Title of the Doctoral Thesis

„Investigations of the microstructural and textural evolution of calcite deformed to high shear strains at pressures in the GPa regime by high-pressure torsion“

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Deformation experiments on rock forming minerals have long been used to link deformation microstructures and textures with the prevailing $P$-$T$ conditions during deformation as well as the applied stress and the resulting strain and strain rate. Calcite is of great interest to researchers studying rock deformation, since, due to its weakness compared to other important rock-forming minerals, strain localization and subsequent formation of shear zones commonly occurs in calcite bearing rocks. Hitherto the main technique to study high strain deformation in the Earth sciences has been the Paterson apparatus, which allows for torsional deformation at confining pressures up to 500 MPa and at temperatures up to 1600 K.

In this thesis high-pressure torsion (HPT) was used to perform high strain deformation experiments on calcite with confining pressures in the GPa range. The microstructure and texture analysis after deformation by means of SEM based electron backscatter diffraction and synchrotron based X-ray line profile analysis extends the knowledge on deformation and dynamic recrystallization mechanisms in calcite deformed to high shear strains at confining pressures in the GPa range. The deformation experiments were performed at room temperature, 235, and 450 °C and confining pressures between 1 and 6 GPa. The high confining pressure facilitated deformation experiments to shear strains exceeding 80 at all temperatures without brittle sample failure. Thus, HPT permits to study the effect of high confining pressures on the microstructural evolution at high applied shear strains in specimens deformed at low temperatures. Furthermore, the HPT experiments allowed to investigate the influence of the stability fields of high pressure CaCO$_3$ polymorphs on the microstructural evolution under well-constrained conditions. The phase transition between calcite and CaCO$_3$-II occurs at 1.7 GPa at room temperature and 1.6 GPa at 450 °C. At room temperature CaCO$_3$-II transforms to CaCO$_3$-IIIb at 1.9 GPa and further to CaCO$_3$-III at 3.3 GPa.

Deformation at 450 °C proceeds primarily by crystal-plastic deformation in the form of dislocation creep and to a lesser extent by mechanical twinning. Dynamic recrystallization by subgrain rotation leads to a fine grained matrix with area weighted mean recrystallized
grain sizes between about 800 nm and 2 µm. The recrystallized grain size and the coherently scattering domain (CSD) size decrease with increasing confining pressures, except when the boundary between the calcite and CaCO$_3$-II stability fields is crossed. The area weighted mean grain size increases from about 1.2 µm at 1.2 GPa to 2 µm at 2 GPa, while the CSD size increases from about 40 nm at 1.4 GPa to about 60 nm at 2 GPa. In the same manner the dislocation density increases with increasing pressure except when the boundary between the calcite and the CaCO$_3$-II stability fields is crossed, where it drops to a lower value. The change in the evolution of microstructural parameters between the calcite and the CaCO$_3$-II stability fields is linked to different recrystallization mechanisms in the two stability fields. While recrystallization eventually leads to a homogeneous distribution of recrystallized grains regardless of the confining pressure, the intermediate stages of recrystallization differ in the calcite and the CaCO$_3$-II stability fields. In the calcite stability field, recrystallization leads to a typical core-mantle microstructure and a saturation of the dislocation density at shear strains $\approx$ 10 regardless of the strain rate, while the recrystallization in the CaCO$_3$-II stability field is strain rate dependent. The recrystallization behavior in the calcite regime concurs with the findings on recrystallization microstructures and steady state flow stresses in earlier studies performed at lower confining pressures. By contrast, the porphyroclasts break up in a more homogeneous manner at low local strain rates in the CaCO$_3$-II stability field, resulting in a microstructure of comparatively smaller porphyroclast remnants, while at higher local strain rates recrystallization leads to core-mantle microstructures with occasional large porphyroclast remnants even at high strains.

Microstructures in samples deformed at 235 °C do not show evidence for significant recovery and dynamic recrystallization by subgrain rotation. Instead, deformation proceeds by cataclasis and limited dislocation glide and twinning in porphyroclasts. The morphology of the mechanical twins depends on the confining pressure, where at lower pressure (≤ 2 GPa) the twins are several µm wide and may show slightly curved boundaries. By contrast, twins at higher pressures (> 2 GPa) are thinner and straight and often show evidence of significant twin boundary migration.

At room temperature deformation proceeds mainly by cataclastic processes. However, the high confining pressure inhibits macroscopic cracking and sample failure during deformation leading to the accumulation of pronounced lattice strain in the porphyroclasts and previously unreported intragranular deformation mechanisms at room temperature. The elevated lattice strain is evident from the high dislocation density ($1-2 \times 10^{-15}$ m$^{-2}$), which does not show saturation with the sample radius even at shear strains >
80 as well as from the significant local lattice misorientation in the porphyroclasts. This high heterogeneous lattice strain leads to apparent high temperature $e$-twin morphologies otherwise associated with deformation temperatures of at least $150 \, ^{\circ}C$. In addition, the porphyroclasts exhibit deformation lamellae that exhibit specific orientation relationships that can be traced to the interaction of two different twin systems.

This study presents new results on the deformation and recrystallization mechanisms in calcite deformed to high strains at confining pressures in the GPa range. The findings reveal that high confining pressures during deformation can significantly affect the microstructural and textural evolution of calcite and pressure effects should be included in the analysis of natural rock microstructures deformed at high confining pressures.
Zusammenfassung


In dieser Arbeit wurde High-Pressure Torsion (HPT) verwendet, um Deformationsexperimente zu hohen Dehnungen an Kalzit unter Drücken im GPa Bereich durchzuführen. Die Analyse der Mikrostrukturen nach den Verformungsexperimenten mittels synchrotron-basierter Röntgenprofilanalyse (XPA) und SEM-basierter Elektronenrückstreubeugung (EBSD) erweitert den Wissensstand bezüglich der Deformations- und Rekristallisationsmechanismen in unter Druck im GPa Bereich zu hohen Dehnungen verformtem Kalzit. Die Deformationsexperimente wurden bei Raumtemperatur, 235, und 450 °C und Drücken zwischen 1 und 6 GPa durchgeführt. Der hohe Druck ermöglichte Experimente zu Scherdehnungen jenseits von 80 bei allen Temperaturen ohne Probenbruch. Auf diese Weise ermöglicht HPT den Effekt des hohen hydrostatischen Drucks auf die mikrostrukturrelle Entwicklung in bei niedrigen Temperaturen zu hohen Dehnungen verformtem Kalzit zu untersuchen. Weiters ermöglichen die HPT Experimente den Einfluss der Stabilitätsfelder von Hochdruck CaCO$_3$ Polymorphen auf die mikrostrukturrelle Entwicklung unter exakt definierten Bedingungen zu untersuchen. Der Phasenübergang zwischen Kalzit und CaCO$_3$-II tritt bei 1.7 GPa bei Raumtemperatur und 1.6 GPa bei 450 °C auf. Bei Raumtemperatur transformiert CaCO$_3$-II zu CaCO$_3$-IIIb bei 1.9 GPa und weiter zu CaCO$_3$-III bei 3.3 GPa.

Mikrostrukturen in Proben, die bei 235 °C verformt wurden, zeigen keine Anzeichen für signifikante Erholung und Rekristallisation durch Subkornrotation. Stattdessen erfolgt die Deformation durch Kataklas, sowie eingeschränkt auch durch Versetzungs- gleiten und Verzwillingung in Porphyroklasten. Die Zwillingsmorphologie ist druckabhängig, wobei Zwillinge bei niedrigem Druck (≤ 2 GPa) mehrere µm breit sind und leicht gekrümmte Grenzen aufweisen. Im Unterschied dazu sind Zwillinge in Proben, die bei höherem Druck (> 2 GPa) verformt wurden, dünner und gerade und zeigen häufig Anzeichen für Rekristallisation durch Zwillingsgrenzenwanderung.

Deformation in Proben, die bei Raumtemperatur verformt wurden, verläuft haupt-

Diese Studie präsentiert neue Erkenntnisse über Deformations- und Rekristallisationsmechanismen in unter hohem Druck im GPa Regime zu hohen Dehnungen verformtem Kalzit. Die Resultate offenbaren, dass hoher Druck während der Deformation die Mikrostruktur- und Texturentwicklung von Kalzit signifikant beeinflussen kann und in die Analyse von natürlichen Gesteinsmikrostrukturen, die bei Verformung unter hohem Druck entstehen, berücksichtigt werden sollte.
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Introduction

1.1 Deformation experiments in the Earth sciences

A profound understanding of the mechanical properties and the deformation behavior of rock forming minerals is necessary to accurately model processes in the deep Earth. The mechanical rock properties are therefore of pivotal interest in the Earth sciences. The analysis of microstructures and textures of naturally deformed rocks has long been established as the foremost technique to understand the influence of deformation conditions on the macroscopic rheology of rocks and the activity of deformation and recrystallization mechanisms. However, the prevailing deformation conditions in natural settings can usually only be poorly constrained and are therefore associated with significant uncertainties. Furthermore, the deformation conditions may vary during deformation or deformation microstructures may be overprinted by subsequent recrystallization.

To provide a better link between the microstructures and textures of naturally deformed rocks with the prevailing deformation conditions and the active deformation and recrystallization mechanisms, well-constrained laboratory experiments are necessary. Experiments allow to control deformation parameters such as differential stress, strain, strain rate, confining pressure and temperature as well as the chemical environment and the initial microstructural state of the investigated specimen. Methodical variation of these parameters allows to access different deformation regimes and to explore the activity of deformation and recrystallization mechanisms under varying conditions. In this manner the microstructures and textures in deformed specimens can be reliably related to the deformation conditions. Thus, deformation experiments on important rock-forming minerals and mineral assemblages have long been used to investigate the rheology of rocks and minerals under well defined experimental conditions and to characterize the post-deformation microstructures and textures.

Calcite is one of the most intensely studied minerals both in natural settings as well as in experiments, since carbonate rocks are frequently the site of deformation localization
1.2 HIGH-PRESSURE TORSION

and shear zone formation in natural settings. Early rock deformation studies on calcite focused predominantly on coaxial deformation such as uniaxial or triaxial compression or tensile tests (e.g. Turner et al. (1954); Griggs et al. (1960); De Bresser and Spiers (1997)). However, geological deformation, in particular in shear zones, usually proceeds by non-coaxial deformation, such as simple shear. Torsional deformation is an ideal method to perform non-coaxial deformation experiments to high strains. Locally, torsion imposes simple shear in the sample, where the shear direction lies normal to both the torsion axis and the radial direction. Since the imposed local strain and strain rate are directly proportional to the distance from the rotation axis, torsional deformation allows to study microstructures produced at different strains and strain rates in a single specimen. Early torsional deformation studies on calcite were performed under poorly constrained experimental conditions (Bridgman, 1936) or to comparatively low strains (Handin et al., 1960). In order to perform torsional experiments under well-constrained conditions to high strains, the Paterson triaxial apparatus was adapted for torsional deformation (Paterson and Olgaard, 2000). This device has become the standard for torsional rock deformation studies in the Earth sciences and has been applied to study the microstructural and textural evolution of calcite (e.g. Pieri et al. (2001a,b); Barnhoorn et al. (2004, 2005); Rybacki et al. (2013)). It allows for deformation experiments at temperatures up to 1300 °C and confining pressures up to 500 MPa.

1.2 High-pressure torsion

Investigating the deformation behavior of calcite at confining pressures in the GPa range is not possible with the Paterson apparatus. However, this pressure range is of high interest for calcite for two reasons. Firstly, it corresponds to possible pressure conditions in the lower crust, where calcite-bearing rocks may be subducted influencing the global carbon cycle (Merlini et al., 2012). Secondly, several pressure induced phase transitions in the CaCO$_3$ system occur in the GPa pressure range (Merrill and Bassett, 1975; Merlini et al., 2012). Furthermore, the high confining pressure suppresses macroscopic fracturing and sample failure and therefore allows for deformation to high strains even at low temperatures. To explore the deformation behavior of calcite deformed to high shear strains at confining pressures in the GPa range, high-pressure torsion (HPT) was employed in this study. HPT is a deformation technique used in materials science to produce bulk nanostructured materials through torsional deformation under quasi-hydrostatic confining pressures between 1 and 10 GPa. The quasi-hydrostatic pressure conditions in HPT
are provided by a special anvil geometry (Zhilyaev and Langdon, 2008). The sample is placed between cavities in the two anvils the combined depth of which is only about 100 µm smaller than the sample height. At the onset of torsional deformation, sample material flows into the gap between the anvils, where it hardens and provides back pressure for the rest of the sample. The deformation experiments in this study were performed at room temperature, 235 and 450 °C and at confining pressures between 1 and 6 GPa.

1.3 Calcite

Calcite is one of the most common minerals in the Earth’s crust and an important rock forming mineral. Due to calcite’s relative weakness compared to other common rock forming minerals such as quartz or feldspar, calcite bearing rocks are often the site of strain localization and the formation of shear zones. Thus, the rheology and microstructural evolution of calcite deformed to high shear strains along non-coaxial strain paths is of pivotal interest. In addition, calcite plays an important role in the Earth’s carbon cycle, where calcite bearing rocks are subducted into the deep Earth. In this respect the deformation behavior of calcite at high pressure conditions is of particular interest.

At elevated temperatures, deformation in calcite bearing rocks is largely facilitated by intracrystalline plastic deformation mechanisms leading to characteristic microstructures and textures (Pfiffner, 1982; van der Pluijm, 1991; De Bresser and Spiers, 1997). Depending on the deformation temperature and applied strain, both mechanical twinning and dislocation creep contribute to the resulting microstructures. Mechanical twinning on e\{01T8\}-planes is a very prominent microstructural element in calcite and has been studied extensively since the mid 19th century. Apart from the very common e-twinning, two other mechanical twin modes have been observed in calcite. Those are twinning on r\{10T4\} and f\{01T2\} planes. The slip systems observed in calcite show three sets of Burgers vectors, namely 1/3\{2021\}, 1/3\{10T1\} and 1/3\{2T0\}, where dislocations with the 1/3\{2021\} Burgers vectors are the most common despite the Burgers vector length. Possible slip planes are the rhombohedral planes r\{10T4\} and f\{01T2\}, the prismatic planes a\{T2T0\} and m\{10T0\} as well as the basal plane c\{0001\}. A list of the slip systems in calcite can be found in Table 2 in chapter 3 (Schuster et al., 2017).

The influence of confining pressures in the GPa range on the deformation behavior of calcite bearing rocks is complicated by the existence of several metastable high pressure polymorphs, that form when calcite is subjected to pressures in the GPa range (Bridgman, 1938; Merrill and Bassett, 1975; Fiquet et al., 1994; Merlini et al., 2012). At room
temperature calcite transforms to \( \text{CaCO}_3\)-II at 1.7 GPa, to \( \text{CaCO}_3\)-IIIb at 1.9 GPa, and to \( \text{CaCO}_3\)-III at 3.3 GPa. The effect of these phase transitions on the deformation of carbonate rocks has heretofore not been studied in-depth.

