear strain / shear strain rate in a radial profile from the center to the edge of the sample. The slabs were prepared by sawing and mechanical polishing, temporarily mounted on glass slides using crystal bond.

Natural mylonites

Circular slabs (10 mm high, 25 mm diameter) were cut from oriented hand specimen, mechanically polished using diamond paste with a particle size of $0.25 \mu\text{m}$ and subsequently ultra-polished for 14 hours with SYTON colloidal silica suspension. The surface was coated with 2-4 nm carbon coating, which was enough to avoid major charging problems during SEM work. Nearly the same areas on the polished slabs were analysed with both EBSD and X-ray texture goniometry.

6.2.3.2 X-ray goniometry

X-ray texture measurements were performed on a standard goniometer (SCINTAG XDS 2000) with Cu-Kα radiation (0.154 nm) and a solid state HPGe-Detector. Energy discrimination enables Kβ-suppression without any physical filter and hence gives higher count rates than with a
Determination of lattice proportional counter and Kβ-filter. For the small flint samples (dimensions around 10 mm), a small (0.5 mm diameter) collimator was used. For the standard samples (diameter 25 mm) a 1 mm collimator was installed, which gives an optimum between sampling area, resolution and count rates.

Due to the absorption of X-rays in matter the depth of analysis is rather limited (in the case of quartz ~ 0.1 mm). Grain statistics were improved by oscillating the samples over a range of 10 mm parallel to the surface resulting in an effective sampling volume of 5 x 10 x 0.1 mm³ on average.

Incomplete reflection pole figures were measured in a 5° raster for 8 diffraction peaks (see Table 6.1 for details). The acquired incomplete and overlapping pole figures were processed by ODF calculation using the discrete WIMV procedure (software Beartex, Wenk et al. 1998). As illustrated for the case of sample RJ17 in Fig. 6.13a, the measured incomplete pole figures and the recalculated complete figures agree well. The fit is quantified by RP-values between 8% and 15% (Table 6.1). The outer unmeasured areas (left empty due to defocusing effects) are successfully integrated into the bulk sample texture without additional measurements of incomplete transmission pole figures. Complete pole figures of major crystal directions and poles were recalculated from the ODF after smoothing with a certain Gaussian width. The diagrams have the same orientation as the microphotographs (Fig. 6.15), normal to the foliation plane and with the lineation in the drawing plane from left to right. This reference system will be kept constant for all pole figures in this paragraph.

<table>
<thead>
<tr>
<th>20° Cu-Kα</th>
<th>(hkl)</th>
<th>Overlap weight (%)</th>
<th>RP0(%)</th>
<th>RP1(%)</th>
<th>PF Min (mrd)</th>
<th>PF Max (mrd)</th>
<th>PF range</th>
</tr>
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<tr>
<td>20.83</td>
<td>10-10</td>
<td>100</td>
<td>14.16</td>
<td>9.43</td>
<td>0.13/0.12</td>
<td>3.27/4.73</td>
<td>60°</td>
</tr>
<tr>
<td>26.64</td>
<td>10-11/01-11</td>
<td>70/30</td>
<td>8.74</td>
<td>8.00</td>
<td>0.44/0.25</td>
<td>2.94/2.92</td>
<td>65°</td>
</tr>
<tr>
<td>36.50</td>
<td>11-20</td>
<td>100</td>
<td>14.60</td>
<td>10.32</td>
<td>0.13/0.12</td>
<td>4.31/4.63</td>
<td>70°</td>
</tr>
<tr>
<td>39.43</td>
<td>10-12/01-12</td>
<td>17/83</td>
<td>9.94</td>
<td>10.18</td>
<td>0.01/0.03</td>
<td>4.11/3.93</td>
<td>70°</td>
</tr>
<tr>
<td>45.77</td>
<td>20-21/02-21</td>
<td>33/67</td>
<td>14.31</td>
<td>10.76</td>
<td>0.13/0.20</td>
<td>2.85/2.82</td>
<td>75°</td>
</tr>
<tr>
<td>50.14</td>
<td>11-21</td>
<td>100</td>
<td>9.42</td>
<td>9.03</td>
<td>0.11/0.15</td>
<td>3.38/2.83</td>
<td>75°</td>
</tr>
<tr>
<td>59.95</td>
<td>21-31/12-31</td>
<td>53/47</td>
<td>14.27</td>
<td>12.01</td>
<td>0.28/0.25</td>
<td>2.67/2.50</td>
<td>80°</td>
</tr>
<tr>
<td>73.42</td>
<td>10-14/01-14</td>
<td>22/78</td>
<td>12.32</td>
<td>8.53</td>
<td>0.01/0.01</td>
<td>5.63/5.05</td>
<td>80°</td>
</tr>
</tbody>
</table>

Table 6.1 Experimental details of X-ray goniometry as applied to the three mylonite samples with data resulting from ODF calculation for sample R17. Diffraction angle 20, lattice plane indices hkl including overlaps, overlap weight, ODF goodness of fit parameters RP0 and RP1, pole figure intensities and ranges.
Fig. 6.13  a) X-ray goniometry from sample RJ17. Measured incomplete pole figures and corresponding complete ones recalculated from ODF. Goodness of fit, as quantified by RP values, is given in table 6.1. b) Comparison between X-ray goniometry and EBSD for sample RJ17. Pole figures of 6 significant planes and directions from X-ray measurement (first row) and from the large and small scan EBSD data sets (second and third row).

6.2.3.3 Synchrotron diffraction

Synchrotron experiments were performed on the Microfocus beamline at the European Synchrotron Radiation Facility in Grenoble (France) to perform local texture measurements along a radial profile in torsion samples. The sample sections of 100 μm thickness were measured in
transmission geometry with a monochromatic beam ($\lambda = 0.78\,\text{Å}$) focused to a diameter of 30 $\mu$m, resulting in a sampled volume of $10^{-4} \, \text{mm}^3$. The samples were rotated around one axis perpendicular to the beam up to ±62.5° in 5° steps. This rotation axis is parallel to the radius of the torsion sample. Polycrystal diffraction patterns (Debye-Scherrer rings) were recorded with a two-dimensional CCD detector, from which incomplete pole figures were constructed for up to eight lattice planes. Those were used to calculate the ODF using the discrete WIMV procedure. Complete pole figures were recalculated from the ODF, after smoothing with a Gaussian of 15° FWHM. Sampling statistics were improved by averaging over several measurements performed at different axial but same radial positions. A detailed description of the texture analysis by synchrotron experiments is given in Heidelbach et al. (1999).

### 6.2.3.4 Electron backscatter diffraction

The automated analysis of EBSD patterns in the SEM offers a unique tool to link the complete crystal orientation to the location being measured on the sample surface, with an angular accuracy of about 1° and a spatial resolution of less than 1 $\mu$m. The measurements were performed on a SEM CamScan CS44LB furnished with an EBSD attachment. Video images of the diffraction patterns were background corrected, frame averaged and contrast enhanced before being transferred on-line into the processing software OIM 2.0 (TSL Inc.) on a SGI Indy workstation. The sample surface is tilted by 70° to the incident beam. EBSD patterns were recorded using 15 kV accelerating voltage and a beam current of approximately 3 nA. Orientation measurements were performed at all points of raster scans of various sizes and spacings.

From the sets of individual orientations, ODF and pole figures were calculated through Gaussian convolution with a 15° smoothing width within the harmonic expansion calculus to a maximum expansion degree of $L=47$ (algorithm HIOR, software Beartex). Fig. 6.13b shows the resulting pole figures represented by density contours for sample RJ 17 for two data sets from a large and a small area scan.

### 6.2.4 Applications

#### 6.2.4.1 Weak and random textures of quartz in flint

##### 6.2.4.1.1 Motivation

Flint from the Upper Cretaceous Chalks of Dover is a fine-grained (less than 1 $\mu$m grain diameter), water-rich (1.3 wt.% H2O) quartz aggregate with a high purity (98.2 wt.% SiO2). Due to its random texture it is a suitable starting material for rock deformation studies. Deformation
experiments on flint were performed in a Paterson gas medium apparatus with torsion capabilities in order to study the evolution of microstructure and texture with strain (see Chap. 5). Grain growth mainly during heat-treatment of the samples prior to deformation resulted in an average grain size of about 5 μm. Rheological and microstructural analysis showed that the samples deformed by granular flow involving mainly the relative movement of rigid grains. Granular flow was accommodated primarily by diffusive mass transfer and grain boundary sliding. Texture measurements should indicate whether and to which extent intracrystalline deformation may have occurred. As this process is certainly not dominating, any effects will be small. The task was to identify whether the texture changed at all during the experiments and to distinguish between random and weak textures.