### 1.4 Aims of the study

The main aim of the study is to investigate the microstructural and textural evolution of calcite deformed to shear strains up to 80 at temperatures between room temperature and 450 °C and at confining pressures in the GPa range and to determine the influence of temperature, pressure, strain, and strain rate on the deformation and recrystallization mechanisms. To this end, a HPT apparatus was adapted for rock deformation experiments on calcite powder aggregates. The quasi-hydrostatic confining pressures of several GPa during HPT deformation allow for the deformation of even brittle samples to high strains without inducing macroscopic sample failure. This allowed to extend the range of calcite high strain deformation experiments to higher pressures and for low deformation temperatures also to higher shear strains than previously achieved.

The resulting microstructures post HPT deformation were analyzed by synchrotron based X-ray diffraction experiments and subsequent X-ray line profile analysis (XPA) as well as by scanning electron microscopy with a focus on electron backscatter diffraction (EBSD). With XPA the evolution of microstructural parameters such as dislocation character and density and coherently scattering domain size was characterized for a wide range of pressure, temperature, strain and strain rate conditions with good statistical reliability. EBSD was used to study the nature and prevalence of deformation and dynamic recrystallization mechanisms and the evolution of the grain size and morphology with strain as well as the development of the deformation texture.

The main issues addressed in the study relate to the effect of high confining pressure during deformation:

- Investigating the utility of HPT for rock deformation experiments. Numerous studies on HPT deformed materials have shown a distinct influence of high confining pressures in the GPa range on the microstructural evolution leading to changes in microstructural, mechanical and functional properties compared to conventionally deformed materials. Therefore, HPT provides the possibility to extend the range of rock mechanics tests to higher pressures and strains, leading to new insights into the deformation behavior of minerals and rocks deformed to high strains under high-pressure conditions.
• The high confining pressure allows to deform even comparatively brittle materials to high strains, due to the inhibition of crack nucleation and propagation and therefore brittle sample failure at moderate strains. This causes the activation of alternative deformation mechanisms, which are not observed in samples deformed at lower pressures.

• High confining pressure acts similarly to low temperatures in suppressing the mobility of point defects necessary for thermally activated dislocation processes, in particular dislocation climb. This may lead to a pressure dependence on recovery and dynamic recrystallization processes in calcite deformed at elevated temperatures and may influence defect densities, texture evolution and deformation microstructures.

• Calcite undergoes several structural phase transitions to high pressure polymorphs in the $P$-$T$ regime investigated in this study. The possible influence of these phase transitions on the deformation behavior and microstructural and textural evolution during deformation is therefore of high interest.

1.5 Experimental and analytical methods

The HPT experiments were performed with the HPT apparatus at the Faculty of Physics at the University of Vienna. Fig. 1.1 shows the experimental assembly after a deformation experiment at elevated temperatures. For a sketch of the HPT process see Fig. 2 in chapter 4 [Schuster et al. (2019)].

In order to generate the high quality XRD data necessary for XPA, two synchrotron sources were used for the diffraction experiments. One set of measurements was performed at the P07-HEMS beamline at PETRA III, Deutsches Elektronen-Synchrotron (DESY, Hamburg) using a monochromatic X-ray beam with an energy of 50 keV [Schell et al. 2014], with additional measurements undertaken at the Microdiffraction beamline at the Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, USA. In contrast to the measurements at DESY the ALS measurements were performed in reflection geometry with a monochromatic beam of 12 keV energy. The SEM measurements were carried out on the FEI QuantaTM 3D FEG Scanning Electron Microscope at the Laboratory for Scanning Electron Microscopy and Focused Ion Beam Applications of the Faculty of Geosciences, Geography and Astronomy at the University of Vienna (Austria). The X-ray texture measurements were performed with an AXS BRUKER D8 diffractome-
1.5. EXPERIMENTAL AND ANALYTICAL METHODS

Figure 1.1: View of a calcite sample, the HPT anvils and induction coils after a deformation experiment at 450 °C

ter at the Faculty of Physics at the University of Vienna with a monochromatic beam of 8 keV energy.
Organization of the thesis

The thesis is organized into four parts. The first three parts are based on three manuscripts investigating the microstructural and textural evolution of HPT-deformed calcite by means of X-ray line profile analysis and EBSD. The fourth is a summary and synthesis, which combines the findings of the individual manuscripts.

• The first manuscript is concerned with microstructure analysis by XPA. XPA revealed $r\{10\bar{1}4\}\langle2021\rangle$ with edge dislocation character as the main slip system for all $P-T$ conditions. In addition, the influence of temperature and pressure during deformation on the evolution of microstructural parameters such as dislocation density and coherently scattering domain size was established. Furthermore, the occurrence of high pressure polymorphs leads to a pronounced qualitative change in the development of dislocation densities.

• The second manuscript is concerned with EBSD based microstructure analysis of samples deformed by HPT at temperatures of 235 and 450 °C. The influence of high confining pressures and the stability fields of the high pressure polymorphs on the active deformation mechanisms, and in the 450 °C case also the dynamic recrystallization mechanisms, was revealed. The EBSD analysis also allowed to determine the characteristic texture evolution at 450 °C, which is different from the textures observed in studies of calcite torsionally deformed at lower confining pressures.

• The third manuscript is concerned with intracrystalline deformation mechanisms in porphyroclasts, with an emphasis on twinning, in samples deformed by HPT at room temperature. The post deformation microstructures were analyzed by means of EBSD. The high hydrostatic pressure component in HPT processing allows to deform even brittle materials to high strains without sample failure, leading to the activation of alternative deformation mechanisms. The occurrence of twin boundary morphologies that previously have only been observed at significantly higher
deformation temperatures could be demonstrated. Furthermore, the existence of two new types of deformation lamellae related to deformation twinning could be observed and characterized.
Manuscript I
Microstructure of calcite deformed by high-pressure torsion: An X-ray line profile study

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Microstructure of calcite deformed by high-pressure torsion: an X-ray line profile study

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Abstract
Calcite aggregates were deformed to high strain using high-pressure torsion and applying confining pressures of 1-6 GPa and temperatures between room temperature and 450 °C. The run products were characterized by X-ray diffraction, and key microstructural parameters were extracted employing X-ray line profile analysis. The dominant slip system was determined as \( \{10\overline{1}4\}\langle\overline{2}0\overline{2}1\rangle \) with edge dislocation character. The resulting dislocation density and the size of the coherently scattering domains (CSD) exhibit a systematic dependence on the \( P-T \) conditions of deformation. While high pressure generally impedes recovery through reducing point defect mobility, the picture is complicated by pressure-induced phase transformations in the CaCO\(_3\) system. Transition from the calcite stability field to those of the high-pressure polymorphs CaCO\(_3\)-II, CaCO\(_3\)-III and CaCO\(_3\)-IIIb leads to a change of the microstructural evolution with deformation. At 450 °C and pressures within the calcite stability field, dislocation densities and CSD sizes saturate at shear strains exceeding 10 in agreement with earlier studies at lower pressures. In the stability field of CaCO\(_3\)-II, the dislocation density exhibits a more complex behavior. Furthermore, at a given strain and strain rate, the dislocation density increases and the CSD size decreases with increasing pressure within the stability fields of either calcite or of the high-pressure polymorphs. There is, however, a jump from high dislocation densities and small CSDs in the upper pressure region of the calcite stability field to lower dislocation densities and larger CSDs in the low-pressure region of the CaCO\(_3\)-II stability field. This jump is more pronounced at higher temperatures and less so at room temperature. The pressure influence on the deformation-induced evolution of dislocation densities implies that pressure variations may change the rheology of carbonate rocks. In particular, a weakening is expected to occur at the transition from the calcite to the CaCO\(_3\)-II stability field, if aragonite does not form.
1 Introduction

Calcite is an important rock-forming mineral in the earth’s crust, and it plays a key role in the earth’s carbon cycle. Due to the relative weakness of calcite compared to other common rock-forming minerals, strain localization and formation of shear zones often occur in calcite-bearing rocks (van der Pluijm, 1991; Fernández et al., 2004; Romeo et al., 2007). Carbonate rocks may undergo ductile deformation at relatively low temperatures and high pressures, as may prevail in old continental lithospheres with low geothermal gradients and may be generated by tectonic overpressure (Peacock and Wang, 1999; Gerya et al., 2008; Vrijmoed et al., 2009; Li et al., 2010; Warren, 2013). In this context, the deformation behavior of calcite at relatively low temperatures and high confining pressures in the GPa range is of central interest.

Experimental rock deformation has provided key information on the conditions and mechanisms of rock deformation in natural systems. Deformation experiments and studies on naturally deformed rocks are tied together by the resulting microstructures (Herwegh et al., 2005). Calcite-bearing rocks are among the most intensely studied rock types both in natural settings (e.g. (Burkhard, 1993; Bestmann and Prior, 2003)) as well as in laboratory experiments (e.g. (Renner et al., 2002; De Bresser et al., 2002)). Initially, deformation experiments on calcite were limited to tensile, compression and triaxial tests (Turner et al., 1954; Griggs et al., 1960; De Bresser and Spiers, 1997) or torsional deformation to comparatively low strains (Handin et al., 1960) or under poorly constrained conditions (Bridgman, 1936). Natural rock deformation is often localized in shear zones where non-coaxial deformation to high strain occurs. Experimental rock deformation must therefore also explore the high-strain case.

Torsion experiments are ideally suited for investigating non-coaxial deformation to high strain. The Paterson deformation apparatus has been the standard device for torsional deformation experiments on geological materials.
(Paterson and Olgaard, 2000). This apparatus allows for torsional deformation to high strains at temperatures up to 1300°C and confining pressures up to 500 MPa. Experiments have been designed using the Paterson apparatus to study the relations between stress and strain-rate, deformation induced microstructure evolution, as well as dynamic and static recrystallization of calcite aggregates at \( P-T \) conditions prevailing in the earth’s crust (Casey et al., 1998; Paterson and Olgaard, 2000; Pieri et al., 2001a,b; Barnhoorn et al., 2004, 2005).

The potential influence of confining pressures in the GPa range on deformation and related microstructures is, however, out of reach with the Paterson apparatus. Nevertheless, deformation of CaCO\(_3\) at high confining pressures in the GPa range is particularly interesting. Apart from several CaCO\(_3\) polymorphs that are stable or metastable at ambient conditions (calcite, aragonite and vaterite) a number of high-pressure polymorphs exist, which form, when calcite is subjected to pressures in the GPa range (Bridgman, 1938; Merrill and Bassett, 1975; Fiquet et al., 1994; Merlini et al., 2012). At room temperature trigonal calcite transforms to CaCO\(_3\)-II at 1.7 GPa and further to CaCO\(_3\)-IIIb at 1.9 GPa and to CaCO\(_3\)-III at 3.3 GPa. The crystal structure of the CaCO\(_3\)-II polymorph was determined as a monoclinic structure with space group \( P2_1/c \) (Merrill and Bassett, 1975) and a density of 2.77 g cm\(^{-3}\) compared to a density of 2.71 g cm\(^{-3}\) for calcite at ambient conditions. The crystal structures of CaCO\(_3\)-III and CaCO\(_3\)-IIIb were determined by Merlini et al. (2012) to be triclinic with space group \( P1 \). The densities of these phases are 2.99 g cm\(^{-3}\) for CaCO\(_3\)-III at a pressure of 2.8 GPa and 2.96 g cm\(^{-3}\) for CaCO\(_3\)-IIIb at a pressure of 3.1 GPa, which is still lower than the density of aragonite indicating that these phases are not the thermodynamically stable phases in this pressure range (Merrill and Bassett, 1975). Recently Schaebitz et al. (2015) have reported the occurrence of CaCO\(_3\)-III and CaCO\(_3\)-IIIb nanocrystals in natural rocks that had been deformed during a land-slide event. The mechanisms of non-coaxial deformation of CaCO\(_3\) at confining pressures in the GPa range and the resulting
microstructures and textures are not known. In particular, the potential influence of high confining pressure on the activation of slip systems and intracrystalline deformation as well as on recovery and recrystallization is of key interest.

At the moderate temperatures that are relevant for this study, intracrystalline plastic deformation in calcite proceeds mainly by mechanical twinning, dislocation glide, climb, and cross slip. Figure 1 shows the commonly observed twinning and slip systems in calcite. Throughout this study we utilize the 4-index Miller Bravais indexation for the hexagonal unit cell of calcite, except for the notation of Bragg reflexions, where we omit the third index. Studies of experimentally and naturally deformed calcite have revealed three different deformation twinning systems, namely twinning on $e\{0\bar{1}8\}$-, $r\{10\bar{1}4\}$- and $f\{01\bar{T}2\}$ planes. The slip systems show three sets of Burgers vectors namely $1/3\langle 2\bar{2}01 \rangle$, $1/3\langle 10\bar{1}1 \rangle$ and $1/3\langle 2\bar{1}\bar{1}0 \rangle$. Possible slip planes are the rhombohedral planes $r\{10\bar{1}4\}$ and $f\{01\bar{T}2\}$, the prismatic planes $a\{2\bar{T}0\}$ and $m\{10\bar{T}0\}$ as well as the basal plane $c(0001)$.

In this study we present results from experimental high-strain torsional deformation of CaCO$_3$ at pressures in the GPa range. To this end, high-pressure torsion (HPT), a deformation method routinely used in materials science for producing bulk nanostructured materials, was used. In HPT a special anvil geometry provides quasi-hydrostatic pressure conditions in the GPa range in the sample during torsional deformation (Zhilyaev and Langdon, 2008).

For investigating the microstructures resulting from the HPT experiments X-ray line profile analysis (XPA) was employed. This technique uses the broadening of Bragg reflections due to deviations of atomic positions in real crystals from their sites in the ideal lattice. In this study we analyzed the peak broadening due to lattice strain caused by dislocations to determine dislocation densities and the active slip systems. In addition, the peak broadening resulting from the finite extent of the coherently scattering domains (CSD) was used to determine the evolution of the CSD size during HPT
Figure 1: Stereographic projection of calcite marked with the plane poles and directions relevant for slip and twinning. Due to the trigonal symmetry of calcite the orientations of plane poles and directions with the same Miller-Bravais indices in the basal plane and normal to it are equivalent and noted as directions in this plot. The grid spacing is 15°. In addition, the known slip and deformation twinning systems in calcite are listed.

deformation. The X-ray diffraction profiles of samples deformed at temperatures between room temperature and 450°C under confining pressures ranging from 1 GPa to 6 GPa to different strains and at different strain rates were analyzed.

2 X-ray Line Profile analysis

The 2D powder pattern of an ideal crystal is given by delta-function shaped diffraction peaks the positions of which are determined by the crystal structure. In contrast, the peaks of powder patterns of real lattices may be shifted
from their ideal position, symmetrically or asymmetrically broadened or de-
viate in some other manner from the ideal peak shape (Warren and Averbach,
1952). These deviations of the X-ray diffraction patterns of real crystals from
the patterns of ideal crystals are due to the displacement of atom positions
in the real lattice from the corresponding atom positions in an ideal lattice as
well as due to the finite size of the crystallites (Warren and Averbach, 1952;
Williamson and Hall, 1953). Atomic displacements or lattice strain may be
cau sed by zero-, one-, or two-dimensional lattice defects, which influence
diffraction patterns in specific manners (Krivoglaz, 1969).

In X-ray Line Profile analysis (XPA) the deviations of the Bragg peaks
from their ideal shape and position are used to extract information on the
nature and quantity of defects in the crystal lattice as well as on the size
and shape of the crystallites. XPA is complementary to electron microscopy,
since it samples larger areas on the surface and, depending on the wavelength
of the X-ray beam applied, it also probes deeper into the sample. This en-
sures better statistical reliability compared to microstructure analysis based
on scanning electron microscopy (SEM) and especially transmission electron
microscopy (TEM). Moreover, XPA can be used for in-situ investigations
at P-T conditions that may not be replicated in an SEM or TEM. Further-
more, XPA is suitable for the study of very high dislocation densities or beam
sensitive materials which cannot be analyzed by TEM.

2.1 Theory

According to the kinematical theory of X-ray diffraction the intensity of the
physical profile of a Bragg reflection $I^P$ is given by the convolution of the
intensities of the profile due to the finite size of the scattering domains $I^S$
with the profile due to lattice strain $I^D$ (Warren and Averbach, 1952).

$$ I^P = I^S * I^D $$

(1)

In Fourier space it is therefore possible to separate the broadening caused
by size and strain giving rise to the Warren-Averbach equation (Warren and
Averbach, 1952):

\[ \ln A^P(L) = \ln A^S(L) + \ln A^D(L), \]  

where \( A^P, A^S \) and \( A^D \) are the Fourier coefficients of the physical profile, the size Fourier coefficients and the strain or distortion Fourier coefficients, and \( L \) is the Fourier length. The size Fourier coefficients depend on the extension of the coherently scattering domain (CSD) along the diffraction vector. In the absence of shape preferred orientation, it is independent of diffraction order. In contrast, the strain broadening coefficients as calculated by Warren and Averbach depend on diffraction order (Warren and Averbach, 1952)

\[ A^D(L) = \exp[-2\pi^2 L^2 g^2 \langle \epsilon^2_{g,l} \rangle], \]  

where \( g \) is the absolute value of the diffraction vector and \( \langle \epsilon^2_{g,l} \rangle \) is the mean square strain. It is therefore possible to distinguish between peak broadening caused by the finite size of the CSD and the broadening caused by lattice strain. For the case, where the lattice distortion is caused by dislocations, \( \langle \epsilon^2_{g,l} \rangle \) was calculated by Wilkens (1970)

\[ \langle \epsilon^2_{g,l} \rangle \approx \frac{\rho C b^2}{4\pi} f(L/R_e), \]  

where \( \rho \) is the dislocation density, \( b \) is the length of the Burgers vector of the active slip system, and \( C \) is the dislocation contrast factor. The contrast factor accounts for the different degrees of “visibility” of the strain field caused by different dislocations. It is determined by the elastic properties of the material and the relative orientations of the line and Burgers vector of the dislocation and the diffraction vector. The Wilkens function \( f(L/R_e) \), the explicit form of which is given in Wilkens (1970), describes the strain field caused by the dislocation for the dislocation arrangement assumed by Wilkens. The outer cut off radius \( R_e \), describing the range of the strain field, varies according to the configuration of the dislocations, which may lead to a partial screening of their strain fields.
2.2 Strain anisotropy

When lattice strain is caused by dislocations, the strain broadening of Bragg reflections increases with the magnitude of the diffraction vector as can be seen in Eq. 3, but it also depends on the orientation of the diffraction vector. The anisotropy in strain broadening is due to the anisotropic nature of the strain fields associated with dislocations. This implies that, similarly to dislocation contrast in TEM, the dislocation contrast changes with varying orientation of the diffraction vector relative to the dislocation. In particular, the dislocation contrast depends on the anisotropy of the elastic properties of the crystal, and for non-cubic crystals it also depends on the respective ratios of the lattice parameters and the angles between the crystal directions. Furthermore, it depends on the orientations of the line- and Burgers vectors of the dislocation and on the orientation of the diffraction vector.

In polycrystals with no or weak texture, slip systems with symmetrically equivalent slip planes and directions are activated to a similar extent. In this case the respective contrast factors may be averaged to obtain the averaged contrast factors \( \overline{C} \) of each set of equivalent slip systems. For crystals with hexagonal symmetry the averaged contrast factors can be parametrized as (Ungár et al., 2001; Dragomir and Ungár, 2002)

\[
\overline{C} = \overline{C}_{hk0}(1 + q_1 x + q_2 x^2),
\]

where \( \overline{C}_{hk0} \) is the averaged contrast factor of \( hk0 \) type reflections, \( x = 2/3(l/ga)^2 \), \( q_1 \) and \( q_2 \) are parameters depending on the lattice parameters, elastic constants and the active slip systems, \( l \) is the Miller index in the direction perpendicular to the basal plane, and \( a \) is the basal lattice parameter. This form allows to fit the dislocation contrast to the broadening of several Bragg reflections of an X-ray diffraction profile. The resulting experimental contrast factors can then be compared to the contrast factors calculated for the possible slip systems. Through this procedure the dominant slip system or the combination of active slip systems can be identified.
2.3 Whole Profile fitting

In whole profile fitting a diffraction pattern is simulated by using physical models that describe both size and strain broadening and incorporate the measured instrumental broadening (Ungár, 2004). The simulated patterns are then fitted to the measured diffraction profiles. In this study the whole profile fitting method was applied. To this end, we used the CMWP-fit software developed by Ribárik et al. (2001, 2004) and Ribárik (2008). In the CMWP-fit software size broadening is accounted for by assuming a lognormal distribution of the CSD-size and either spherical or ellipsoidal CSD shape. The probability density function of this distribution is given as

\[ f(x) = \frac{1}{\sqrt{2\pi}\sigma_x } \exp \left[ -\frac{(\log(x/m))^2}{2\sigma^2} \right]. \tag{6} \]

For spherically shaped crystallites the size broadening is therefore described by the parameters \( m \) and \( \sigma \). The \( m \) parameter is the scale parameter and median of the lognormal distribution, whereas \( \sigma \) is its shape parameter. For modeling the strain induced broadening the expression for the mean square strain in Eq. (4) is used. The fitting parameters, that are adjusted to construct the strain portion of the simulated diffraction pattern, are the dislocation density \( \rho \), the effective outer cut-off radius \( R_e \) as well as the \( q_1 \) and \( q_2 \) parameters. Eq. (5) was used to account for strain anisotropy.

3 Experimental

3.1 Sample preparation

The starting material was prepared from a block of highly pure Carrara marble, which was crushed and sieved to a particle size of 63 - 100 \( \mu \)m. The powder was dried and then compacted into cylindrical pellets with 8 or 10 mm diameter at room temperature using a cold press. The amount of powder was chosen as to obtain a pellet with 0.8 mm thickness assuming zero porosity. The pre-pressed powder samples show a weak texture with
Figure 2: Schematic cross-section of an HPT assembly; the cylindrical sample is placed in the cavity between two anvils. The top anvil is fixed after the pressure is applied while the bottom anvil is rotated. The sample confinement is provided by sample material, which flows into the narrow gap between the two anvils and hardens at the onset of the torsion deformation thereby providing the necessary back-pressure for the quasi-hydrostatic pressure conditions. The temperature regulation is managed by a controller, which is coupled with the induction furnace and a pyrometer focused on point (T) on the upper anvil. The induction coils extend about 2 cm above and below the sample. The HPT apparatus is held at room temperature by water cooling about 10 cm above and below the sample, ensuring well-constrained temperature conditions during deformation.

a preferred orientation of the c-axes parallel to the compaction direction i.e. normal to the basal plane of the cylindrical sample. The a-axes of the crystallites that have their c-axis aligned with the compaction direction are randomly orientated within the basal plane of the cylindrical pellet.

### 3.2 High Pressure Torsion

A high pressure torsion (HPT) apparatus at the Faculty of Physics, University of Vienna was used for the torsion experiments. During HPT deformation cylindrical samples are subjected to quasi-hydrostatic pressure of
several GPa in addition to concurrent torsional deformation (Zhilyaev and Langdon, 2008). Quasi-hydrostatic-pressure is facilitated by the geometry of the pressure anvils. Both anvils contain a cylindrical cavity with the same diameter as the sample into which the samples are fitted (see Fig. 2). The combined depth of the two cavities is slightly smaller than the initial sample height, leaving a gap of about 100 µm between the anvils. At the onset of a deformation experiment sample material flows into the gap between the anvils, where it hardens due to friction thereby providing the back pressure necessary for the quasi-hydrostatic pressure conditions (Vorhauer and Pippin, 2004). This provides homogeneous pressure conditions for the specimen except for the very rim of the sample, which was not analyzed in this study (Lee et al., 2014). The quasi-hydrostatic-pressure conditions permit deformation experiments to arbitrarily high strain, while the sample geometry is largely retained.

The HPT machine used allows to deform cylindrical samples of up to 10 mm diameter and 0.8 mm height at pressures from about 1 GPa up to 8 GPa. Deformation at elevated temperatures up to about 450°C is facilitated by induction heating of the HPT-anvils (see Fig. 2). The temperature was measured with a pyrometer coupled to the heating control regulating the power output of the induction coils. The pyrometer was focused on the surface of the upper anvil 2 mm above the sample. Given the slow angular velocity of 0.02 rotations per minute (RPM) during HPT-processing, a possible temperature increase in the sample due to deformation heating is negligible (Figueiredo et al., 2012). Similarly, the small sample thickness and the high heat capacity of the anvils ensure a uniform temperature distribution. To check for possible slippage between sample and anvils during HPT-deformation, test runs were performed at various $P - T$ conditions, where marks were applied along the sample radius on the bottom and top surfaces before deformation. All tests showed that no slippage occurred and that the specified torsion was completed along the entire radius. The local
shear strain $\gamma$ in the sample after deformation is given by

$$\gamma = \frac{2\pi nr}{t},$$

(7)

where $n$ is the number of rotations, $r$ is the distance from the rotation axis, and $t$ is the thickness of the sample. The equivalent von Mises strain $\epsilon$ is then calculated as

$$\epsilon = \frac{\gamma}{\sqrt{3}}.$$ 

(8)

Samples were deformed at room temperature, 235°C and 450°C at pressures between 1 and 6 GPa. The sample diameter was 10 mm for samples deformed at 1 GPa and 8 mm for samples deformed under higher confining pressures. The sample thickness post-deformation was 0.6 mm for all samples. All samples were deformed at a constant twist rate of 0.02 RPM, which corresponds to a maximum equivalent strain rate of about $1 \times 10^{-2}$ s$^{-1}$ at the edge of a sample with 10 mm diameter and of about $8 \times 10^{-3}$ s$^{-1}$ at the edge of a sample with 8 mm diameter. After deformation at elevated temperatures the samples were cooled under pressure to 50°C before the pressure was released. Observation by light-optical microscopy and SEM showed no porosity in the samples post-deformation regardless of the deformation temperature.

3.3 X-ray diffraction experiments

High-quality X-ray diffraction patterns were obtained from diffraction experiments performed at the P07-HEMS beamline at PETRA III, Deutsches Elektronen-Synchrotron (DESY, Hamburg) (Schell et al., 2014) using a monochromatic X-ray beam with an energy of 50 keV. The diffraction experiments were carried out in transmission geometry parallel to the rotation axis with a spot size of 500 μm by 200 μm. The measurements were taken every 500 μm from the center to the rim along a radial profile normal to the rotation axis. The diffractograms were recorded with a 2D Perkin Elmer XRD 1621 detector.

Additional measurements were carried out at the Microdiffraction beamline at the Advanced Light Source, Lawrence Berkeley National Laboratory,
Berkeley, USA. In contrast to the measurements at DESY the ALS measurements were performed in reflection geometry with a monochromatic beam of 12 keV energy and 30 µm spot size on the sample, where, similarly to the experiments at DESY, profiles along the sample radius were measured. The diffractograms were recorded with a 2D Pilatus 1M detector. For all measurements the resulting Debye-Scherrer rings were then azimuthally integrated with the Fit2D software (Hammersley, 1997; Hammersley et al., 1996) to obtain diffraction patterns.

Due to the relatively large footprint of the beam at the DESY beamline, the measurements sampled over relatively large radial distances and thus incorporated a range of strains and strain rates. This effect is particularly pronounced for measurements close to the sample center. Assuming that the beam is placed exactly on the center of a sample deformed for one rotation at 0.02 RPM, the von Mises equivalent strain $\epsilon$ in the illuminated region ranges from 0 to 1.5 with an average of 0.8. The von Mises equivalent strain rate $\dot{\epsilon}$ ranges from 0 to $5.1 \times 10^{-4}$ s$^{-1}$ with an average of $2.6 \times 10^{-4}$ s$^{-1}$. Due to the comparatively small footprint of the beam at ALS, $\epsilon$ varies from 0 to 0.2 and $\dot{\epsilon}$ from 0 to $6.1 \times 10^{-5}$ s$^{-1}$ over the sampled area. On the other hand, the large illuminated volume of the DESY measurements ensures better statistical reliability than the smaller footprint of the ALS measurements. Table 1 lists the samples that were measured at DESY and ALS. Figure 3 shows a typical readout of the 2D detector at DESY as well as two diffractograms resulting from integration of the raw data with Fit2D. The diffractograms show the qualitative difference in the peak broadening of two samples deformed at room temperature and at 450°C applying the same confining pressure of 2 GPa, shear strain of $\gamma = 31$, and shear strain rate of $1 \times 10^{-2}$ s$^{-1}$. The diffractograms show significantly more pronounced peak broadening resulting from higher defect densities in samples deformed at room temperature than at 450°C.
Figure 3: X-ray diffraction data. (a) raw data from the 2D Perkin Elmer XRD 1621 detector at DESY of a sample deformed at 2 GPa at room temperature taken 3 mm from the rotation axis. (b) integrated diffractograms of the raw data from (a) in blue as well as from a sample deformed under 2 GPa at 450°C taken 3 mm from the rotation axis, in red.

### 3.4 Evaluation

The positions and intensities of the Bragg reflections were determined with the software “Fityk” (Wojdyr, 2010). For the XPA processing of the line profiles the CMWP-fit software and the software “multi_eval” (Kerber et al., 2009), which allows to vary the set of starting values for the fit parameters in CMWP-fit, were used. Stacking faults and twinning were not included in the evaluation. Peak broadening due to the presence of twins depends on the frequency of twin boundaries. For peak broadening due to twinning to be detectable by XPA in the presence of other defects, a twin boundary density of more than about 0.05 % would be required (Ungár et al., 2008). Considering e-twinning in calcite, this would correspond to a mean spacing of less than 400 nm between the twin boundaries. SEM measurements showed that even after deformation at room temperature the twin boundary densities are much lower and therefore in our samples the Bragg peak broadening due to twinning is not resolvable by XPA. Instrumental broadening was incorporated into the evaluation by measuring the widths of Bragg peaks in the relevant 2θ range of unstrained standard samples at both beamlines.

While the CMWP-fit evaluation of most patterns gave values of about
10 nm for the outer cut-off radius, in some cases the evaluation resulted in unrealistic values for the outer cut-off radius and therefore unreliable dislocation densities. To ensure the comparability of the dislocation densities across all diffraction patterns, the outer cut-off radius was fixed to 10 nm for all CMWP-fit evaluations.

The contrast factors for the slip systems observed in naturally and experimentally deformed calcite (De Bresser and Spiers, 1997; Pieri et al., 2001a; Bestmann and Prior, 2003) were calculated using the GNU Octave script “contrastfactor” written by Spieckermann (2010) on the basis of the work of Martinez-Garcia et al. (2009) for pure edge and screw dislocation character. The dislocation contrast factors for arbitrary crystal symmetries and Bragg reflections can be calculated with this script using the compliance or stiffness matrix and lattice parameters of the investigated material as well as the slip planes and Burgers vectors of the relevant slip systems as input.