6.2.4.1.2 Results

Textures were measured on experimental samples by X-ray texture goniometry, EBSD and synchrotron experiments. Pole figures for the c- and a-axes were obtained by each of the three techniques for a heat-treated sample and a sample experimentally deformed to \( \gamma = 3.3 \). They are correlated to the number \( N \) of grains in the respective measured volumes, which was estimated by dividing the irradiated sample volume (5 mm\(^3\) for normal collimator, 1 mm\(^3\) for small collimator goniometry, 10\(^{-4}\) mm\(^3\) for synchrotron) by the average grain volume. For EBSD measurements the scanning step size of 7.5 μm means, that nearly each raster point has hit a different grain, and thus the number grains measured was about equal with the total number of data. The EBSD measurements were filtered by a minimum confidence index of 0.2 resulting in \( N = 13'000 \) (for the heat-treated sample) and \( N = 2'000 \) (for the deformed sample), both out of a total data set of about 25'000.

The heat-treated sample shows a nearly perfect random texture for all three measurement techniques (Fig. 6.14 left). Goniometry pole figures compare very well with the ones obtained by synchrotron experiments. In the EBSD data a spurious c-axis concentration appears in the middle of the pole figure.

The deformed sample shows a weak but clearly developed and reproducible texture for all three techniques (Fig. 6.14 right). Again, texture goniometry and synchrotron measurements gave very consistent results. A c-axes maximum is oriented in the tectonic XZ-plane at about 70° to the shear zone boundary (SZB) against the sense of shear. The a-axes [11-20] (and also prism m-poles (10-10)) form girdles perpendicular to the c-axis maximum, therefore at about 20° to the SZB. The observed obliqueness of the c-axis maximum is opposite to that often observed in natural quartz.
Fig. 6.14 Model curves of texture index $J_N(b,w)$ vs. % LPO for $N = 300, 2'000, 6'000, 10'000, \infty$ and smoothing width $b = 15^\circ$. Indicated are empirically determined error bars for 6 different data files at different % LPO and corresponding standard deviations 1$\sigma$, 2$\sigma$ (shaded areas). Pole figures: Experimentally heat-treated sample (left) and deformed sample (right, $\gamma = 3.3$, dextral sense of shear) of Dover flint, measured with three different methods (EBSD, Synchrotron experiments, texture goniometry), contour intervals in logarithmic scale at 0.85, 0.92, 1.00, 1.08, 1.18, 1.28, 1.38, 1.50, upper hemisphere, equal area projections, smoothing width 15$^\circ$. Symbols indicate % LPO in the samples derived from the texture indices and the estimated numbers of measured grains $N$. Open symbols are heat-treated (undeformed) sample, filled ones are deformed sample.
mylonites (Schmid and Casey, 1986). In the EBSD pole figures the c-axis maximum is spread around the periphery primarily normal to the SZB.

6.2.4.1.1 Discussion

The texture indices obtained from the three measurements are compared with the model curves of texture index $J_N(b=15^\circ, w)$ for various numbers of data $N$ against the amount of preferred orientation $w$ (% LPO, Fig. 6.14 middle). For all three techniques, a higher % LPO is obtained for the deformed sample compared to the heat-treated sample. The texture indices from goniometry and synchrotron experiments suggest less than 1% LPO in the heat-treated sample and between 1 and 2% LPO for the deformed sample. The texture indices from the EBSD data indicate always a little higher % LPO for both samples. In order to verify this trend, we compared texture indices of four different data sets ($N=300, 2000, 6000, 10'000$) derived from different EBSD scans on the deformed sample. The data set with $N=300$ was actually indexed manually, covering an area of $8\times10\,\text{mm}^2$ with about $500\,\mu\text{m}$ step size to ensure that completely uncorrelated data are taken. All four data sets yield about 4% LPO, indicating that the EBSD measurements are self-consistent within this wide range of data sets.

It is interesting to note that the texture strength seems to be representatively described by only 300 reliable measurements, after appropriate scaling according to the size of the data set. In fact, for a finite data set of $N=300$, the texture index cannot be much lower than 1.7 even for a perfectly random data set. Thus the index of 2.080 for the deformed sample still means a rather small amount of preferred orientation (4 % LPO). However, for a large set with thousands of data, the same texture index would translate to nearly 10 % LPO.

The discrepancy in % LPO between EBSD and goniometry as well as synchrotron shows that it is ambiguous to rely only on the absolute % LPO extracted from Fig. 6.14. The texture index is only one number characterizing a continuous probability distribution with 3 degrees of freedom. Also the applied model is the most simple idealization of a non-random orientation distribution. On the other hand, the % LPO estimations verify the trends suggested from a visual interpretation based on the contoured pole figures, which indicate a slightly stronger LPO in the EBSD data than in the others for both samples. Further tests must be performed to determine, whether the applied system for EBSD pattern indexing may introduce some minor bias in favour of certain orientations. This may never be visible in strongly textured data sets, but could appear for nearly random samples and in scans with a high percentage of low confidence indexations.
6.2.4.2 Strong LPO in quartz mylonites

6.2.4.2.1 Sample description

Mylonites represent highly deformed rocks from shear zones at the deeper levels of faults. Microstructural analysis of mylonites has proved to be extremely useful to reconstruct rheological properties of fault zones and to provide additional information on the kinematics and type of flow associated with the fault. In mylonitic zones, quartz is a very common mineral, often occurring in nearly monomineralic quartzites and quartz veins. It is therefore a suitable material to investigate the path and kinematics of deformation in major displacement zones as well as the grain-scale deformation mechanisms.

The quartz microstructure and texture of three lower greenschist facies mylonites were investigated. The studied rocks belong to the mylonitic belt of the Pejo fault, a late Cretaceous extensional fault of the Austroalpine nappe system in the Italian central-eastern Alps. A geological overview was given by Martin et al. (1991) and Werling (1992). However, the structural frame of the fault is more complex than reported by those authors (Viola, 2000), with at least three different phases of tectonic activity and multiple reactivation of older faults and structures. In the following section, samples are described in the order of decreasing amount of recrystallization, which is inferred to be the order of decreasing deformation temperature and/or finite strain.

6.2.4.2.2 Optical microstructures

Sample RJ4 is a strongly recrystallized tectonite. The sample presents a very sharp c-axis preferred orientation evident in the dominant blue interference color. The optical microstructure (Fig. 6.15) is characterized by elongated ribbon grains a few hundred micrometers wide and several millimeters long alternating with bands of newly recrystallized grains, formed presumably by subgrain rotation recrystallization. The boundaries of the ribbon crystals define a dominant grain-shape fabric SA, which is parallel to the foliation observed in the field. Subgrains with an average grain size of 100 μm can be easily recognized in the ribbons, together with a weakly developed but distinct undulose extinction. Subgrain boundaries are at high angle (~70°) to the dominant foliation SA. The recrystallized grains between the ribbons have an average grain size of 20 μm. Their shape fabric is due to slightly elongate grains and asymmetric grain-boundary bulges and defines a weakly developed oblique foliation SB. No shear bands are present in this quartz vein. Based on these microstructural features, as well as on field geological and petrographic indications, a deformation temperature of 350-400°C (623-673 K) is inferred.
Fig. 6.15 Optical microstructures and selected pole figures for mylonite samples RJ4, RJ17 and RJ20. In sample RJ4 the dominant foliation is $S_A^*$ defined by elongate ribbon grains. $S_B$ is the oblique shape fabric defined by slightly elongated recrystallized grains and grain-boundary bulges.
The bulk texture shows an oblique and asymmetric c-axis cross girdle, typical for shear deformation under medium to low metamorphic conditions. However, in contradiction to the simple shear deformation inferred from field evidence, the observed texture pattern clearly deviates from the monoclinic sample symmetry typically expected for simple shear deformation. A kinematic history, characterized by the superposition of more than one non-coaxial deformations in one or subsequent phases, may explain this lack of symmetry.

**Sample RJ17** shows a microstructure, where quartz has undergone a less profound, but still significant dynamic recrystallization and forms a well-defined LPO (Fig. 6.15). The optical microstructure displays large stretched relic quartz grains (aspect ratios of 10:1) with strong intragranular deformation visible through deformation bands and pronounced undulose extinction. The long stretched crystals are separated by domains of small (10 µm) dynamically recrystallized grains. This feature defines typical "core and mantle" structures, with a less defined foliation.

The c-axis pole figure presents an asymmetric pattern, slightly oblique, with some possible remnants of a cross-girdle type I.