The lattice parameters of calcite at room temperature and 1 bar atmospheric pressure were taken as 4.99 Å for the $a$ parameter and 17.06 Å for the $c$ parameter (Antao et al., 2009). The stiffness matrix of calcite at room temperature and 1 bar atmospheric pressure was taken from (Dandekar, 1968).

4 Results

The measured diffractograms do not show any reflections pertaining to aragonite or another calcium-carbonate polymorph other than calcite demonstrating that, if high pressure polymorphs were present during the HPT experiments, they were not preserved in the quenched samples.
Figure 4: Theoretically calculated contrast factors for slip systems in calcite for edge (e) and screw (s) dislocations (see Table 2). The $r\{10\bar{1}4\}\langle \overline{2}021 \rangle$-edge and $f\{\bar{1}012\}\langle 10\bar{1}1 \rangle$-edge slip systems are shown as heavy symbols to highlight their similarity.
Table 1: Samples measured at DESY and ALS. The column ‘Phase’ indicates the stability fields of the CaCO₃ polymorphs corresponding to the $P-T$ conditions during deformation (Kondo et al., 1972; Pippinger et al., 2015), where calcite is denoted as phase I.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Rotations</th>
<th>Phase</th>
<th>Beamline</th>
</tr>
</thead>
<tbody>
<tr>
<td>rt-1.4-1</td>
<td>RT</td>
<td>1.4</td>
<td>1</td>
<td>I</td>
<td>DESY</td>
</tr>
<tr>
<td>rt-2-1</td>
<td>RT</td>
<td>2</td>
<td>1</td>
<td>IIIb</td>
<td>DESY</td>
</tr>
<tr>
<td>rt-4-1</td>
<td>RT</td>
<td>4</td>
<td>1</td>
<td>III</td>
<td>DESY</td>
</tr>
<tr>
<td>rt-4-2</td>
<td>RT</td>
<td>4</td>
<td>2</td>
<td>III</td>
<td>DESY</td>
</tr>
<tr>
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<td>1.4</td>
<td>1</td>
<td>I</td>
<td>DESY</td>
</tr>
<tr>
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<td>450°C</td>
<td>2</td>
<td>1</td>
<td>II</td>
<td>DESY</td>
</tr>
<tr>
<td>450-4-1/12</td>
<td>450°C</td>
<td>4</td>
<td>1/12</td>
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<td>DESY</td>
</tr>
<tr>
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<td>450°C</td>
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<td>1</td>
<td>II</td>
<td>DESY</td>
</tr>
<tr>
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<td>1</td>
<td>I</td>
<td>ALS</td>
</tr>
<tr>
<td>235-2-1</td>
<td>235°C</td>
<td>2</td>
<td>1</td>
<td>II</td>
<td>ALS</td>
</tr>
<tr>
<td>235-2-2</td>
<td>235°C</td>
<td>2</td>
<td>2</td>
<td>II</td>
<td>ALS</td>
</tr>
<tr>
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<td>235°C</td>
<td>3</td>
<td>1</td>
<td>III</td>
<td>ALS</td>
</tr>
<tr>
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<td>235°C</td>
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<td>1</td>
<td>III</td>
<td>ALS</td>
</tr>
<tr>
<td>235-4-2</td>
<td>235°C</td>
<td>4</td>
<td>2</td>
<td>III</td>
<td>ALS</td>
</tr>
<tr>
<td>235-6-1</td>
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<td>1</td>
<td>III</td>
<td>ALS</td>
</tr>
<tr>
<td>450-1-1</td>
<td>450°C</td>
<td>1</td>
<td>1</td>
<td>I</td>
<td>ALS</td>
</tr>
<tr>
<td>450-2-2</td>
<td>450°C</td>
<td>2</td>
<td>2</td>
<td>II</td>
<td>ALS</td>
</tr>
<tr>
<td>450-3-1</td>
<td>450°C</td>
<td>3</td>
<td>1</td>
<td>II</td>
<td>ALS</td>
</tr>
</tbody>
</table>
Table 2: Theoretical contrast factors for the known slip systems as given in (De Bresser and Spiers, 1997) and the \( r\{10\overline{1}4\}\{\overline{2}0\overline{2}0\} \) slip system proposed in (Pieri et al., 2001b) for the first 11 Bragg reflections in calcite for pure edge (e) and screw (s) dislocations:

<table>
<thead>
<tr>
<th>Slip system</th>
<th>0 1 2</th>
<th>1 0 4</th>
<th>0 0 6</th>
<th>1 1 0</th>
<th>1 1 3</th>
<th>2 0 2</th>
<th>0 2 4</th>
<th>0 1 8</th>
<th>1 1 6</th>
<th>2 1 1</th>
<th>1 2 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a{\overline{1}2\overline{1}0}{\overline{2}0\overline{2}1} \rangle_e )</td>
<td>0.142</td>
<td>0.107</td>
<td>0.392</td>
<td>0.354</td>
<td>0.207</td>
<td>0.322</td>
<td>0.142</td>
<td>0.320</td>
<td>0.131</td>
<td>0.355</td>
<td>0.252</td>
</tr>
<tr>
<td>( c(0001){\overline{1}2\overline{1}0} \rangle_e )</td>
<td>0.142</td>
<td>0.246</td>
<td>0.217</td>
<td>0.193</td>
<td>0.196</td>
<td>0.233</td>
<td>0.142</td>
<td>0.198</td>
<td>0.202</td>
<td>0.202</td>
<td>0.177</td>
</tr>
<tr>
<td>( f{\overline{1}0\overline{1}2}{2201} \rangle_e )</td>
<td>0.123</td>
<td>0.290</td>
<td>0.270</td>
<td>0.154</td>
<td>0.185</td>
<td>0.215</td>
<td>0.123</td>
<td>0.245</td>
<td>0.228</td>
<td>0.167</td>
<td>0.140</td>
</tr>
<tr>
<td>( f{\overline{1}0\overline{1}2}{10\overline{1}1} \rangle_e )</td>
<td>0.071</td>
<td>0.266</td>
<td>0.519</td>
<td>0.077</td>
<td>0.109</td>
<td>0.122</td>
<td>0.071</td>
<td>0.374</td>
<td>0.198</td>
<td>0.086</td>
<td>0.068</td>
</tr>
<tr>
<td>( m{10\overline{1}0}{\overline{1}2\overline{1}0} \rangle_e )</td>
<td>0.128</td>
<td>0.250</td>
<td>0.000</td>
<td>0.346</td>
<td>0.278</td>
<td>0.413</td>
<td>0.128</td>
<td>0.021</td>
<td>0.173</td>
<td>0.363</td>
<td>0.291</td>
</tr>
<tr>
<td>( r{10\overline{1}4}{\overline{2}0\overline{2}1} \rangle_e )</td>
<td>0.134</td>
<td>0.229</td>
<td>0.466</td>
<td>0.121</td>
<td>0.137</td>
<td>0.132</td>
<td>0.134</td>
<td>0.349</td>
<td>0.199</td>
<td>0.123</td>
<td>0.120</td>
</tr>
<tr>
<td>( r{10\overline{1}4}{\overline{1}2\overline{1}0} \rangle_e )</td>
<td>0.166</td>
<td>0.219</td>
<td>0.113</td>
<td>0.285</td>
<td>0.242</td>
<td>0.313</td>
<td>0.166</td>
<td>0.113</td>
<td>0.182</td>
<td>0.293</td>
<td>0.255</td>
</tr>
<tr>
<td>( \langle 2\overline{1}10 \rangle_s )</td>
<td>0.089</td>
<td>0.280</td>
<td>0.000</td>
<td>0.132</td>
<td>0.184</td>
<td>0.227</td>
<td>0.089</td>
<td>0.086</td>
<td>0.207</td>
<td>0.152</td>
<td>0.115</td>
</tr>
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<td>( \langle 20\overline{2}1 \rangle_s )</td>
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<td>0.646</td>
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<td>0.207</td>
<td>0.524</td>
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<td>0.391</td>
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<tr>
<td>( \langle 10\overline{1}1 \rangle_s )</td>
<td>0.071</td>
<td>0.266</td>
<td>0.519</td>
<td>0.077</td>
<td>0.109</td>
<td>0.122</td>
<td>0.071</td>
<td>0.374</td>
<td>0.198</td>
<td>0.086</td>
<td>0.068</td>
</tr>
</tbody>
</table>
4.1 Slip system analysis

The contrast factors for the 012, 104, 006, 110, 113, 202, 024, 018, 116, 211 and 122 Bragg reflections were calculated for the c(0001)<1210>, r{1014}<T201>, r{1014}<T210>, f{T012}<2201>, f{T012}<1014>, a{T201}<2201> and m{1010}<T210> slip systems for both pure edge and pure screw dislocation character with the aforementioned script “contrastfactor”. The contrast factors of the individual slip systems were then averaged assuming identical activity of each individual slip system belonging to one particular set of equivalent slip systems. For example, in the case of the r{1014}<T210> slip system the contrast factors of the individual Bragg reflections for the three equivalent slip systems r(1014)<T201>, r(1014)<1201> and r(0114)<2100> were averaged to compute the averaged contrast factors \( \bar{C} \) for the r{1014}<T210> set of slip systems. Table 2 lists the averaged contrast factors for the first eleven Bragg reflections for the known slip systems in calcite for both pure edge and pure screw character as given in (De Bresser and Spiers, 1997) and the r{1014}<T210> slip system proposed in (Pieri et al., 2001b).

The active slip systems were determined by comparing the theoretical contrast factors with the dislocation contrast extracted from the measured line profiles. Equation (5) was used to obtain the contrast factors of the individual Bragg reflections from the fitting parameters \( q_1 \) and \( q_2 \).

The comparison of the experimentally determined and the theoretically calculated contrast factors shown in Figures 5 and 4, respectively, reveals that only the edge dislocations of the r{1014}<2201> slip system and of the f{T012}<1014> slip system exhibit a similar anisotropy as the measured contrast factors. Even though the difference in the dislocation contrast of these two slip systems is too small to reliably distinguish between them (see Fig. 4), earlier studies on the deformation behavior of calcite have shown that for strain rates relevant to this study and deformation temperatures up to about 500°C the f{T012}<1014> slip system is very unlikely to play a major role, whereas the r{1014}<2201> slip system is dominant (De Bresser and Spiers, 1997). Thus, from our slip system analysis we infer that, apart from twin-
Figure 5: Experimentally determined contrast factors (right axis) and calculated contrast factors for the $r\{10\bar{4}\}\langle 2021 \rangle$ and $f\{1012\}\langle 1011 \rangle$ slip systems for edge dislocations (left axis). The experimentally determined contrast factors show the same strain anisotropy as the two slip systems but with diminished extent.

4.2 Dislocation Density

The dislocation density shows a systematic variation with temperature, pressure and radial distance from the rotation axis, hence, with strain and strain rate (see Fig. 6). For a given strain and strain rate, lower temperatures and higher pressures generally result in higher dislocation densities, whereby the influence of varying pressures is more pronounced at higher temperatures.
Figure 6: Dislocation densities after HPT-deformation as a function of distance from the rotation axis. (a) samples deformed at room temperature under 1.4, 2 and 4 GPa confining pressure respectively for one rotation and one sample deformed at 4 GPa for two rotations. (b) samples deformed at 450°C for one rotation under 1, 1.4, 2, 3 and 4 GPa confining pressure. (c) samples deformed at 450°C under 2 GPa for 1 and 2 rotations and under 4 GPa for 1/12 and 1 rotations respectively. (d) samples deformed at 235°C under 2 GPa confining pressure for 1 and 2 rotations.
than at lower temperatures. Samples deformed at room temperature show a monotonic increase in dislocation density with increasing radial distance from the rotation axis. In contrast, samples deformed at 235°C and 450°C exhibit a more complex behavior. After an initial increase of the dislocation density with distance from the rotation axis in samples deformed for up to one rotation the dislocation density saturates and even decreases with increasing distance from the rotation axis. At 235°C the saturation of dislocation density is reached at a higher radial distance than at 450°C.

4.2.1 Deformation at room temperature

The monotonic, almost linear increase of dislocation density with increasing distance from the sample center at room temperature can be seen in Fig. 6a. The samples deformed under 4 GPa for one and two rotations do not show any systematic differences in dislocation density except for strains smaller than about 10 (corresponding to a radial distance of < 1 mm), where the dislocation density is slightly higher after two rotations than after one rotation. The similarity of dislocation densities from one and two rotations at radial distances larger than 1 mm indicates that the shear strain rate rather than strain is the parameter controlling dislocation density. In addition, the dislocation density shows a weak dependence on the confining pressure. The samples deformed under the highest applied pressure of 4 GPa exhibit a higher dislocation density than the samples deformed under 1 and 2 GPa pressure. Interestingly, the sample deformed under 1.4 GPa displays consistently a slightly higher dislocation density than the one deformed under 2 GPa pressure, for most measurement points this effect is within the experimental error, though.

4.2.2 Deformation at 450°C

For samples deformed at elevated temperatures, the confining pressure has a more pronounced influence on the resulting dislocation densities (see Fig. 6b). Two different pressure regimes can be distinguished based on the evo-
olution of dislocation density with applied strain: At 1 and 1.4 GPa confining pressure and one rotation the dislocation density saturates with increasing radial distance from the center after an initial increase along the first mm, where the dislocation density is higher at 1.4 GPa than at 1 GPa (see Fig. 6b empty symbols).

Samples deformed under confining pressures ranging from 2 to 4 GPa for one rotation show a markedly different behavior (see Fig. 6b filled symbols). After an initial increase with distance from the center the dislocation density saturates only at higher strains and even decreases towards the edge of the sample. Similarly to the samples deformed in the low-pressure regime, the dislocation density shows a clear pressure dependence. With increasing pressure the dislocation density increases for a given radial distance, and the maximum in the dislocation density shifts towards successively higher radial distances from the center.

In both, the low-pressure and the high-pressure regimes, higher confining pressures lead to higher dislocation densities. The trend of increasing dislocation densities with increasing confining pressure is, however, persistent only within each of the two pressure regimes. The pressure effect shows a discontinuity at the boundary between the two regimes between 1.4 and 2 GPa, where a jump from dislocation densities of $9 \pm 1.4 \times 10^{14} \text{ m}^{-2}$ in the high-pressure limit of the low-pressure regime to a maximum of $3.5 \pm 0.5 \times 10^{14} \text{ m}^{-2}$ in the low-pressure limit of the high-pressure regime occurs.

### 4.2.3 Deformation at 235°C

Due to the small footprint of the beam at the ALS beamline used for measuring the samples that were deformed at 235°C, the data on the dislocation density are rather scattered. Nonetheless, some insight into the evaluation of the dislocation density during deformation at 235°C could be gained. Fig. 6d shows two samples deformed under 2 GPa confining pressure for one and two rotations, respectively. As expected, the dislocation densities obtained from deformation at 235°C are between those of the samples deformed at room
temperature and at 450°C. The dislocation density shows an initial increase with radial distance from the rotation axis before it saturates and decreases again. This behavior is similar to what has been observed in the samples deformed at 450°C and pressures of at least 2 GPa. In contrast to the samples deformed at 450°C, in the samples deformed at 235°C the dislocation density is higher and decreases only further away from the rotation axis and not as strongly.