**Sample RJ20** presents a distinct optical microstructure, characterized by very elongated quartz grains with aspect ratio in the order of 15-20:1 and with average length of several millimeters (Fig. 6.15). They define the dominant foliation. Intracrystalline deformation is recognizable in deformation bands and in widespread undulose extinction. At the grain boundaries there is evidence of incipient recrystallization by bulging and subgrain rotation recrystallization forming few new grains with an average grain size of 10 µm. The rock is overprinted by numerous conjugate sets of calcite-filled fractures (not visible in the figure). Compared to the previous samples, RJ20 is characterized by the lowest deformation temperature (around 300°C (573 K)).

The sample shows a sharp lattice preferred orientation with two asymmetric maxima forming an incomplete c-axis girdle in large angle to the lineation.

6.2.4.2.1  **Results from texture analysis**

For each of the three samples, the LPO from X-ray goniometry is compared to two different sets of EBSD measurements. In the "large scan", an area of 25 mm² (5 mm x 5 mm) was analysed on a square raster with a 50 µm scanning step size, for a total of 10'201 individual orientations measured. An additional "small scan" covers an area of 0.8 mm² (0.8 mm x 1 mm). A scanning step size of 8 µm was used resulting in a total of 12'726 measurements. We will use the results from texture goniometry as a reference in order to facilitate comparison with the EBSD data.
Pole figures for RJ17, obtained from texture goniometry data and EBSD analysis for both large and small scans, are qualitatively compared at the same scale in Fig. 6.13b. Goniometry pole figures compare especially well with the pole figures obtained from the EBSD large scans, whereas in the small scan pole figures, the average peak intensities are higher. Also the c-axis girdle differs slightly from the two other distributions, displaying a stronger asymmetry and less intensity normal to the foliation.

Despite the large number of data acquired in the EBSD scans, the covered sample volume is still small compared to the volume contributing to X-ray pole figure measurements. Hence, it is necessary to develop a criterion capable of indicating the minimum number of necessary measurements. It is obvious that the necessary number of measured grains depends on the texture itself. A very sharp texture is satisfyingly characterized by only few measurements, whereas a random texture will only be revealed after many thousands. In practice a measure is needed, which is based on the counted finite data set itself.

Given the relatively strong textures, the texture index \( J \) should be an efficient tool to compare the texture strength of the different samples on a quantitative basis. We analysed the texture index behavior against the smoothing width used in the ODF calculations (Fig. 6.16). All possible curves are restricted to an area bound by the horizontal axis (corresponding to a random texture \( J=1 \)) and the dotted curve for a single crystal orientation, which represents the strongest possible texture. An excellent agreement is obtained regardless of the smoothing width for the texture indices from goniometry data (WIMV calculations) and from the EBSD large scan data. In all three examples, an EBSD scan over an area of 25 mm\(^2\) (with a 50 \( \mu \)m scanning step) provides about the same information about the texture of the sample than that obtained through X-ray texture analysis. It might therefore be considered representative for the sample texture at that scale. Only slightly different \( J \) values are obtained for extremely low (< 5°) smoothing width values, which is below the angular resolution of the goniometry pole figures and ODF calculation. For the harmonic treatment of EBSD data, truncation of the series expansion at \( L=47 \) results in an underestimated texture index for very small smoothing widths, where it should theoretically diverge to infinity at zero smoothing.

However, the \( J \) values for the small scans tend to be much more sensitive to the smoothing width. For smoothing with more than 30° they are not too different from those computed for the large scans and the texture goniometry analysis. However, with decreasing smoothing width, the small scan curves deviate dramatically from the other two. Therefore, no reliable information on the bulk texture can
Fig. 6.16 Texture index versus smoothing width $b$ for the three mylonite samples in comparison between WIMV (X-ray goniometry), large scan and small scan EBSD and single crystal.
be extracted from such small areas of investigation (less than 1 mm$^2$). Nonetheless, these scans are extremely useful in order to gain highly detailed information on spatial orientation correlations across subgrain and grain boundaries and to map the orientation variations within individual grains. This may help to understand small-scale processes such as recrystallization mechanisms, but is beyond the scope of this contribution.

It is also worth noting that, according to the structural and fabric descriptions given in the previous sections, the J values are highest in sample RJ 4, which displays the strongest microstructural fabric.

6.2.5 Discussion

6.2.5.1 Significant and redundant measurements

Comparison of the EBSD large scans with X-ray goniometry showed, that LPO can be reasonably measured by either technique. The total scan size and the step size for EBSD must be chosen with respect to the average grain size and its homogeneity within the sampled area. For pure texture determination, there is no reason to scan with a smaller step size than the grain size. This ensures, that almost any raster point will hit another grain, and that an area as large as possible will be scanned with the minimum necessary effort. Considering the various grain sizes in the investigated samples, it is obvious that the size of the EBSD scanning grids alone does not provide an objective measure for sampling statistics. It is demonstrated by the EBSD small scans, that adding lots of (redundant) data by reducing the step size much below the grain size does not improve the statistical content of the data set, but rather complicates an extrapolation to infinitely large data sets as proposed above (Fig. 6.17).

According to Eq. (6.10) the texture index derived from a finite data set will systematically decrease with increasing number of data. However, the extrapolation of $J_N(b)$ to $N=\infty$ should remain constant after a relatively small number of measurements. Fig. 6.17 shows the evolution of the texture index $J_N(b)$ (filled symbols) and the asymptotically extrapolated texture index $J_\infty(b)$ based on the curve $J_n(b)$ for $n=1...N$ (empty symbols) with increasing number $N$ of measurements for each of the six large and small scan data sets. For these plots, the $N$ orientations are always arbitrarily picked out of the complete scan file, so that the data enter the set in the least correlated manner. Starting at some high values for small numbers of data, the indices stabilize with a few hundred to thousand measurements. The indices $J_N(b)$ remain noisier and decrease much slower than their asymptotic extrapolations, but eventually approach stationary values as well. The smaller the smoothing width applied and therefore the higher the desired angular resolution of the ODF, the more data it takes to reach stationary indices.
Fig. 6.17 Texture index $J_\gamma(b)$ (filled symbols) and asymptotic extrapolation $J_\infty(b)$ (empty symbols) versus number of measurements $N$ for large and small EBSD scans for the three mylonite samples. Smoothing width $b = 5^\circ, 10^\circ, 15^\circ, 30^\circ$ and $45^\circ$ applied to ODF calculations.
The large scan data set of RJ4 barely satisfies stationary conditions for smoothing of 15° and certainly not below, whereas an ODF calculated with 30° smoothing would represent the coarse texture quite well, even based only on half of the data set. The two other large scan data sets RJ17 and RJ20 reach a representative size well after about 5,000 measurements, when judged for the commonly applied smoothing width of 15°.

On the other hand, the value, at which the extrapolated index stabilizes, should be possible to use as a reasonable estimate for the texture strength of the sample. This should not need measuring as many orientations, until the finite index actually reached a steady value. However, this is only valid, as long as the measured orientations are uncorrelated data, i.e. each entry in the list is completely independent from all the previous entries.

None of the small scan data sets satisfies this criterion of independence despite the vast number of measurements indicating a large redundancy in these data. For example, in the RJ4 small scan, all the curves have stabilized already after about 1,000 measurements, and the further 90% of data do not modify them anymore. In that case, the indices may be stationary, but are not at all representative of the larger scale bulk texture.

An evaluation of the "minimum necessary" number of data needs to be calibrated by the ratio of average grain size to scanning step size. The same area of a small scan at 8 μm step size covered by the 12'726 grid points is scanned by 12'726*(8/50)^2 = 326 measurements in the large scan at 50 μm step size. If this large scan hits each grain on average already at least once, there is no further improvement possible by the refined raster of a small scan. In fact, the texture indices for the complete small scan data sets compare well to those in the large scan diagrams for a few hundred measurements.

6.2.5.2 Smoothing and angular resolution

The slope at which the texture approaches a stationary situation with increasing number of measurements depends significantly on the smoothing width b during data processing. Any contouring procedure contains such a smoothing parameter, either explicitly stated or implicitly hidden. For goniometry and synchrotron experiments, it is at least the angular distance between individual sample positions of 5°, which is also the numerical resolution of the WIMV procedure for ODF calculation. Typically an additional smoothing of 15° is applied. For the EBSD data, the smoothing width should at least not be smaller than the angular precision of the pattern indexation procedure of about 1°, which may be the way of choice for specific problems. In general practice a much larger smoothing (often 15° and larger) is applied for several reasons:
Data sets are typically noisy, and smoothing suppresses some artificial detail in the presentation, which may actually distract from the main trends in the LPO.