4.3 Coherently scattering domain size

We describe the CSD-size distribution as determined by line profile analysis with a single parameter. To this end, the area averaged mean crystallite size $\langle x \rangle_{\text{area}}$ is used. It characterizes the CSD-size by an area weighted mean grain diameter similar to the size parameters extracted from grain size evaluations by microscopy. It can be derived from the $m$ and $\sigma$ parameters of the fitted size distribution according to (Ungár, 2004):

$$\langle x \rangle_{\text{area}} = m \exp(2.5\sigma^2)$$  (9)

Similarly to the dislocation density, the CSD size shows a strong dependence on both the pressure and temperature conditions prevailing during deformation, where low temperatures and high pressures generally lead to small CSD sizes (see Fig. 7).

4.3.1 Deformation at room temperature

Just as is the case with the dislocation density, the domain size does not show a saturation but decreases linearly with increasing radial distance from the center in samples deformed at room temperature (Fig. 7a). The decrease in $\langle x \rangle_{\text{area}}$ is not due to a shift in the median $m$ of the size distribution function, it is rather due to the decreasing width of the distribution, demonstrating that the distribution of the CSD size becomes more narrow with increasing radial distance from the center. This can be seen in Fig. 7d, where the $\sigma$ parameter, which reflects the width of the distribution for a given value of $m$, decreases
Figure 7: CSD size expressed as area weighted size parameter $\langle x \rangle_{area}$ (a-c) and width of the CSD size distributions (d) after HPT deformation as a function of the distance from the rotation axis. (a) samples deformed at room temperature under 1.4, 2 and 4 GPa confining pressure, respectively, for one rotation and one sample deformed at 4 GPa for two rotations. (b) samples deformed at 450°C for one rotation under 1, 1.4, 2, 3 and 4 GPa confining pressure and under 2 GPa for 2 rotations and under 4 GPa for 1/12 rotation. (c) samples deformed at 235°C under 1, 2, 3, 4 and 6 GPa confining pressure for 1 rotation and 2 and 4 GPa for two rotations. (d) Width of the CSD size distribution $\sigma$ for samples deformed for one rotation at room temperature and at 450°C applying confining pressures of 1.4, 2 and 4 GPa and at 235°C applying confining pressures of 1, 2 and 4 GPa.
down to a value of about 0.5 in concordance with the CSD size. Yet this value is still high given the small CSD size, exemplifying the heterogeneous character of the CSDs caused by deformation at room temperature. The samples deformed at 4 GPa for one and two rotations respectively display no significant difference, showing that at room temperature the CSD size evolution is controlled by the strain rate rather than by strain. Both the CSD size and the distribution width show the same weak influence of the confining pressure as the dislocation density, where higher pressures generally lead to smaller CSD sizes and narrower distributions. Just as in the case of the dislocation density, the pressure dependence exhibits an anomaly between 1.4 and 2 GPa, where the CSD size and width are slightly smaller (within the measurement error) at 1.4 than at 2 GPa.

4.3.2 Deformation at 450°C

The evolution of the CSD size distribution during deformation at elevated temperatures differs markedly from the room temperature case. Fig. 7b shows the CSD sizes of samples deformed at 1, 1.4, 2, 3 and 4 GPa at 450°C for one rotation. The CSD size decreases with increasing pressure in the range from 2 to 4 GPa confining pressure similar to the samples deformed at room temperature, but at 450°C the pressure dependence is more pronounced. The CSD size of the samples deformed at 1 and 1.4 GPa confining pressure lies in between the values for the samples deformed under 2 and 4 GPa. With the exception of the sample deformed at 1.4 GPa, the CSD size saturates after an initial distinct decrease with distance from the center.

To investigate the strain and strain rate dependence of the CSD-size evolution, one sample was deformed under 4 GPa confining pressure to 1/12 of a rotation, whereas another sample was deformed under 2 GPa confining pressure to 2 rotations. It is seen in Figure 7b that neither data points with equal strain rate but different strain nor data points with equal strain but different strain rates exhibit the same CSD size. This indicates that, in contrast to the room temperature case, neither strain nor strain rate alone are
the controlling parameters.

The width of the CSD size distribution is smaller than for the room temperature case despite of larger CSD sizes, and it displays a marked pressure dependence. It shows the same strain dependence as the \( \langle x \rangle_{\text{area}} \) parameter, remaining constant after an initial decrease. The size distribution broadens with decreasing pressure, with the sample deformed under 1 GPa pressure exhibiting the broadest distribution (see Fig. 7d).

### 4.3.3 Deformation at 235°C

As expected, the values for the CSD size parameter of samples deformed at 235°C lie between those of the samples deformed at room temperature and those deformed at 450°C. Fig. 7c shows the CSD size for samples deformed under 1 to 6 GPa confining pressure for one rotation as well as for samples deformed under 2 and 4 GPa confining pressure for two rotations. Similar to the situation at 450°C the CSD size saturates after an initial decrease with radial distance from the center. In contrast to the samples deformed at 450°C, the effect of pressure variations is more muted and becomes insignificant beyond 3 GPa, where the CSD is 25-30 nm at radial distances beyond 1 mm. The samples deformed at 2 GPa exhibit a significantly larger CSD size, which is still smaller than the corresponding values of the samples deformed at 450°C by almost a factor of 2. In addition, the initial decrease of the CSD size with increasing distance from the center is much more pronounced than at higher pressures. The sample deformed under 1 GPa pressure displays a different behavior, just as it is the case for the other deformation temperatures. Its CSD size does not show any dependence on the measurement position, and close to the center it is smaller than the CSD size of the samples deformed at 2 GPa pressure.

To differentiate between the effect of strain and strain rate two samples were deformed under 2 and 4 GPa pressure for two rotations. As Fig. 7c shows, the two samples deformed under 4 GPa demonstrate no significant difference regarding their CSD size indicating that after the initial deforma-
tion stage the CSD size is independent of strain and strain rate similar to the room temperature case. In contrast, the CSD size of the sample deformed under 2 GPa for two rotations is notably smaller than the CSD size of the sample deformed for one rotation. This conforms with the samples deformed at 450°C, where neither strain nor strain rate are the sole defining parameters for the CSD size.

The width of the CSD size distribution of these samples is well below the room temperature case and similar to the width of the CSD size distribution of the samples deformed at 450°C. Fig. 7d shows that the size distribution becomes more homogeneous with increasing pressure albeit not as pronouncedly as in the 450°C case. The width of the CSD size distribution shows a weak dependence on the radius, this dependence further decreases with increasing pressure.

5 Discussion

5.1 Slip system analysis

The identification of \( r\{10\overline{1}4\}\langle2021\rangle \) as the dominant active slip system agrees well with earlier studies on experimentally deformed calcite (Turner et al., 1954; De Bresser and Spiers, 1997; Barber et al., 2010). In these studies slip on \( r\{10\overline{1}4\}\langle2021\rangle \) was found to be one of the most important mechanisms of plastic deformation in calcite at temperatures up to 800 K. According to De Bresser and Spiers (1997) this slip system has the lowest critically resolved shear stress (CRSS) among the known slip systems in calcite for the deformation temperatures and strain rates relevant to this study.

The anisotropy of the experimentally determined dislocation contrast factors reflects the anisotropy of the theoretically calculated contrast factors very well in a qualitative sense. The magnitude of the strain anisotropy is, however, significantly lower for the experimentally determined than for the theoretically calculated contrast factors (see Fig. 5). It is known from TEM
investigations on calcite that in bright field images the dislocation contrast used for the Burgers vector analysis does not vanish, as it is the case in metals, when the Burgers and diffraction vectors are perpendicular (Barber et al., 2007). One of the reasons for the difference between the dislocation contrast derived from the model and the experimental values lies in the non-negligible proportion of covalent bonding in calcite. While the bonds between the calcium ions and the carbonate groups are primarily of ionic character, the bonds between the carbon and oxygen within the carbonate groups are of more covalent nature. Therefore a non-negligible fraction of the electron density in the carbonate groups lies between the C- and O-ions. This is in conflict with the model assumption of a spherically symmetric electron density around the ions underlying the kinematical theory of diffraction used in XPA (Ungár, 1999).

Moreover, due to the reduced mobility of point defects during plastic deformation under high confining pressure, the concentration of vacancies during HPT deformation is much higher than the equilibrium concentration at the same pressure and temperature conditions (Zehetbauer et al., 2003, 2006). High concentrations of point defects in the vicinity of dislocation cores naturally leads to a relaxation of the strain fields and dampening of the strain broadening of the Bragg peaks (Bullough and Newman, 1970), which diminishes the anisotropy of the dislocation contrast determined in diffraction experiments (Barber et al., 2007).

It is important to note, that several experiments were performed at $P-T$ conditions, where the metastable high-pressure polymorphs of CaCO$_3$ were present during deformation, yet no change in dislocation contrast was observed when crossing from the stability field of calcite into the stability fields of the high-pressure polymorphs. Our results suggest that in the high-pressure polymorphs dislocation glide operates in a similar manner as in calcite. In particular, our results indicate that in the high pressure polymorphs the glide planes and directions correspond to the $r\{10\overline{1}4\}$ lattice plane and the $\langle 2021 \rangle$ direction in calcite.
Twinning on \( \{10\bar{1}8\} \) planes is an important deformation mechanism in calcite. In particular, at room temperature the CRSS for \( \{10\bar{1}8\} \) twinning is substantially lower than for dislocation glide on \( r\{10\bar{4}\}\)\(\{2021\}\). Twinning on \( \{10\bar{1}8\} \) planes certainly contributed to deformation during the HPT experiments. The maximum shear strain that can be accommodated by \( e\)-twinning in calcite is 0.69 (Schmid et al., 1987). In comparison, the local shear strain attained during HPT of one rotation for a radial distance of 1 mm from the rotation axis is about 10. Therefore, in our experiments the contribution of twinning to the bulk deformation is minute. In addition, due to the low density of twin boundaries the contribution of twinning to Bragg peak broadening is negligible. Therefore, in our case information on twinning cannot be extracted from XPA, and no quantitative relationship between the contribution from twinning and from dislocation glide can be given.

5.2 Influence of temperature on microstructure evolution

It emerges from our experiments that the temperature has a strong influence on microstructure evolution during deformation (see Figs. 6, 7, and 8). Not only are the dislocation densities higher and the CSD sizes smaller

Figure 8: Temperature influence on (a) CSD size and (b) dislocation density in samples deformed under 2 GPa confining pressure for one rotation.
after deformation at room temperature than after deformation at elevated temperatures, but there are also systematic differences in the evolution of these parameters as a function of the applied strain. In samples deformed for one rotation at room temperature the dislocation density shows a monotonic increase with increasing strain, that is with radial distance from the rotation axis, and does not exhibit a saturation with increasing strain even at shear strains of 40 or higher (Fig. 8b). In contrast, if samples are deformed for one rotation at elevated temperatures, the dislocation density saturates at a certain strain and beyond saturation even decreases with increasing strain. Similarly, at room temperature the CSD size steadily decreases with increasing strain in samples deformed for one rotation, whereas at elevated temperatures it saturates after an initial decrease with increasing strain (see Figs. 7 and 8a). The experimentally observed microstructure evolution reflects successive accumulation of defects and diminution of the CSD size during deformation at low temperature and considerably more efficient recovery and eventually attainment of a dynamic equilibrium between nucleation and annihilation of dislocations during deformation at elevated temperatures.

Microstructure evolution during deformation is determined by the competition between deformation-induced nucleation of dislocations and recovery through their organization into energetically favorable arrangements such as (sub)grain boundaries and eventually annihilation, both of which require dislocation glide and climb (Passchier and Trouw, 1996). The strong influence of temperature can be explained by the temperature-dependence of the mobility of dislocations. Dislocation climb is a non-conservative motion of a dislocation in the sense that it requires supply or removal of point defects at the dislocation core by diffusion and is thus a thermally activated process. Although during deformation by HPT the concentration of point defects is substantially higher than in thermodynamic equilibrium (Zehetbauer et al., 2006), their mobility is very limited at low temperature. This renders dislocation climb extremely sluggish, and formation of energetically favorable dislocation structures via polygonalization and the annihilation of
dislocations are very limited. In contrast, these processes are very efficient at elevated temperatures. In addition, even though dislocation glide is a conservative mode of dislocation motion and does not involve long-range diffusion of point defects, it still shows considerable temperature dependence (De Bresser and Spiers, 1997).

The CSDs that are observed after deformation at 450°C may be interpreted as the characteristic sizes of dislocation cells, consisting of strain-free domains separated by thin regions of high dislocation density, which are produced during recovery of deformed materials (Mughrabi, 1983). The CSD size obtained by XPA in HPT-deformed metals and alloys very likely corresponds to the size of these dislocation cells (Ungár, 2005). TEM studies on deformed calcite have revealed the formation of dislocation cell structures similar to those found in metals (Barber and Wenk, 1979; Barber et al., 2010; Rybacki et al., 2013). The heterogeneous arrangement of dislocations in these dislocation cells leads to a reduction of lattice strain caused by dislocations, due to the screening of the strain fields of dislocations by neighbouring dislocations with opposite orientation. Higher deformation temperatures promotes the formation of these cell structures in calcite in a twofold manner. On the one hand, the CRSS of slip systems in calcite is strongly temperature dependent, especially so at low temperatures (De Bresser and Spiers, 1997). In order to build dislocation cell structures multiple slip systems need to be active. This may necessitate, depending on the grain orientation, secondary slip on a slip system other than one of the three $r\{10\bar{1}4\}\{20\bar{2}1\}$ slip systems, which is enhanced at high temperatures. On the other hand, arrangement of dislocations into the energetically favorable cell arrangements requires dislocation climb, which is thermally activated. A lack of active thermally activated crystal-plastic deformation mechanisms at low temperatures is reflected by the relatively small CSD sizes and their rather wide distribution after deformation at room temperature as compared to larger and more homogeneously distributed CSD sizes in the samples deformed at 450°C (see Fig. 7). The saturation of the CSD size with increasing strain after deformation at 235°C
and 450°C is similar though less pronounced to the strain-dependence of crystallite sizes in HPT deformed copper (Hebesberger et al., 2005).

The high dislocation densities observed after deformation at room temperature do not necessarily imply that dislocation glide is the prominent deformation mechanism. Calcite twinning is favored compared to dislocation glide at low temperatures, since the CRSS for twinning is much lower than for dislocation glide. TEM and etching studies have shown that mechanical twinning in calcite is accompanied by high dislocation densities around the twin boundaries and within the twins (Keith and Gilman, 1960; Barber and Wenk, 1979). The high dislocation density may therefore result from sessile dislocations that are at least in part due to twinning.