While the orientation relative to a sample fixed reference can be measured precisely, it is often an individual choice to define the structural reference system of foliation and lineation below a precision of 5-10°.

Even if the above sources of errors can be neglected it requires much more data to define a LPO with high spatial resolution, than a smooth texture. The average angular distance of orientations in a random data set decreases very slowly with increasing number of data. In the case of quartz (trigonal sample symmetry) it is approximately \( N = \frac{8\pi}{b^3} \) (with \( b \) in radians), that means \( N = 38'000, 5'000, 1'400, 170 \) for \( b = 5°, 10°, 15°, 30° \), respectively. If a weak or random texture should be declared with a certain resolution, at least the above number of (independent) measurements are needed. (For comparison, the equivalent relation for axes on the sphere reads approximately \( N = \frac{8}{b^2} \), with \( N = 1'000, 260, 117 \) for \( b = 5°, 10°, 15° \).)

It is obvious from several curves presented here, that the convergence of the texture indices is much faster after smoothing with 15° than with smaller widths, where a stationary situation may not have been reached yet at all.

If smoothing is performed through harmonic expansion, the maximum necessary expansion degree \( L \) increases about inversely proportional to the smoothing width \( b \). The software package Beartex allows for a maximum \( L = 47 \), corresponding to an angular resolution of about 8°.

With all the argument above in mind, it is crucial for any quantitative and even for a qualitative comparison of LPO data from different sources, that the data are processed using an equivalent smoothing procedure with comparable width. It is demonstrated here how data sets of different size may be possibly compared. However, it is certainly more difficult to compare LPOs that are in addition processed using different smoothing parameters. Therefore it is strongly recommended to indicate the method and width of smoothing for any LPO data published, what has been a matter of course for analysis of directional data like c-axes on the sphere.

**6.2.6 Summary and conclusions**

Orientation data sets of different sizes can be compared after appropriate normalization to an infinite number of data. The necessary number of independent data increases with decreasing strength of the texture itself and with increasing angular resolution (decreasing smoothing width) in the derived distributions.
Weak and random textures in flint can be reliably measured by EBSD, goniometry as well as synchrotron experiments and distinguished based on the evaluation of texture index with respect to the sampling number. Crystallographic fabrics of quartz mylonites were successfully analyzed using both X-ray goniometry and automated EBSD and the results compare well for data sets representing similar numbers of independent grains.

Statistical relevance of EBSD data can be evaluated by the analysis of texture index and its asymptotic extrapolation behavior versus number of measurements. The stationary value of the asymptotic extrapolation (if any) is useful to compare texture strength of data sets obtained from different samples. On-line evaluation of the asymptotic extrapolation during data acquisition would allow the operator to optimize statistical reliability of data sets.
Chapter 7

7 Experiments on different starting materials

7.1 Introduction

Besides of Dover flint, two other starting materials were tested for deformation in torsion: hot-pressed silicic acid (synthetic quartz aggregate) and Arkansas novaculite (natural quartz aggregate). The advantage of using synthetic quartz aggregates is to have a starting material in which water content and grain size can be varied in order to study the effect of these factors on the deformation behavior. The disadvantage is that the fabrication of a homogeneous synthetic quartz aggregate is not easy, as will be discussed in this chapter. The sample preparation for natural quartz aggregates is relatively fast and easy, since the starting material already exists in nature. This offers the possibility to conduct many deformation experiments in a relatively short amount of time. Arkansas novaculite was used since it is a fine-grained, homogeneous and isotropic material. The disadvantage is that natural quartz aggregates generally contain some impurities, which may have unpredictable consequences on the rheology. Also, grain size and water content may vary in samples from the same block and even more from different locations. The microstructure from the starting material can be influenced only in very restricted ways prior to the deformation experiments.

This chapter describes the approaches (1) to fabricate a homogeneous synthetic quartz aggregate by using the isostatic hot-pressing procedure (Kingery et al., 1976) and (2) to deform synthetic quartz aggregate as well as (3) Arkansas novaculite in torsion. It was found that the two types of starting material were not suitable for this study due to the following reasons:

(1) The fabrication of the synthetic quartz aggregate did not give a satisfactory starting material.

(2) The deformation of synthetic quartz aggregates was ambiguous due to the presence of cristobalite in the prepared starting material. Furthermore, the samples had a very high strength preventing shear strains of $\gamma > 0.1$.

(3) Arkansas novaculite was too strong to be deformed in torsion.
7.2 Fabrication and deformation of synthetic quartz aggregates

7.2.1 Motivation

The first attempts to deform quartz in torsion were made by using hot-pressed silicic acid as starting material. Silicic acid was chosen because it was already successfully hot-pressed and subsequently deformed in compression in a Paterson gas medium apparatus by Luan (1989). In his experiments, samples were deformed at 1300 K, 300 MPa and a strain rate of $10^{-5}$ s$^{-1}$ and showed strain hardening behavior. The maximum flow stress was about 200 MPa. The microstructure showed undulatory extinction and grain flattening, suggesting that deformation occurred by intracrystalline plasticity (Luan and Paterson, 1992).

In this study, the same procedure for hot-pressing silicic acid was applied. We hoped to obtain a homogeneous starting material which could be deformed in torsion to high shear strain.

7.2.2 Starting material

Silicic acid (SiO$_2$*xH$_2$O) manufactured by Johnson Matthey & Brandenberger AG was tested. According to the manufacturer’s label, silicic acid is amorphous and composed of 99.98 wt.% SiO$_2$ with a 100 mesh particle size (about 150 μm). The initial water content was determined to be 5.2 wt.% from weight loss on heating at 1473 K, 1 atm for 10 h. The powder is white in colour and very flaky.

7.2.3 Experimental procedure

Before cold-pressing, silicic acid was predried by heating for 1 h at 1273 K and 1 atm except two, which were cold-pressed as-received (P176, P180). Water content after predrying was around 2 wt%. The density of the pellets after cold-pressing was typically around 0.9 gcm$^{-3}$. The pellets were very difficult to remove from the iron jacket without damaging them. Therefore, the cold-pressing assembly was directly used for the subsequent hot-pressing by inserting at both ends of the pellet a porous (drained conditions) or non-porous spacer (undrained conditions; see Fig. 4.2, Chap 4). Pore pressure valves were always opened. Details on the cold-pressing and subsequent hot-pressing are given in Chap. 4.

The conditions and results of hot-pressing silicic acid are shown in Tab. 7.1. Hot-pressing was carried out in the Paterson rig at 300 MPa and 1300 K or 1400 K for several hours under drained or undrained conditions. In two of the experiments (P173, P174), an axial load of 1 Nm was applied in order to enhance crystallization. All of the samples showed a strong decrease in volume...
(about 50-60%) during hot-pressing. According to Luan (1989), this shrinkage is due to a combination of phase transformation, water loss and compaction. After hot-pressing, samples were either immediately deformed, or the experiment was terminated by cooling down and depressurizing to room conditions. For one of the samples (P175), the iron jacket was mechanically peeled off after hot-pressing. Afterwards the planar end surfaces of the sample were machined parallel to each other (within ± 5 μm) and oriented exactly perpendicular to the cylinder axis (± 1°) by diamond polishing on a lathe. Then the sample was inserted in a standard sample assembly again for subsequent deformation experiments (P179, P181, P182).

Deformation experiments were performed in torsion at 300-350 MPa and 1300-1400K under undrained or drained conditions (Table 7.2). Strain rates ranged from $1 \times 10^{-5}$s$^{-1}$ to $2 \times 10^{-4}$s$^{-1}$.

The composition of the hot-pressed and deformed aggregates was verified by X-ray diffraction and microscopic observations after the experiments. Water content was determined by loss on ignition for 24 h at 1273 K and 1 atm. In the deformation experiments of Luan (1989) on hot-pressed silicic acid at similar conditions, the stress exponent $n$ was determined to be around $n = 4$. Therefore, an exponent $n = 4$ was also assumed here to convert the torque to shear stress assuming a constant flow law through the whole sample (see Paterson and Olgaard, 2000 and Pieri et al., 2001).