5.3 Effect of hydrostatic pressure on deformation

Our experiments that have been performed over a pressure range from 1 to 6 GPa reveal that apart from the temperature also the confining pressure applied during HPT has a significant influence on the evolution of the microstructural parameters. Four different polymorphs of CaCO$_3$ are expected to have been present during deformation at the different temperatures and confining pressures applied (see Table 1). According to Pippinger et al. (2015) calcite is stable at low pressures, and at about 1.2 to 1.6 GPa, depending on the temperature, it transforms to CaCO$_3$-II, and at pressures in excess of about 2.2 GPa CaCO$_3$-III and CaCO$_3$-IIIb become the stable polymorphs, where CaCO$_3$-III and CaCO$_3$-IIIb are confined to temperatures below about 250°C. The boundary between the stability fields of calcite and CaCO$_3$-II has been studied for temperatures up to 700°C by Kondo et al. (1972), who place it at 1.5 GPa for 250°C and at 1.6 GPa for 450°C. For both, the experiments done in the low-pressure regime in the stability field of calcite and for the experiments done in the high-pressure regime, within the stability fields of CaCO$_3$-II, CaCO$_3$-III and CaCO$_3$-IIIb an increase in the confining pressure leads to an increase of the dislocation densities and a decrease of the CSD sizes, where the effect is more pronounced at high temperatures than at
Figure 9: Pressure influence on CSD size and dislocation density in samples deformed at 450°C for one rotation. The measurements were taken 3 mm from the center corresponding to a shear strain of 31 and a shear strain rate of $1 \times 10^{-2} \text{s}^{-1}$. 
low temperatures. This pressure effect is due to the influence of pressure on the crystal lattice and the elastic anisotropy (Poirier, 1985). The formation of dislocations and point defects leads to excess volume, and work must be done against the applied pressure during the creation and movement of such defects (Zehetbauer et al., 2003). Elevated hydrostatic pressure therefore influences the mobility of dislocations in a similar way as reduced temperature. The pressure effect is generally less significant for glide-controlled creep than for thermally activated recovery processes (Poirier, 1985). A qualitative indication of the similarity between the effects of reduced temperature and elevated pressure is given by the shift of the maximum dislocation density towards higher radial distances, which is similarly produced by either a pressure increase from 2 to 3 or 4 GPa at 450°C or a temperature decrease from 450°C to 235°C at 2 GPa (see Fig. 6b,d).

The trend of increasing dislocation density and decreasing CSD size with increasing pressure is broken at the supposed pressure of the calcite to CaCO$_3$-II transformation. In our experiments, the dislocation density shows a sharp drop and the CSD size shows a sharp increase with a change in pressure from 1.4 to 2 GPa at room temperature and at 450°C (see Fig. 9) and with a change in pressure from 1 to 2 GPa at 235°C. The anomaly in the pressure effect is more pronounced at high temperatures than at low temperatures. At room temperature the CSD size at 1.4 GPa is consistently smaller by about 10-20 % than at 2 GPa for similar local strain, which is close to the measurement error of 15 %. The relative difference in the dislocation density is even smaller. At 450°C the CSD sizes at 1 and 1.4 GPa are 20-30 % and 30-80 %, respectively, smaller than at 2 GPa. The effect on the dislocation density at 450°C is even more pronounced with the dislocation densities being 40 % and 150 % higher at 1 and 1.4 GPa, respectively, than at 2 GPa.

In addition to the quantitative change, the evolution of the dislocation density with strain is also qualitatively different for deformation in the low- and high-pressure regimes (see Fig. 6). In the low-pressure regime of 1 and
1.4 GPa the dislocation density develops in accordance with the results from earlier studies on deformation in the stability field of calcite. For example, based on torsion experiments on Carrara marble at 1000 K and at 300 MPa confining pressure Pieri et al. (2001a,b) found that a steady state flow stress, a stable texture and an equilibrium grain size are reached at shear strains between 2 and 5. This agrees well with the dislocation density evolution in our samples, where the saturation is reached at a shear strain of about 5. In the high-pressure regime at pressures of 2 GPa and higher the dislocation density does not reach a saturation for samples deformed for one rotation even though the shear strain on the sample rim exceeds 40. Comparison of the samples deformed under 2 GPa for one and two rotations, respectively, reveals that after two rotations the dislocation density attains saturation, where the dislocation density at saturation is slightly higher than the maximum value for one rotation (see Fig. 6c). Furthermore, in the sample deformed under 4 GPa to $30^\circ$ (1/12 rotation) the dislocation density shows similar qualitative behavior as in the sample deformed at 4 GPa for one rotation, with the only difference that for a given strain rate the dislocation density is lower in the sample deformed for 1/12 rotation than in the sample deformed for one rotation (see Fig. 6c). This peculiar behavior cannot be explained solely based on XPA. Referring to preliminary results from crystal orientation imaging with electron backscatter diffraction (EBSD) it may, however, be hypothesized that at high strain-rates, that is at large radial distance from the rotation axis, the deformation is preferentially accommodated by dynamic recrystallization and the associated formation of high-angle grain boundaries. Immediately after their formation the grains that are newly generated during this process have lower dislocation densities than the relict porphyroclasts. The porphyroclasts are more likely preserved at low strain and strain rate, that is at lower radial distances from the rotation axis. The variation of the dislocation densities observed with increasing radial distance is thus likely due to the combined effects of two processes. The initial increase in the dislocation density with radial distance reflects the successive loading with dislocations
during progressive crystal plastic deformation of the pre-existing grains. This trend of increasing dislocation density is then truncated by the successive formation of new grains by dynamic recrystallization at high strains and strain rates occurring at higher radial distances from the rotation axis. This effect is likely to be obliterated through the progressive transformation of the porphyroclasts into recrystallized grains and the successive generation of dislocations within the recrystallized grains during ongoing deformation, as is indicated by the rather homogenous distribution of dislocation densities after deformation for two rotations (see Fig. 6c).

5.4 Implications for natural deformation

When deformation proceeds by dislocation creep, the relationship between dislocation density and applied stress can be used to infer the applied stress from deformation microstructures. Microphysical models for dislocation creep predict that the flow stress is proportional to the square root of the dislocation density (Kohlstedt and Weathers, 1980). This naturally implies that once steady state flow is reached, the dislocation density stays constant and vice versa (Kohlstedt and Weathers, 1980; De Bresser, 1996). Our results indicate that at 450°C in the CaCO$_3$-II stability field steady state deformation and thus constant microstructural parameters are only attained at significantly higher strain than at 450°C in the calcite stability field and that the microstructural parameters associated with steady state deformation are strain rate sensitive at least at strain rates between $10^{-2}$ and $10^{-3}$ s$^{-1}$. In addition, the jump in the dislocation density between 1.4 and 2 GPa suggests a weakening of carbonate rocks, when the boundary between the calcite and CaCO$_3$-II stability fields is crossed in the absence of aragonite formation.

Although the temperatures in the earth’s crust pertaining to the lithostatic pressures, at which the high-pressure polymorphs of CaCO$_3$ form, usually exceed the deformation temperatures used in this study, the pertinent $P - T$ conditions may nonetheless be reached in nature under specific circumstances. In the case of subduction of old lithosphere into the mantle,
extremely low geothermal gradients have been observed. Peacock and Wang (1999) calculated that the temperature of the Pacific plate subducted beneath north-east Japan reaches 200°C only at 50 km depth. Even at more common, higher geothermal gradients of 10 K/km the $P - T$ conditions of our experiments may locally be generated by tectonic overpressure. Field observations of high-pressure minerals in rocks typical for low-pressure metamorphism (Warren, 2013) and numerical modeling (Mancktelow, 2008; Vrijmoed et al., 2009; Li et al., 2010) have shown that significant overpressures of up to 40 % of the lithostatic pressure may occur for pressures up to 2 GPa. In addition, unusually high pressures may also be generated locally during deformation events on the earth’s surface as was inferred from the presence of nanocrystalline CaCO$_3$-II and CaCO$_3$-III in rocks deformed during landslide events (Schaebitz et al., 2015).

Moreover, we could demonstrate that high confining pressure in the GPa range can have a significant influence on the deformation behavior and resulting microstructure also aside from the impact of phase transitions. Earlier studies on deformation at lower confining pressures showed only a minute influence of confining pressure on the flow stress (De Bresser, 2002). It was found by De Bresser (2002) that the flow stress increases by about 1.6 % per 100 MPa in uniaxial compression tests at 800-1000°C and confining pressures between 100 to 600 MPa. In contrast, the influence of varying confining pressures on the inferred flow stress appears to be substantially more pronounced for deformation at about 1 GPa. Applying the aforementioned square root relationship between dislocation density and flow stress to our experiments at 450°C, an increase of the steady state flow stress of about 30 % is inferred for a pressure increase from 1 to 1.4 GPa, which corresponds to an increase of the flow stress of 7.5 % per 100 MPa. At pressures in excess of about 2 GPa the influence of the confining pressure on the inferred flow stress decreases with increasing pressure. This is evident from the fact that in the samples deformed at 450°C for one rotation the flow stress inferred for the maximum dislocation density increases only by about 30 % with a pressure increase
from 2 to 3 GPa (3 % per 100 MPa) and by about 10 % with a pressure increase from 3 to 4 GPa (1 % per 100 MPa).

6 Conclusions

Calcite powder was pressed and deformed to high strain at confining pressures of 1 to 6 GPa and temperatures ranging from room temperature to 450°C using high-pressure torsion. The resulting microstructures were characterized by synchrotron based X-ray diffraction experiments and analyzed by X-ray line profile analysis.

The analysis of the strain anisotropy as obtained from Bragg peak broadening showed that \( r\{10\overline{1}4\}\{2021\} \) with edge character is the dominant slip system for deformation under the pressure, temperature and strain rate conditions applied in this study. The dislocation contrast does not show any change, when the \( P - T \) conditions of deformation are shifted from the stability field of calcite to the stability fields of the high pressure polymorphs CaCO\(_3\)-II, CaCO\(_3\)-III\(b\) and CaCO\(_3\)-III, indicating that slip in these phases operates in a similar manner as in calcite.

In addition, the influence of pressure and temperature on the evolution of the microstructure during HPT could be established. Higher temperature allows for the development of a homogeneous and stable CSD size whereas at room temperature recovery and dynamic recrystallization are greatly hindered leading to much broader CSD size distributions. With respect to the effect of pressure a low-pressure regime defined by the stability field of calcite and a high-pressure regime coinciding with the stability fields of the high pressure CaCO\(_3\) polymorphs is discerned. Within the stability field of either calcite or of the high-pressure CaCO\(_3\) polymorphs increasing pressure leads to higher dislocation densities and smaller CSD sizes, where the effect diminishes with lower temperature and higher pressure. This trend is, however, broken at the calcite to CaCO\(_3\)-II transformation, where an increase in pressure leads to a sudden increase in CSD size and a concomitant drop in the
dislocation density. This effect is more pronounced at elevated temperatures than at room temperature.

Furthermore, at pressures below the calcite to CaCO$_3$-II transition the dislocation density saturates after an applied shear strain of about 10 in agreement with earlier studies on deformation at lower pressures. At pressures above the calcite to CaCO$_3$-II transition the strain and strain-rate dependence of microstructural parameters is more complex and governed by the effects of several competing processes including the successive accumulation of lattice strain within coherently scattering domains and potentially the formation of high-angle grain boundaries through dynamic recrystallization.

The effect of varying confining pressures is secondary to changes in temperature, but can still be relevant even within the stability field of a single phase. It is most significant at high temperatures and at pressures of about 1 GPa, and it diminishes with decreasing temperatures and with decreasing and increasing pressures. The drop of the dislocation densities with increasing pressure at the calcite to CaCO$_3$-II transition implies a weakening of carbonate-bearing rocks at these conditions.

Acknowledgements

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Manuscript II
Microstructural and textural evolution of calcite deformed to high shear strain by high-pressure torsion


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Microstructural and textural evolution of calcite deformed to high shear strain by high-pressure torsion

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Abstract

Calcite powder aggregates were deformed to shear strains up to 80 by high-pressure torsion at temperatures of 235 and 450 °C and confining pressures of 1 to 4 GPa. At 235 °C the deformation occurs by twinning and limited dislocation creep as well as by brittle processes. In contrast, subgrain rotation recrystallization is the predominant deformation mechanism at 450 °C. The high confining pressures affect the microstructural evolution by inhibiting crack nucleation and propagation and by constraining the mobility of point defects. While at 1.2 GPa confining pressure transient core-mantle microstructures are produced for all strain-rates, the recrystallization is strain-rate dependent at 2 to 4 GPa confining pressure. Core-mantle microstructures are produced at high strain-rates, whereas the porphyroclasts deform more homogeneously at low strain rates. This change in microstructural evolution is ascribed to the phase transition from calcite to CaCO$_3$-II at 1.6 GPa. Within the stability field of CaCO$_3$-II an increase in the confining pressure leads to reduction of the recrystallized grain size. Irrespective of the confining pressure a strong crystallographic preferred orientation is developed during deformation at 450 °C, which is compatible with dislocation glide on the $\{10\bar{1}4\}\langle\bar{2}021\rangle$ slip systems.
1 Introduction

The deformation of rocks is often characterized by the localization into shear zones with non-coaxial deformation kinematics, where high strains are attained (Etheridge and Wilkie, 1979). The microstructures and textures resulting from deformation and recrystallization in shear zones contain key information on the deformation conditions and on the processes underlying the high-strain deformation of rocks (Urai et al., 1986; Bestmann and Prior, 2003). Performing deformation experiments, where temperature, stress, strain, strain rate and confining...
pressure are accurately controlled, is crucial for the understanding of the links between microstructures, textures and deformation mechanisms.

Calcite is one of the most common minerals in the Earth’s upper crust and it plays an important role in the Earth’s carbon cycle. Calcite-bearing rocks may be subducted to great crustal and mantle depth, and, in this context, the deformation behavior of calcite under elevated pressures is of particular interest. The deformation behavior of calcite and of calcite-bearing rocks has been studied extensively. Both, natural and experimental settings have been addressed, and a wide range of deformation conditions has been covered (Turner et al., 1954; Schmid et al., 1980, 1987; Rutter, 1995; De Bresser and Spiers, 1997; Pieri et al., 2001a,b; Bestmann and Prior, 2003; Barnhoorn et al., 2004; Barber et al., 2007). Twinning on \( \{01\bar{1}8\} \)-planes and less commonly on \( \{10\bar{1}4\} \)-planes was established as an important deformation mechanism especially at low temperatures (Reusch, 1867; Baumhauer, 1879; Turner et al., 1954). Furthermore, dislocation creep is an important deformation mechanism in calcite, which becomes dominant with increasing temperatures. The known slip systems in calcite are \( \{10\bar{1}4\} \langle 2021 \rangle \), \( \{10\bar{1}4\} \langle 12\bar{1}0 \rangle \), \( \{T012\} \langle 2\bar{2}01 \rangle \), \( \{T012\} \langle 10\bar{1}1 \rangle \), \( c \langle 0001 \rangle \langle T2\bar{T}0 \rangle \), \( a \langle T2\bar{T}0 \rangle \langle 2021 \rangle \) and \( m \langle 10\bar{T}0 \rangle \langle T2\bar{T}0 \rangle \) (Turner et al., 1954; De Bresser and Spiers, 1997; Pieri et al., 2001a). The slip planes and directions relevant to this study are illustrated in Fig. 1.