**Table 7.1** List of hot-pressing experiments on silicic acid.

<table>
<thead>
<tr>
<th>Run</th>
<th>Predrying$^1$ (K)</th>
<th>Spacer top</th>
<th>Spacer bottom</th>
<th>Heat-treatment time (h), T (K)</th>
<th>Pc$^2$ (MPa)</th>
<th>Water content (wt%)</th>
<th>Minerals</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P173</td>
<td>1273</td>
<td>np</td>
<td>np</td>
<td>3.5, 1300</td>
<td>300</td>
<td>?</td>
<td>Qtz, Cr, a.s.</td>
<td>Hot-pressed with axial load (1 Nm)</td>
</tr>
<tr>
<td>P174</td>
<td>1273</td>
<td>np</td>
<td>np</td>
<td>5.0, 1300</td>
<td>300</td>
<td>?</td>
<td>Qtz, Cr, a.s.</td>
<td>used for P179$^3$</td>
</tr>
<tr>
<td>P175</td>
<td>1273</td>
<td>np</td>
<td>np</td>
<td>7.0, 1300</td>
<td>300</td>
<td>?</td>
<td>Qtz, Cr, a.s.</td>
<td>loose like sand</td>
</tr>
<tr>
<td>P176</td>
<td>none</td>
<td>np</td>
<td>np</td>
<td>5.0, 1300</td>
<td>300</td>
<td>0.38</td>
<td>Qtz</td>
<td>used for P186$^3$</td>
</tr>
<tr>
<td>P180</td>
<td>none</td>
<td>p</td>
<td>np</td>
<td>5.0, 1300</td>
<td>300</td>
<td>0.08</td>
<td>a.s., Cr</td>
<td></td>
</tr>
<tr>
<td>P183</td>
<td>1273</td>
<td>np</td>
<td>np</td>
<td>3.0, 1400</td>
<td>300</td>
<td>?</td>
<td>?</td>
<td>used for P195$^3$</td>
</tr>
<tr>
<td>P184</td>
<td>1273</td>
<td>np</td>
<td>np</td>
<td>1.5, 1400</td>
<td>300</td>
<td>0.37</td>
<td>Qtz, Cr</td>
<td></td>
</tr>
<tr>
<td>P194</td>
<td>1273</td>
<td>np</td>
<td>p</td>
<td>2.5, 1400</td>
<td>300</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

1. Predrying temperatures before cold-pressing (for 1 h at 1 atm)
2. Confining pressure
3. see Tab. 7.2

*Qtz* Quartz, *a.s.* amorphous silica, *np* non-porous, *Cr* Cristobalite, *p* porous
Table 7.2   List of deformation experiments on hot-pressed silicic acid.

<table>
<thead>
<tr>
<th>Run</th>
<th>Hot-pressing</th>
<th>Set-up</th>
<th>Def. T (K)</th>
<th>Pc (MPa)</th>
<th>Strain rate (10^-4 s^-1)</th>
<th>Water content (wt%)</th>
<th>Minerals</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>P179</td>
<td>P175</td>
<td></td>
<td>1300</td>
<td>300</td>
<td>2</td>
<td>?</td>
<td>Qtz, Cr</td>
<td>slip</td>
</tr>
<tr>
<td>P181</td>
<td>P175</td>
<td></td>
<td>1400</td>
<td>300</td>
<td>-</td>
<td>?</td>
<td>?</td>
<td>leak</td>
</tr>
<tr>
<td>P182</td>
<td>P175</td>
<td></td>
<td>1400</td>
<td>300</td>
<td>0.1</td>
<td>0.1</td>
<td>?</td>
<td>slip</td>
</tr>
<tr>
<td>P186</td>
<td>P183</td>
<td>see Fig. 7.6</td>
<td>1400</td>
<td>350</td>
<td>0.3</td>
<td>?</td>
<td>Qtz, Cr</td>
<td>slip</td>
</tr>
<tr>
<td>P195</td>
<td>P194</td>
<td></td>
<td>1400</td>
<td>300</td>
<td>0.1</td>
<td>0.08</td>
<td>Qtz, Cr</td>
<td>shear fracture</td>
</tr>
</tbody>
</table>

1. Number of hot-pressing run
2. Confining pressure
Qtz Quartz  Cr Cristobalite  ? not available

7.2.4  Heat-treatment

Several different procedures were tested in order to obtain a suitable starting material, which are described and discussed chronologically in the following.

Step 0a: Predried powder, 1300 K hot-pressed, undrained (P173, P174 and P175). After the experiment, P173 and P174 had a very irregular shape, probably resulting from the application of an axial load. A set of typical X-ray patterns illustrating the crystallization sequences of silicic acid is shown in Fig. 7.1a-c, the corresponding microstructures in Fig. 7.2a,b. All of the three samples synthesized only partially: A gradient of amorphous silica, cristobalite and quartz was observed from sample bottom to sample top.

Carr and Fyfe (1958) investigated the crystallization of silicic acid under low temperatures (up to 721 K) and a pressure range of 100 to 400 MPa under hydrothermal environments. They found that the crystallization followed the path amorphous silica → cristobalite → keatite → quartz. Keatite is a tetragonal silica polymorph which has no field of thermodynamic stability. Luan (1989) found that the crystallization processes were faster with high water content than low water content.

In our study, a crystallization path as described in Carr and Fyfe (1958) was found except that keatite was not detected. We believe that during hot-pressing, water was flowing towards the sample top and enhanced there the crystallization process. This hypothesis was confirmed by the experiments P176 (step 0b) and P180 (step 0c):

Step 0b: As-received powder, 1300 K hot-pressed, undrained (P176). As-received silicic acid was used for cold-pressing in order to have a higher initial water content during hot-pressing. During hotpressing, the sample synthesized fully to quartz (Fig. 7.1d). The cohesion of the grains
was very low: except in an outer crust of about 100 \( \mu m \) width, the sample was loose like sand and disaggregated into small pieces when the jacket was peeled off. In optical microscopy, the grain size was strongly heterogeneous: it varied from 5 to 200 \( \mu m \) (Fig. 7.2c). In regions with a coarse grain size, pores were abundant (Fig. 7.3). The water content was relatively high.

Faster crystallization of the as-received silicic acid confirmed that water enhances crystallization processes at least during the first stages of hot-pressing. It was suspected, that the strong heterogeneity in grain size and porosity was related to inhomogeneous water distribution within the sample. Locally elevated water content might have promoted grain growth and the formation of pores. In order to prevent the build-up of a high pore pressure, the next attempt was made by allowing some drainage of the sample.

**Step 0c: As-received powder, 1300 K hot-pressed, partly drained** (P180). A porous spacer at the top of the cold-pressed powder allowed some of the water to escape the sample during hot-pressing. X-ray diffraction of the hot-pressed sample showed that it consisted mainly of amorphous silica. Some cristobalite was detected only towards the sample bottom. The water content was low.

Obviously, most of the water left the sample early during hot-pressing leading to very slow crystallization kinetics. None of the above attempts to produce a suitable starting material at 1300 K were therefore successful due to (1) the presence of cristobalite and/or amorphous phase or (2) strongly heterogeneous porosity and grain size.

Luan (1989) suggested that crystallization of silicic acid to quartz is enhanced by increasing not only the water content, but also the temperature. Therefore, the next three samples of this study were hot-pressed at 1400 K:

**Step 0d: Predried powder, 1400 K hot-pressed, undrained** (P183, P184) and partly drained (P194). P184 crystallized to quartz and cristobalite. The grain size was rather homogeneous (50-150 \( \mu m \)) than in P180 (step 0c), no pores were detected in optical microscopy (Fig. 7.2d). Texture measurements were performed by X-ray goniometry on P184. The texture is very weak with a texture index of \( J = 1.2 \) and a higher probability of the c-axis towards a maximum around the Y-axis (Fig. 7.4). P183 and P194 were immediately deformed in torsion after hot-pressing.
Fig. 7.1 2θ diffraction scans (using Cu-Kα) performed using the texture goniometer on planar bulk samples after hot-pressing from silicic acid (count rates normalized to 100%). Indicated are the most important peaks for quartz (Qtz), cristobalite (Cr) and the broad band for amorphous silica (a.s.). P174 (predried powder). Scans were taken at sample top (a), center (b) and bottom (c). Note decreasing crystallization from sample top to bottom. d) P176 (as-received powder).
Fig. 7.2  Microphotos in plane polarized light (a, b) and crossed polarized light (c-f) of only hot-pressed (a)-(d) and hot-pressed and deformed silicic acid (e)-(f). Qtz = quartz; Cr = cristobalite; a.s. = amorphous silica; u.p. = unknown phase; p = pores. a)-b) P174 (predried powder, hot-pressed with axial load). Partially crystallized at sample bottom (a), fully crystallized to quartz and cristobalite at sample top (b). c) P176 (as-received powder). Note inhomogeneous grain size and porosity. d) P184 (predried powder, 1400 K). Fairly homogeneous grain size. e) P182. Deformed to $\gamma < 0.1$. f) P195. Deformed to $\gamma < 0.1$. 
The most homogeneous starting material was obtained by using predried silicic acid for cold-pressing and by subsequently hot-pressing it at 1400 K under undrained conditions. However, the presence of cristobalite next to quartz could not be avoided, and the range in grain size was still rather high.