Most rock deformation experiments, particularly those done at elevated pressures, have been performed using methods of coaxial deformation such as uniaxial compression or tensile tests. Since rock deformation in natural settings is usually non-coaxial, experiments involving non-coaxial deformation are crucial for a better understanding of rock deformation in nature (Paterson and Olgaard, 2000). One of the most commonly used and best suited methods for non-coaxial deformation to high strains is torsional deformation, which has been employed to study the deformation and the associated microstructure and texture evolution in calcite at confining pressures up to 500 MPa (Paterson and Olgaard, 2000; Pieri et al., 2001a,b; Rybacki et al., 2003; Barnhoorn et al., 2004; Barber et al., 2007). Pieri et al. (2001b) and Barnhoorn et al. (2004) related the components of the deforma-
tion and recrystallization textures that occur in torsionally deformed calcite to the activity of slip and twinning systems and established the temperature dependence of the texture evolution at 300 MPa.

The effect of confining pressures in the kbar and GPa range on the deformation behavior of CaCO$_3$ has usually been assumed to be of secondary importance (De Bresser, 2002), but it has not been studied comprehensively. The influence of high confining pressures on the deformation mechanisms in calcite-bearing rocks is, however, of particular interest, because high-pressure polymorphs of CaCO$_3$ may come into play (Merrill and Bassett, 1975; Merlini et al., 2012; Pippinger et al., 2015). Moreover, it has been shown for a variety of materials that high confining pressure in the GPa range may impede recovery and recrystallization during deformation. As a consequence, deformation at high confining pressures may lead to different microstructures and textures than deformation at similar temperatures and strain rates but at sub-GPa pressures (Zehetbauer et al., 2003). These potential effects of high confining pressure have not been investigated in any systematic manner for the deformation of calcite. In addition, if a high confining pressure in the GPa range is applied during deformation, this suppresses cataclasis and sample failure by fracturing and thus allows for high-strain deformation by crystal plasticity even at relatively low temperatures, which is not possible at lower confining pressures (Barnhoorn et al., 2004).

In this study we expand on the previous work on calcite deformation and investigate the development of microstructures and textures in polycrystalline Carrarra marble aggregates subjected to high-strain torsional deformation under confining pressures of 1 to 4 GPa and at temperatures of 235 and 450 ºC. We performed deformation experiments using high pressure torsion (HPT), a technique that allows for torsional deformation to arbitrarily high strains at temperatures of up to about 500 ºC and under quasi-hydrostatic confining pressures of up to 10 GPa (Zhilyaev and Langdon, 2008). These $P-T$ conditions conform to low temperature subduction zones or may be locally generated by tectonic overpressure in warmer subduction zones (Peacock and Wang, 1999; Warren, 2013; Schuster et al., 2017). We employed electron backscatter diffraction (EBSD) for crystal orientation anal-

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ysis on HPT deformed samples. EBSD provides direct and spatially resolved access to microstructures and crystal orientations which allowed us to unravel the influence of high confining pressures in the GPa range on the deformation mechanisms, microstructure- and texture evolution during HPT deformation of CaCO$_3$. The study complements an earlier study that employed X-ray line profile analysis (XPA) to investigate the evolution of the dislocation density and the size of the coherently scattering domains (CSD) with increasing strain in HPT deformed calcite (Schuster et al., 2017). For given temperature, strain rate and strain the dislocation density was found to increase and the CSD size was found to decrease with increasing pressure. This trend is only broken at the phase transition from calcite to the high-pressure polymorph CaCO$_3$-II, where the dislocation density drops and the CSD size increases with increasing pressure. In addition, qualitatively different behavior with increasing strain was observed during deformation at 450 °C in the stability fields of calcite and CaCO$_3$-II. In both pressure regimes the dislocation density increases with increasing strain but reaches a maximum at relatively low strains during deformation in the calcite stability field, whereas it only saturates at comparatively high strain during deformation in the stability field of CaCO$_3$-II. Although Schuster et al. (2017) provided important insights into the deformation of calcite at high confining pressures in the GPa range, the study is limited by the fact that relatively large volumes were sampled in the X-ray experiments, and direct information on the microstructures and textures on the scale of individual grains is missing.

2 Deformation experiments

The procedure of sample preparation and of the HPT experiments followed the one in the previous study by Schuster et al. (2017). For the starting material highly pure Carrara marble from the same block that was used in the previous study was crushed and subsequently sieved to a particle size of 63 - 100 µm. The powder was dried and then compacted into cylindrical pellets with 8 or 10 mm diameter at room temperature using a cold press. The amount of powder was chosen so as
Figure 2: Schematic cross-section of the HPT assembly; the sample is placed in the cavity between two anvils. The top anvil can move vertically to apply the set pressure. After the pressure is applied the top anvil is fixed, while the bottom anvil rotates to apply the shear stress. The sample confinement in the gap between the anvils is provided by the sample material that flows into the gap at the onset of the torsional deformation. The sample material in the gap hardens and provides the necessary back-pressure for the quasi-hydrostatic pressure conditions in the rest of the sample. The temperature is regulated by a controller, which is coupled with the induction furnace and a pyrometer focused on point (T) on the upper anvil. The induction solenoid surrounding the anvils extends about 2 cm above and below the sample. The HPT apparatus is held at room temperature through water cooling about 10 cm above and below the sample, ensuring well-constrained temperature conditions during deformation. Modified after Fig. 2 in (Schuster et al., 2017)

to obtain a pellet with 0.8 mm thickness assuming zero porosity. The pre-pressed powder samples show a weak texture with a preferred orientation of the \( c \)-axis parallel to the compaction direction i.e. normal to the base plane of the pellet. Accordingly, the \( a \)-axes show a slight aggregation within the base plane of the pellet but are otherwise randomly oriented (Schuster et al., 2017).

The deformation experiments were performed using the HPT apparatus at the Faculty of Physics, University of Vienna. The quasi-hydrostatic pressure component in the GPa range during HPT processing allows for the deformation of
cylindrical samples to arbitrarily high strains without sample failure and without significant change of the sample geometry. The quasi-hydrostatic pressure conditions are ensured through the geometry of the pressure anvils (Fig. 2). Both anvils contain cavities into which the sample is fitted. The sample is slightly thicker than the combined depth of the cavities, so that a gap of about 100 µm remains between the anvils. During the initial stage of the torsional deformation, after the compressive stress has been applied, sample material flows into the gap between the anvils, where it hardens and provides the back pressure necessary for maintaining quasi hydrostatic pressure conditions in the rest of the sample. The uniaxial load on the HPT anvils that induces the quasi-hydrostatic pressure conditions in the sample is monitored during deformation with an accuracy of about 3 %. The control system keeps the pressure on the sample surface within about 10 % of the set value.

The applied shear strain $\gamma$ increases with the distance from the rotation axis according to

$$\gamma = \frac{2\pi nr}{t},$$

(1)

where $n$ is the number of rotations, $r$ is the radial distance from the rotation axis and $t$ is the sample thickness. Locally the shear strain is simple shear with the shear plane normal to the rotation axis and the shear direction normal to the radial direction. For a more detailed description of the HPT technique the reader is referred to Zhilyaev and Langdon (2008).

In this study we used samples of 8 or 10 mm diameter that exhibited a final thickness (after deformation) of about 0.6 mm. The experiments were performed at 235 and 450 °C with the applied confining pressures ranging from 1 to 4 GPa (Table 1). The twist rate was 0.02 rotations per minute in all experiments corresponding to an equivalent strain rate of about $1.7 \times 10^{-2}$ s$^{-1}$ and of about $1.4 \times 10^{-2}$ s$^{-1}$ at the outer rim of the samples with 8 and 10 mm diameter, respectively. Test runs, where radially oriented line markers were applied to the basal and top surfaces of the pellet, revealed that the entire torsion was accommodated by shear deformation within the specimen, and no slip occurred at the contacts between the specimen and the anvil.

The deformed samples were embedded into epoxy resin so that the final spec-
imen surface was parallel to the plane normal to the rotation axis. This sample geometry ensured that the entire range of strains and strain rates present in the samples could be accessed. The surfaces were ground and subsequently polished with silicon carbide-, diamond- and aluminum oxide-suspensions down to a particle size of 0.05 µm to obtain the surface quality that is required for EBSD measurements. To establish electrical conductivity during the measurements in the SEM, the embedded samples were coated with a thin layer of amorphous carbon. In some cases the resin was painted with a layer of graphite paste.
Table 1: List of samples deformed by HPT and analysed by EBSD showing the deformation conditions and EBSD mapping parameters. Rot. is the number of rotations and r corresponds to the distance from the rotation axis where the EBSD data were collected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>P (GPa)</th>
<th>T (°C)</th>
<th>Rot.</th>
<th>Scan (mm)</th>
<th>r (mm)</th>
<th>Gain</th>
<th>Exposure (ms)</th>
<th>Indexing rate (s⁻¹)</th>
<th>Rho (%)</th>
<th>Peak count</th>
<th>Min peak dist. [px]</th>
<th>Step size (µm)</th>
<th>Size (µm)</th>
<th>Time (min)</th>
<th>γ</th>
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<td>76.25</td>
<td>12.9</td>
<td>87</td>
<td>3-15</td>
<td>150</td>
<td>10</td>
<td>0.1</td>
<td>92x65</td>
</tr>
<tr>
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<td>235</td>
<td>2</td>
<td>1</td>
<td>0.3</td>
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<td>11.4</td>
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<td>11.3</td>
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<td>0.12</td>
<td>45x105 50</td>
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<td>1</td>
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<td>11.3</td>
<td>85</td>
<td>3-14</td>
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<td>0.12</td>
<td>45x105 50</td>
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<td>85</td>
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<td>5</td>
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<td>3.29</td>
<td>74.24</td>
<td>13.3</td>
<td>85</td>
<td>3-14</td>
<td>200</td>
<td>8</td>
<td>0.08</td>
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<td>71.53</td>
<td>13.8</td>
<td>87</td>
<td>3-15</td>
<td>200</td>
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<td>86</td>
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<td>86</td>
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</table>
3 EBSD analysis

The EBSD measurements were performed on an FEI QuantaTM 3D FEG Scanning Electron Microscope. The EBSD patterns (EBSPs) were recorded with an EDAX Digiview IV EBSD camera mounted at an elevation angle of 5°. The OIM Data Collection 6.2 software was used for data collection and indexing. Electron beam settings were at an acceleration voltage of 15 kV, and a probe current of approximately 4 nA at a beam incidence angle of 20°, and a working distance of 14 mm. The EBSD camera binning was 4×4, Hough space settings were at a binned pattern size of 140, a θ step size of 1°, while a 9×9 convolution mask was employed. Crystal orientation maps were collected on a hexagonal grid. The texture of the pre-pressed pellet not subjected to HPT deformation was measured using an AXS BRUKER D8 diffractometer at the Faculty of Physics, University of Vienna utilizing Cu Kα1 radiation with a spot size of 0.5 mm.

3.1 Data treatment

The EBSD data were cleaned using cleaning procedures implemented in the EDAX OIM analysis software version 6.2. Firstly the grain confidence index (CI) standardization procedure, where the CI (= difference between the number of triangles between each 3 reflectors found for the first and second orientation solution, divided by the total number of triangles found) of data points inside a grain is changed to the maximum CI value found inside that grain. Subsequently, one step of the neighbour orientation correlation procedure was used and lastly one or two steps of grain dilation were applied. Mis- or non-indexed data points thus were assigned the orientation of one of the pertinent grains assuring neighbouring grains were in direct contact with one another. After the cleanup procedures data points with a CI smaller than 0.03 and grains consisting of only one data point were excluded. Grains were defined so that they were separated by high-angle grain boundaries with a misorientation angle of at least 15° with neighbouring grains.

For the texture analysis the MTEX 4.4 toolbox for Matlab was used (Bach-
The orientation distribution functions (ODF) were calculated by imposing no sample symmetry using a de la Vallee Poussin kernel with a halfwidth of 5° and a resolution of 2.5°. The X-direction in the pole figures (north) points towards the rotation axis, the Y-direction (east) follows the shear direction, and the Z-direction is parallel to the rotation axis pointing out of the sample plane. All pole figures belonging to one EBSD map are normalized to the same scale given in multiples of a random distribution (m.r.d.). The grid spacing is 15°. Additionally, pole figures projected in the YZ plane are provided in the supplement to aid the comparison with previous studies on deformation textures in calcite.

The twin boundaries were identified based on the misorientation between the grains sharing the boundary. The twin misorientations were defined by a 180° rotation about the respective pole of the twinning plane. In addition, mechanical twins in calcite are coherent twins, implying that the boundary plane coincides with the twin plane. The orientations of the traces of the twin planes in both, the host and the twin domains were compared to the orientation of the boundary trace yielding a second criterion for identifying twin boundaries. The tolerance angle for the misorientation was set to 10°. The relatively high tolerance angle is necessary to include most twin boundary segments, since the high lattice strain in the porphyroclasts may lead to a significant deviation from the ideal misorientation relations, in particular for early twins, which were exposed to large deformation after their formation. The specific misorientations of twins and deformation lamellae are color coded in the IPF maps. Arbitrary low and high angle boundaries with misorientation angles between 2° and 5°, 5° and 15°, and larger than 15° are colored in yellow, orange and white, respectively. Boundaries with misorientations corresponding to $e$-, $r$-, and $f$-twins are shown as thick lines colored black, blue and green, respectively.

For determining the grain size and the grain-size distribution we used the EDAX OIM analysis 6.2 software. The grain size distribution was calculated by defining grains as domains with a misorientation angle of at least 15°. The grain size was characterized by an equivalent diameter, corresponding to the diameter...
of a circle with the same area as the cut through the grains in the measurement plane, with a resolution of 10 bins per µm. The probability distribution

\[ p(x) = \frac{0.1}{\sqrt{2\pi}\sigma_x} \exp \left[ -\frac{(\log(x/m))^2}{2\sigma^2} \right], \]  

(2)

was fitted to the data using the 'Fityk' software (Wojdyr, 2010), where \( m \) is the median and \( \sigma \) is the shape parameter of the lognormal distribution. The factor of 0.1 accounts for the binning density of 10 bins per µm. Finally, the area weighted size parameter \( \langle x \rangle_{\text{area}} \)

\[ \langle x \rangle_{\text{area}} = m \exp(2.5\sigma^2). \]  

(3)

was calculated from the grain-size distribution, to derive a single parameter that characterizes the grain size.

4 Results

4.1 The effect of temperature on microstructural evolution

Pre-pressed calcite aggregates were subjected to high strain torsional deformation at 235 and 450 °C and confining pressures of 1 to 4 GPa using HPT. X-ray diffraction measurements revealed that regardless of the \( P-T \) conditions applied during deformation none of the samples contains aragonite or any other high-pressure polymorph of CaCO\(_3\) after the pressure release (Schuster et al., 2017).

The microstructures of the samples deformed at 235 °C and 450 °C show distinctly different characteristics in SEM (see Fig. 3). The microstructures produced at 235 °C are dominated by the presence of porphyroclasts with a high density of grain-internal lamellar structures. The porphyroclasts often are bounded by cleavage planes or rupture surfaces rather than by regular grain boundaries indicating that the powder was not fully consolidated during deformation. The matrix between the porphyroclasts is comprised of smaller grains, which supposedly formed by cataclasis. These domains exhibit a remarkable surface roughness, which cannot be removed by grinding and polishing and makes them unsuitable
Figure 3: SE images showing the microstructures typical for samples deformed at 235 °C (a) and 450 °C (b). (a) microstructure in a sample deformed by 1 rotation at 235 °C and 2 GPa pressure; image taken 3 mm from the center showing porphyroclasts of similar size as the initial grains and fine-grained domains in between. The porphyroclasts are pervaded by straight and wavy lamellar structures. (b) overview of the central region of a sample deformed by 2 rotations at 450 °C and 4 GPa, where the axis of rotation corresponds to the bottom left corner. The microstructure is characterized by porphyroclast remnants (dark) embedded in fine-grained recrystallized matrix (middle grey). The porphyroclast remnants further away from the center (upper right) show a shape preferred orientation parallel to the local shear direction.

for EBSD analysis. Therefore we obtained crystal orientation data only from the porphyroclasts in the samples deformed at 235 °C.