Fig. 7.4 Pole figures of synthetic quartz aggregate hot-pressed at 1400 K, 300 MPa for 1.5 h (P184). Sample orientation parallel to cylinder axis. Orientation densities in multiples of random distribution (m.r.d.) in logarithmic scale, upper hemisphere, equal area projections with smoothing width 15°. Texture indices are indicated for the overall textures (based on ODF).

7.2.5 Deformation in torsion

The observed stress-stain behavior in four runs in torsion is given in Fig. 7.5. All of the experiments were terminated by slippage at the sample-spacer interface except one (P195), which failed by formation of a shear fracture. As indicated by the strain marking scratches on the iron jacket, the deformation accommodated by the samples themselves was always $\gamma < 0.1$. Different sample assemblies and conditions were tested in order to avoid slippage (Fig. 7.6). They are described in chronological steps:
Fig. 7.5 Shear stress versus shear strain for torsion experiments performed under various conditions. Run number and step as indicated. Shear stress was calculated from the measured torque assuming a power law creep with stress exponent of $n = 4$.

Step 1: Rejacketing, undrained (P179). At a shear stress of 80 MPa, slippage at the top sample-spacer interface occurred.

The slippage can be explained by the increase in pore pressure reducing the effective pressure and therefore the friction at the sample-spacer interface. In torsion, the specimen is loaded by the friction on its end as function of the effective pressure. If the latter is low, high torque values are
prevented by slip along the sample-spacer interface. In order to avoid this effect, the torsional setup for wet samples should allow some drainage. However, since quartz strength is strongly reduced in the presence of water by different mechanisms (see Chapter 3), some of the water should still remain within the sample. Therefore a setup which allows some buffering of the pore pressure was required.

This was done in experiment P182 (step 2) by inserting a non-porous spacer at the sample top, but a porous one at the sample bottom. Further below a non-porous spacer was added. It was thought that the porous spacer would act as a pore fluid buffer, (1) allowing to reduce the pore pressure at the sample-spacer interface, but (2) preventing that all of the water leaves the assembly:

**Step 2: Rejacketing, partly drained** (P182). Again, slip occurred at about $\gamma < 0.1$ but at much higher shear stress (about 150 MPa) than in the undrained experiment P179. The slip was at the interface between sample and bottom porous spacer.

It was calculated that the porous spacer saturated quickly with water and could not prevent the build-up of a high pore pressure at the sample-spacer interface.

After hot-pressing, the synthesized quartz samples were tightly stacked to the adjacent spacers after peeling off the iron jacket mechanically. It was thought that during hot-pressing the crystallizing silicic acid perhaps reacted with the spacer surfaces and may have formed some kind of a "glue" between sample and spacers. Hence, the two subsequent deformation experiments were performed immediately after hot-pressing, without any interruption by cooling, depressurization, and particularly without rejacketing of the samples:

**Step 3: No rejacketing, undrained** (P186). Slip occurred at high shear stress (200 MPa) after a shear strain of $\gamma < 0.1$ at the top sample-spacer interface.

**Step 4: No rejacketing, drained** (P195). Similar conditions as P186, but a porous spacer was used at the sample bottom. Strain weakening occurred at a shear stress of 150 MPa and a shear strain of $\gamma = 0.05$. A macroscopic examination of the jacketed sample revealed a shear fracture inclined at about 16° clockwise to the SZB (Fig. 7.7). No displacement at the sample-spacer interfaces was detected.

This means that weakening in P195 was not due to slippage but formation of a shear fracture. Therefore, the maximum attained shear stress before fracture and slippage could not be evaluated in this experiment.
The microstructures of the three deformed samples were very similar (Fig. 7.2e,f): Grain size is quite heterogeneous ranging from about 5 to 200 μm. Grain boundaries are polygonal. Except for some grains with undulous extinction, no intracrystalline deformation features were observed. Amorphous silica was not detected, but cristobalite was still present next to quartz (Fig. 7.8). The water content was low.

In summary, the highest shear stresses before slippage could be reached by immediately deforming the samples after hot-pressing. However, the achievable shear strain was never higher than $\gamma = 0.1$. 

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Fig. 7.7  Sample P195 (step 4) of synthetic quartz after torsion test at 1400 K, 300 MPa, $1 \times 10^{-5} \text{ s}^{-1}$ within (a) and without iron jacket (b). Shear sense as indicated. Development of a shear fracture.

Fig. 7.8  $2\theta$ diffraction scan (using Cu-Kα) performed using the texture goniometer on planar bulk sample after deformation in torsion at 1300 K, 300 MPa and $2 \times 10^{-4} \text{ s}^{-1}$ (count rates normalized to 100 %). Indicated are the most important peaks for quartz (Qtz) and cristobalite (Cr).
7.2.6 Conclusions

1. No satisfactory starting material could be obtained by isostatically hot-pressing silicic acid under different conditions. The main unresolved problems were to avoid (1) the formation of cristobalite and/or amorphous silica and (2) a strongly heterogeneous grain size and porosity.

2. The deformation of synthetic quartz aggregates in torsion was ambiguous due to the presence of cristobalite in the prepared starting material. As shown in Chapt. 5, the presence of cristobalite may strongly influence the rheological behavior of a sample by reducing its flow strength. Furthermore, the maximum attainable shear strain was only $\gamma < 0.1$ due to slippage at the sample-spacer interface. The slippage was probably caused by the following reasons: (1) In the undrained experiments, some of the water from the sample accumulated at the sample-spacer interface, leading to a reduction in effective pressure on this interface and subsequent slippage at relatively low shear stress. (2) In the experiments performed at 1400 K (step 2-4), the shear stresses were higher than 150 MPa, but the samples still did not deform. The final water content was relatively low ($< 0.1$ wt.%). Since quartz strength is strongly dependent on water content (see Chapt. 3), this low water content was probably responsible for the high strength of the samples.
7.3 Deformation of Arkansas novaculite

7.3.1 Motivation

It was found that the deformation of Dover flint was strongly influenced by the presence of water in the samples (Chapt. 5): at lower temperatures (1250, 1300 K) water promoted deformation by granular flow, whereas at higher temperatures (1400 K) melt was probably present along grain boundaries, leading to granular flow enhanced by melt. The initial water content of Arkansas novaculite (around 0.1 wt%) is much lower than the one of Dover flint (around 1.3 wt%), but both materials are characterized by a homogeneous and fine-grained microstructure. It was expected that another strain accommodating mechanism (e.g. intracrystalline plasticity) might be dominant in novaculite due to the lower water content. Arkansas novaculite was already successfully deformed in compression in a solid-medium apparatus (e.g. Hirth and Tullis, 1991): the samples showed a flow stress of about 250 MPa at 1123 K, 1160 MPa and a strain rate of $10^{-6}$ s$^{-1}$. The dominant deformation mechanism was intracrystalline plasticity.

7.3.2 Starting material and experimental procedure

Arkansas novaculite consists of $>99\%$ SiO$_2$ with 0.1-0.4% Al$_2$O$_3$ and 0.1-0.3% Fe$_2$O$_3$ (Holbrook and Stone, 1978). The loss on ignition after drying at 1273 K and 1 atm for 10 h was around 0.1 wt.%. Samples with different grain sizes are available depending on the metamorphic grade of the novaculite. The samples of this study had a grain size of 1 μm and 30 μm.

Two experiments were performed: P284 had a standard sample assembly with an inner sleeve of gold (see Chapt. 4, Fig. 4.2). In P299 the sample and adjacent spacers had only a diameter of 7.6 mm. Nickel was used as sleeve material.

The experimental conditions are given in Tab. 7.3. Samples were heat-treated under drained conditions for 1 h at the deformation conditions in order to obtain a stable furnace profile. The torque in this study was converted to shear stress assuming a constant flow law with a stress exponent $n = 4$ through the whole sample (see Paterson and Olggaard, 2000 and Pieri et al., 2001).
Table 7.3  List of experiments on Arkansas novaculite. Drained conditions, confining pressure 350 MPa.

<table>
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<tr>
<th>Run</th>
<th>Sleeve</th>
<th>Sample diameter (mm)</th>
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<th>Def.-T (K)</th>
<th>Strain rate ((10^{-4} \text{ s}^{-1}))</th>
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<td>1400</td>
<td>0.05</td>
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</table>

7.3.3 Results

The rheological behavior of the experiments is shown in Fig. 7.9. P299 did not show any deformation at all; all of the angular displacement was accommodated by slip at the top and bottom spacers. The abrupt weakening was related to sliding on the top sample-spacer interface. P284 slipped at the top sample-spacer interface at \(\gamma < 0.1\). The apparent steady-state behavior at \(\gamma > 0.1\) is attributed to sliding on the sample-spacer interface. At this interface, a leak developed at a shear strain of about \(\gamma = 0.8\), which terminated the experiment.

![Graph showing shear stress versus shear strain](image)

*Fig. 7.9*  Shear stress versus shear strain for experiments on novaculite performed under drained conditions. Run number, temperature and shear strain rate as indicated. Shear stress was calculated from the measured torque assuming a power law creep with stress exponent of \(n = 4\). Increase in confining pressure led to shear stress steps in P284 at \(\gamma \approx 0.4\) and 0.6.

The microstructure of P284 shows the development of cracks inclined at 40° clockwise to the shear zone boundary (Fig. 7.10a). They form a pervasive pattern throughout the thin section. No offset of the grains was detected along the cracks (Fig. 7.10b), suggesting that no movement
occurred along them. No evidences were found whether the cracks developed before or just at leakage.

![Fig. 7.10 Microphotos in crossed polarized light of Arkansas novaculite deformed in torsion at 1300 K, 350 MPa, $3 \times 10^5$ s$^{-1}$ (P284). a) Oriented cracks. b) Grains with no offset along crack.]

**7.3.4 Conclusions**

In contrast to Dover flint, which deformed by granular flow, Arkansas novaculite was too strong to be deformed in torsion within the available range of experimental conditions and setup. This material was thus abandoned.
8 Summary and conclusions

8.1 Summary

The purpose of this study was to investigate the rheological, microstructural and textural evolution of quartz aggregates at high temperature and high shear strain. Three different quartz-rich aggregates (Dover flint, Arkansas novaculite, hot-pressed silicic acid) were tested in order to find a suitable starting material. Torsion experiments were carried out using a Paterson gas-medium apparatus operated at temperatures in the range of 1250 to 1400 K (977-1127 °C), confining pressures of 300 to 350 MPa and various strain rates (ranging from 5*10^-6 s^-1 to 1*10^-4 s^-1) under drained or undrained conditions. The suitability of different sample assemblies was explored. Textures and microstructures were investigated using texture goniometry, scanning electron microscopy with EBSD, synchrotron experiments, optical microscopy and transmission electron microscopy. Texture goniometry had to be optimized for small and fine-grained (<1 μm) samples which are generally not accessible to EBSD analysis.

The study leads to the following results.

1. Texture measurements by X-ray goniometry require careful defocusing corrections. The instrumental setup could be optimized for small and rectangular samples with a grain size of < 1 μm. The optimized setup consists in using a small collimator (diameter 0.5 mm) and no sample oscillation. Weak and oblique textures were reliably measured with this setup on Dover flint samples experimentally deformed in torsion.

2. The concept of texture index can be applied to quantitatively compare textures obtained by different measurement techniques.

3. Dover flint provides an isotropic standard to determine texture corrections for quartz.

4. Heat-treatment of Dover flint performed at 1300 K (1027 °C) or 1400 K (1127 °C) at confining pressures of 150 MPa or 350 MPa for different amounts of time resulted in an initial dilation with an isotropic distribution of water-filled pores followed by compaction with continuous reduction in porosity and grain growth.

5. Natural quartz aggregates (Dover flint) were successfully deformed in torsion to high shear strains (\(\gamma = 4\)) under drained conditions. Under undrained conditions, samples failed by tensile fracturing (at \(\gamma < 0.2\)) indicating that the pore pressure exceeded the confining pressure.
6. In experiments where only an iron jacket was used, the formation of a fayalite rim around the sample increased the strength and hydrogen embrittlement of the iron jacket caused leakage and termination of experiments at $\gamma < 1.5$. By using an inner sleeve of platinum and/or nickel, no fayalite rim formed and leak development could be avoided up to $\gamma > 3.5$.

7. At 1300 K ($1027 \, ^{\circ}\text{C}$), torsion deformation of wet Dover flint was characterized by three typical successive stages of granular flow.  

**Stage I.** Apparent steady-state flow stress up to a shear strain of around $\gamma = 0.2$. Prior to deformation, water was isotropically distributed in pores. The pores redistributed into an anisotropic arrangement in planes oriented at $\pm 25^\circ$ to the maximum principal stress direction $\sigma_1$.

**Stage II.** Sudden hardening for shear strains up to $\gamma = 2.5$. Hardening was associated with the interconnection of some pores to form continuous bands in a synthetic Riedel (R1) orientation with no discernible lateral offset along them. These R1 bands served as pathways enhancing local fluid drainage of the samples. Decreasing pore fluid pressure and thus increasing effective pressure in the drained volumes led to an increase of the overall sample strength. Strain was mainly accommodated within the matrix by granular flow.

**Stage III.** Sliding after unloading and subsequent reloading. Deformation occurred primarily by displacement along the existing R1 bands with their evolution into shear planes.

8. At 1400 K ($1127 \, ^{\circ}\text{C}$), simple shear deformation of wet Dover flint occurred also by granular flow, but it was probably enhanced by melt along grain boundaries. Flow stress was steady up to $\gamma = 2$, then progressive hardening occurred. Hardening was correlated with the development of cracks, which allowed fluids to escape faster. Deformation was strongly heterogeneous, probably due to heterogeneous melt distribution.

9. At a shear strain of $\gamma = 0.2$, an oblique c-axis girdle opposite to the sense of shear had developed, which remained in the same position for larger strain (up to $\gamma = 3.3$). Such textures are different from those of naturally deformed quartz mylonites though they agree with model simulations based on dislocation glide on multiple slip systems. The textures were still close to random even at high strains ($\gamma = 3.3$ with texture index $J = 1.06$). Such a low texture index corresponds to only 2-4% of the grains having a preferred orientation, while the other 96 - 98% of the sample volume have random lattice orientations.

10. No satisfactory starting material could be obtained by isostatically hot-pressing silicic acid. Depending on water content of the samples, the synthesized samples showed either the presence of cristobalite and/or amorphous silica, or they had a strongly heterogeneous grain size and porosity.
Chapter 8 173 Summary and conclusions

11. Hot-pressed silicic acid as well as Arkansas novaculite were too strong to be deformed in torsion within the available range of experimental conditions and setup. This was probably due to the low water content of these two starting materials. The most serious limitation of those experiments was the maximum available confining pressure of 350 MPa.

8.2 Geological implications

In geology, the term "superplastic deformation" is commonly used to describe "a deformation in which very high strains are reached without development of a lattice preferred orientation or elongated grains" (Passchier and Trouw, 1996). The micromechanisms of superplasticity involve the movement of the grains relative to each other and thus can be regarded as a type of granular flow (Paterson, 1995). Such granular flow has been inferred to occur in nature for example in recrystallized orthopyroxene (Boullier and Gueguen, 1975), limestone (Schmid, 1982), and albite-rich mylonites (Stünitz and Fitz Gerald, 1993). In quartzites, Behrmann (1985) investigated a fine-grained mylonite (< 10 μm) from the Betic movement zone (southern Spain) with a weak texture, development of voids at grain boundaries and only slightly elongate grain shapes. He suggested that the mylonite developed first by dynamic recrystallization of originally coarser grained aggregates, and that the small recrystallized grain size allowed a subsequent switch in deformation mechanism from dislocation creep to granular flow. Such a change in deformation mechanism could cause weakening of deformation zones leading to shear localization (Schmid, 1982; Paterson, 1990b).

Up to now, granular flow of quartz aggregates up to high shear strain had not been observed in laboratory tests. It remained unclear whether granular flow is a stable mechanism for attaining high strains. All of the studies mentioned above mainly pointed to the role of a small grain size for achieving granular flow. However, it has been speculated that also pore pressure can have an important effect in promoting granular flow: thus even at considerable depth, a pore-fluid pressure approaching the minimum compressive stress could permit granular flow (Twiss and Moore, 1992).

In our study on Dover flint, we have demonstrated for the first time that quartz aggregates can deform in the laboratory to high shear strains by granular flow. Granular flow was promoted by a relatively high sample porosity and a high water content which may not only lubricate grain boundaries but also lower the effective pressure. A decrease in sample porosity and water content with progressive deformation supports the development of brittle features (Riedel bands), suggesting that granular flow is unstable under drained conditions after some amount of
deformation. The development of a weak LPO in our samples is in contradiction to the common opinion that grain size sensitive flow should not produce any texture (e.g., Schmid, 1982).

Textures of quartz are commonly used to deduce the relative sense of displacement in shear zones. Field observations indicate that the c-axis maximum is generally inclined in the sense of shear (e.g., Burg and Laurent, 1978; Schmid and Casey, 1986). However, the opposite sense (e.g. Carreras et al., 1977; Lister and Price, 1978) as well as perfectly symmetric patterns (Law et al., 1984) have also been reported. In the shear experiments of Dell’Angelo and Tullis (1989) a c-axis maximum displaced against the sense of shear developed at low strains, where no recrystallization was identifiable in the sample. A maximum displaced with the sense of shear was observed at high strains, where significant recrystallization occurred. We have clearly shown that the c-axis maximum is inclined opposite to the sense of shear when the main deformation mechanism is granular flow with a minor amount of recrystallization. In the comparison of textures from naturally and experimentally deformed samples it is essential to establish that the microstructures indicate the same operative deformation mechanisms. Furthermore the amount of recrystallization has to be considered.

Riedel structures are frequently found within a variety of fault rocks deformed under very different physical conditions and over a range of scales. Major displacements commonly take place within them and they are useful shear sense indicators. Similar structures have been recognized in laboratory studies on different rock types approaching simple shear conditions, like on clay cakes (Morgenstern and Tchalenko, 1967) and in shear-box experiments on sand and other granular materials (Mandl et al., 1977). In Dover flint samples, Riedel structures are comparable to those in nature and laboratory studies. In contrast to the common opinion, we have shown that deformation does not necessarily localize along Riedel structures. If fluid present in the rock is allowed to escape, Riedel structures enhance local drainage, which may lead to overall strengthening of the material.

8.3 Further work

1. In this study, the maximum shear strain reached on Dover flint deformed at 1300 K (1027 °C) was \( \gamma = 3.5 \). At this point, numerous Riedel shears in a R1 geometry were present and the texture consisted of a c-axis maximum inclined opposite to the sense of shear. It is not clear if this fabric represents a steady-state situation. It is necessary to conduct experiments to higher shear strains in order to see whether the microstructure and texture would still evolve with progressive strain.
2. Experiments on quartz aggregates in torsion could only be performed under drained conditions without slippage at the sample-spacer interface. Since quartz strength is strongly influenced by the amount of water, it is interesting to conduct torsion experiments on quartz under undrained conditions to high shear strain. This could be done by using non-porous spacers at each sample end and by mechanically keying the sample and spacers together. The water content of the starting material should not be too high in order to prevent high pore fluid pressures. A suitable starting material might be Dover flint, heat-treated for 12 h at 350 MPa.

3. In this study, the formation of Riedel bands in samples deformed at 1300 K (1027 °C) could be correlated with the interconnection of water-filled pores. However, the process that leads to the initiation of the Riedel band formation remains unexplored. The operation of brittle mechanisms in a deforming material produces transient acoustic waves, so-called acoustic emission (AE). AE signals can be detected and analyzed using an acoustic emission detection system. Such a system could be used in future experiments to investigate when brittle events occur in the deformation history. Further information about the mechanism of Riedel band initiation could be gained by performing experiments to different stages in the Riedel band development together with detailed microstructural investigations of the deformed samples using TEM.

4. Porosity in Dover flint was influenced in our study by varying the confining pressure during heat-treatment at 1300 K (1027 °C). We tested two confining pressures (150 MPa and 350 MPa) for heat-treatment. In subsequent torsion experiments, it was found that for samples heat-treated at 150 MPa, Riedel band formation was suppressed up to a shear strain of $\gamma = 1.3$, whereas in the samples heat-treated at 350 MPa, Riedel bands developed already after $\gamma = 0.2$. It would be useful to perform a series of experiments could be performed with different confining pressures during heat-treatment resulting in different porosities of the starting material. This would allow (1) to explore the effect of porosity on granular flow and Riedel band formation and (2) to determine rheological parameters for granular flow in order to deduce a flow law.

5. All of the experiments on Dover flint at 1300 K (1027 °C) were performed in torsion. It would be interesting to see if a similar rheology and microstructure would develop in compression experiments. Furthermore, confining pressures an order of magnitude higher could be used (e.g. by deforming the samples in a Griggs rig) in order to investigate whether granular flow will be substituted by intracrystalline plasticity as deformation mechanism at high confining pressures.

6. In this study, the behavior of granular flow at constant strain rate was investigated. Development of Riedel structures might be suppressed in constant stress experiments which would allow to reach very high shear strains with a pure granular flow mechanism. It would be important to investigate if a steady-state configuration could be attained.
7. Arkansas novaculite was too strong to be deformed in torsion in this study, even at a shear strain rate as low as $5 \times 10^{-6} \, \text{s}^{-1}$. It should be tested whether fine-grained novaculite gets weaker in the presence of water, i.e. in a hydrothermal environment. This could be done by drilling a hole through the centre of a cylindrical sample and fill the hole with a mineral that dehydrates at high temperatures (e.g. talc). The water may diffuse into the novaculite, enhance grain growth, but also weaken the aggregate.
References


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References


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### Dover Flint, Heat-Treatment

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### Heat-treated Dover Flint, Deformation

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- Remarks: Thermocouple broken at 1223K

---

Appendix A: List of experiments and experimental conditions
## Arkansas novaculite, deformation

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<th>Radius R (mm)</th>
<th>Length L (mm)</th>
<th>Set-up</th>
<th>Heat-treatment time, Pc, T (h, MPa, K)</th>
<th>Deformation Pc, T (MPa, K)</th>
<th>Strain rate (10^-4 s^-1)</th>
<th>Twist rate (10^-4 s^-1)</th>
<th>Shear strain</th>
<th>Comments</th>
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## Silicic acid, hot-pressing

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<th>Spacer top</th>
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## Hot-pressed silicic acid, deformation

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<th>Spacing bottom</th>
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<th>Twist rate (10^-4 s^-1)</th>
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\(d =\) drained; \(u =\) undrained; \(p =\) porous; \(np =\) non-porous
Appendix B: Experimental details of x-ray goniometry (on SCINTAG XDS2000, ETH Zurich) used for texture determinations on quartz aggregates from incomplete reflection pole figures.

1. Standard conditions. Batch file: ALLQTZR.BT. Round sample (25 mm diameter), normal collimator (1 mm diameter), 5 mm sample oscillation.

Table B.1  
**Diffraction angle 2θ, lattice plane indices (hkil) including superpositions, overlap weight, maximum tilt angle, position of the background measured left and right of the diffraction peaks, scan rate and scan mode.**

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<th>(hkil)</th>
<th>Overlap weight (%)</th>
<th>Tilt stop</th>
<th>Background left</th>
<th>Background right</th>
<th>Scan rate</th>
<th>Scan mode</th>
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cont. = continuous

Table B.2  
**Previous tilt correction table (DMS Table 1)**

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2. Small sample conditions. Batch file: SCQTZR6.BT. Small rectangular sample (8 * 10 mm²), small collimator (0.5 mm diameter), no sample oscillation (standard conditions).

Table B.4  Diffraction angle 2θ, lattice plane indices (hkil) including superpositions, overlap weight, maximum tilt angle, position of the background measured left and right of the diffraction peaks, scan rate and scan mode.

<table>
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<tr>
<th>2θ Cu-Kα</th>
<th>(hkil)</th>
<th>Overlap weight (%)</th>
<th>Tilt stop</th>
<th>Background left</th>
<th>Background right</th>
<th>Scan rate</th>
<th>Scan mode</th>
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<td>70/30</td>
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<td>17/83</td>
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<td>62.5°</td>
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cont. = continuous

Table B.5  Tilt correction table (DMS Table 4)

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Curriculum vitae

MARTIN SCHMOCKER

Personal:

Address: Pfirsichstrasse 7
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Switzerland
Phone: ++411 363 79 56

Date of birth 14.03.1972
Nationality Swiss
Marital status single

Education:

1998-2000 PhD studentship in Structural Geology, ETH Zürich. Title of thesis: "Rheology and microfabrics of quartz: Experimental deformation in torsion".

1993-1998 Studentship in Geology, Universität Freiburg (Schweiz). Title of thesis: "Mikrostrukturelle und petrologische Untersuchungen am Augengneis Typ Mönchalp, Silvrettakristallin (Graubünden)".

1988-1993 Gymnasium Interlaken (Switzerland), Maturität in Typus A (Greek and Latin).