Contrastingly, the samples deformed at 450 °C do not show evidence of brittle processes. Instead, deformation proceeds by crystal-plastic mechanisms accompanied by dynamic recrystallization. The microstructures evolve with the applied shear strain from the initial microstructure, which is dominated by porphyroclasts, towards a microstructure comprised of equiaxed recrystallized grains with a unimodal size distribution. Microstructures at intermediate strain either comprise typical core-mantle microstructures or exhibit more homogeneous grain size distributions.
4.2 Porphyroclast microstructures in samples deformed at 450 °C

The microstructures in regions deformed to low shear strains (≤ 10) at 450 °C are dominated by porphyroclasts and porphyroclast remnants, that largely retain the isometric grain shape of the powder particles of the cold pressed powder. However, at confining pressures (≤ 2 GPa) recrystallization in the innermost regions of the samples (r ≤ 1 mm) may lead to the development of domains with shape preferred orientations within the porphyroclast remnants (Fig. 4b). The elongated porphyroclast domains are characterized by abundant low-angle grain boundaries and e-twins, which separate the elongated domains into more equi-axed subgrains. At higher strain the subgrains evolve to equiaxed recrystallized grains. The shape preferred orientation of the deformed porphyroclasts does not follow the macroscopic shear direction (Fig. 4b). By contrast, at higher strains the porphyroclast remnants regularly show shape preferred orientations with the long axes oriented parallel to the local direction of shear (Fig. 3b).

Deformation in the porphyroclasts proceeds by e-twinning and dislocation activity evident from the considerable grain-internal lattice rotation and the formation of subgrain boundary networks. Gradual grain-internal orientation changes may lead to cumulative misorientations in the porphyroclasts of up to 1° per µm for 10 µm without the formation of subgrain boundaries. Subgrains at the porphyroclast margins in core-mantle microstructures are of similar size as the adjacent recrystallized grains. In the inner region of the porphyroclasts, the subgrains are much larger than the recrystallized grains and exhibit lobate boundaries. Twins in the porphyroclasts are broad and curved with lensoid shape and taper out towards the grain boundaries. The twins are inhomogeneously distributed and in any given porphyroclast usually only one set of e-twins is activated. Like the host crystals, the twin lamellae show evidence of plastic deformation, albeit somewhat diminished, both in the form of localized subgrain boundaries as well as gradual lattice rotation. Apart from the broad e-twins, some isolated twin boundaries due to twinning on r- and to a smaller extent on f- and e-planes can be observed at
intermediate strains (see Fig. 4). These twin boundary sections are interpreted as remnants of twins that have formed in the porphyroclasts at an early deformation stage and were overprinted by grain refinement through recrystallization.

Figure 4: EBSD inverse pole figure (IPF) maps showing transient stages of recrystallization in samples deformed at 450 °C. (a-b) Sample deformed by 1 rotation under 2 GPa showing areas located 1 mm ($\gamma \approx 10$, $\dot{\gamma} \approx 3.5 \times 10^{-3}$ s$^{-1}$) and 2 mm ($\gamma \approx 21$, $\dot{\gamma} \approx 7 \times 10^{-3}$ s$^{-1}$) to the south of the rotation axis, respectively. (c) Sample deformed under 4 GPa for 0.25 rotations showing an area 3 mm southwest of the rotation axis ($\gamma \approx 8$, $\dot{\gamma} \approx 1 \times 10^{-2}$ s$^{-1}$). (d) IPF map color coding key.
Table 2: Parameters of the lognormal fits to the observed size distribution of recrystallized grains as obtained from the EBSD maps of the samples deformed at 450 °C with a significant population of recrystallized grains (>100 grains) and a step size of 150 nm or below. Maps that were generated using larger step sizes exhibit a bias towards larger grain sizes and were excluded. In addition to the median $m$ and the shape parameter $\sigma$ of the size distribution, the area weighted size parameter $\langle x \rangle_{area}$ (Eq. 3), the number of rotations during HPT deformation (Rot.), the distance of the map from the rotation axis (r) and the step size (ss) used for the map are shown in the table.

<table>
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<tr>
<th>EBSD map</th>
<th>P (GPa)</th>
<th>m (µm)</th>
<th>$\sigma$</th>
<th>$\langle x \rangle_{area}$ (µm)</th>
<th>Rot.</th>
<th>r (mm)</th>
<th>$\dot{\gamma}$ (s$^{-1}$)</th>
<th>ss (nm)</th>
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<td>0.60</td>
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<td>1</td>
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<td>0.58</td>
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<td>1</td>
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<td>31</td>
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</table>
4.3 Recrystallized microstructures in samples deformed at 450 °C

The recrystallized grains are isometric and therefore do not show any shape preferred orientation. They exhibit a different texture than the porphyroclasts and are devoid of internal twins on the hundreds of nanometre scale that can be resolved with our EBSD measurements. In every sample the size of the recrystallized grains decreases successively with increasing distance from the rotation axis until it reaches a limiting value between several µm down to a few 100 nm depending on the confining pressure (see Table 2). In contrast, the distribution of the remaining porphyroclasts is more heterogeneous, so that even at high strains relics of the original grains can be discerned (see Fig. 3b and Fig. 5).

4.4 Effect of pressure on the dynamic recrystallization at 450 °C

While dynamic recrystallization at 450 °C eventually leads to a matrix of fine grained recrystallized grains irrespective of the applied confining pressure (Fig. 6), the microstructures at intermediate stages of the recrystallization process exhibit a pressure dependence. Two different types of microstructures are observed in samples deformed at confining pressures \( \geq 2 \) GPa for one rotation (Fig. 5). In regions close to the sample rim recrystallization leads to the formation of a core-mantle microstructure with a distinct bimodal size distribution (Fig. 5c). The large grain size fraction (several 10 µm sized grains) is represented by porphyroclast remnants and the matrix is represented by comparatively small (several 100 nm to a few µm sized) recrystallized grains. In regions closer to the rotation axis (up to about 2 mm from the rotation axis) the formation of small recrystallized grains around the porphyroclasts is accompanied by the break-up of the porphyroclasts into domains separated by low- and high-angle boundaries leading to a more homogeneous grain size distribution (Fig. 5a,b).

The comparison of samples deformed for different numbers of rotations and therefore different strains at a given distance from the rotation axis (i.e. identical
Figure 5: Microstructures and textures of a sample deformed by 1 rotation at 450 °C and 4 GPa. The EBSD IPF maps were collected 1 mm (a), 2 mm (b) and 3 mm (c) south of the rotation axis, corresponding to \( \gamma \) equal to 10, 21 and 31, respectively, and \( \dot{\gamma} \) equal to \( 3.5 \times 10^{-3} \text{ s}^{-1} \), \( 7 \times 10^{-3} \text{ s}^{-1} \) and \( 1 \times 10^{-2} \text{ s}^{-1} \), respectively. The corresponding pole figures are shown in (d), (e), and (f), respectively. All pole figures are upper hemisphere equal angle projections. For the color key of the EBSD maps see Fig. 4. For pole figures projected in the YZ plane see the supplement.

strain rates) demonstrates that the change in microstructural evolution with increasing distance from the rotation axis is due to the change in strain rate and not strain. The microstructure close to the sample rim (3 mm from the rotation axis) in the specimen deformed for only 1/4 of a rotation (Fig. 4c) closely resembles the core-mantle microstructure similar to the sample rim (3 mm from the rotation axis) in the sample deformed for one rotation (Fig. 5c). The difference between the two microstructures lies in the higher area fraction of recrystallized grains in the high strain case (\( \gamma \approx 31 \)) compared to the low strain case (\( \gamma \approx 8 \)). Furthermore,
Figure 6: EBSD IPF map showing a region with almost complete recrystallization in a sample deformed by 1 rotation at 450 °C at 3 GPa pressure. Corresponding pole figures are shown below. The EBSD data were collected 3 mm S of the rotation axis ($\gamma \simeq 31, \dot{\gamma} \simeq 1 \times 10^{-2} \text{ s}^{-1}$). For the color key of the EBSD map see Fig. 4. For pole figures projected in the YZ plane see the supplement.

in samples deformed at pressures $\geq 2$ GPa the porphyroclast remnants close to the rim are frequently larger than any porphyroclast remnants in regions closer to the rotation axis, which demonstrates that the high strain rate microstructures cannot develop from the low strain rate microstructures.

By contrast, samples deformed at 1.2 GPa exhibit core-mantle microstructures everywhere except for the innermost 1 mm of the sample (Fig. 7). With
Figure 7: EBSD IPF map showing a core-mantle microstructure in a sample deformed by 1 rotation at 450 °C and 1.2 GPa pressure. The EBSD data were collected 1 mm S of the rotation axis (γ ≃ 10, ˙γ ≃ 3.5 × 10⁻³ s⁻¹). For the color key see Fig. 4.

The exception of the very center of the sample the microstructures do not show any qualitative dependence on the strain rate. The only systematic difference between the microstructures mapped at different radial distances from the rotation axis are that the size of the recrystallized grains decreases and the area fraction of recrystallized grains increases with increasing radial distance (Table 2).
4.5 Size distribution of the recrystallized grains at 450 °C

Figure 8: Size distribution of the recrystallized grains as derived from EBSD maps of samples deformed at 450 °C. (a) samples deformed for one rotation at pressures of 2, 3 and 4 GPa at a distance of 3 mm from the rotation axis and 1.2 GPa at a distance of 2.5 mm from the rotation axis. (b) samples deformed under 4 GPa pressure for 1/4 and 1 rotations at 1 and 3 mm distance from the rotation axis. The data points from EBSD analyses were fitted to a lognormal distribution with the software ‘Fityk’.

Microstructures, where the area fraction of recrystallized grains exceeds \( \sim \) 25 %, exhibit recrystallized grains with a unimodal size distribution. The area weighted grain size parameter \( \langle x \rangle_{\text{area}} \) decreases with applied shear strain until it reaches a limiting minimum value, which depends on the confining pressure (Table 2).

The recrystallized grain size given in terms of \( \langle x \rangle_{\text{area}} \) varies between 750 nm and 2.3 µm (Table 2). In the range of confining pressures between 2 and 4 GPa the grain size decreases with increasing pressure. However, the sample deformed at 1.2 GPa exhibits a minimum grain size that lies in between the minimum grain sizes in the samples deformed at 2 and 3 GPa. In contrast to the pressure dependence, the influence of strain and strain rate on the grain size yields a more complex picture (Fig. 8). While the grain size decreases with increasing radius in all samples, different local strain rates lead to different grain sizes for the same local shear strain. In particular, regions affected by similar strain exhibit smaller grain sizes at a higher strain rate.
4.6 Texture components at 450 °C

All samples deformed at 450 °C develop a similar texture with increasing strain regardless of the confining pressure, where three major texture components, one pertaining to the porphyroclasts and two pertaining to the recrystallized grains, can be discerned (Fig. 9). The texture becomes more pronounced with increasing strain in every sample (Fig. 5). The strength of the texture increases faster in core-mantle microstructures than in the microstructures with more homogeneous recrystallization that develop at low strain rates at confining pressures ≤ 2 GPa. The strength of the two texture components associated with the recrystallized grains increases with the degree of recrystallization (Fig. 5). A fully recrystallized microstructure exhibits only the two texture components associated with the recrystallized grains (Fig. 6). All three texture components show orientation maxima, that are dispersed alongside specific directions.

The porphyroclast texture component consists of two elements that are symmetrically equivalent with regard to the local shear direction (Fig. 9). The c-axes maxima of the two elements lie in the XZ plane and are rotated away from +Z by about 15° towards +X and -X, respectively. Both c-axes maxima are dispersed over an angle of up to 40° almost parallel to the shear direction where the sense of rotation is towards +Y. This dispersion is due to a rotation about the pole of the {1101} plane, which is aligned parallel to X. One of the associated a-axes lies in the XY plane with a maximum parallel to Y, while the other a-axes enclose a small angle with the XY plane and an angle of 60° with ± Y. The dispersion rotates the a-axes from their orientation in or close to the XY plane towards the XZ plane. All twins in porphyroclasts associated with the porphyroclast texture component are twinned on the same e-plane and only the porphyroclast domains corresponding to the texture component maximum are twinned. Therefore, the crystallographic orientations of the porphyroclast twins do not show dispersion.

The c-axis maximum of the first texture component of the recrystallized grains lies parallel to Z, while one of the a-axes lies parallel to X and one of the m{1010}-poles parallel to Y (Fig. 9). The texture component is dispersed parallel towards the shear direction Y over an angle of up to 45°. The rotation axis responsible
for the dispersion is parallel to X and coincides with the corresponding $a$-axes maximum. The $c$-axes maximum of the first texture component of the recrystallized grains coincides with the $c$-axes maximum of the texture of the cold-pressed samples before HPT-deformation. There, the $c$-axes maximum is, however, rather weak and the $a$-axes do not show any preferred orientation. In contrast, the new texture is characterized by a strong $c$-axes maximum and by additional preferred alignment of the corresponding $a$-axes indicating that this texture component is not inherited from the pre-pressed samples but has been formed during HPT deformation. The $c$-axes maximum of the second texture component of the recrystallized grains lies in the YZ plane enclosing an angle of $45^\circ$ with +Z and -Y, while one of the $a$-axes lies parallel to X, one $\langle 2021 \rangle$ direction lies parallel to Y and one $r\{10\bar{1}4\}$ pole lies parallel to Z (Fig. 9). This texture component is dispersed by a rotation about the $\langle 2021 \rangle$ direction, which is aligned parallel to Y. Therefore, the $c$-axes of this component are dispersed at a high angle with respect to the shear direction, where most grains pertaining to this orientation are dispersed by an angle of up to $15^\circ$ in either rotation sense. The dispersion by rotation about a $\langle 2021 \rangle$ direction normal to X is also observed for the first texture component of the recrystallized grains, especially when the recrystallization is intense (Fig. 6). In that case the $c$-axes of the recrystallized grains that are dispersed from Z towards Y are also dispersed at a high angle with respect to Y.
Figure 9: Texture components of a sample deformed by 0.25 rotations at 450 °C and 4 GPa. The EBSD map is located 3 mm southeast of the rotation axis corresponding to $\gamma = 8$ and $\dot{\gamma} = 1 \times 10^{-2}$ s$^{-1}$. The corresponding EBSD IPF map is shown in Fig. 4c. All orientations were rotated 45° clockwise around the sample normal, so that in the pole figures the Y-direction corresponds to the direction of shear, X points towards the rotation axis, and Z is parallel to the rotation axis pointing out of the plane. (a) Image Quality (IQ) map overlayed with color highlighting of certain orientation ranges. (b) IPF plot using the shear direction (Y) as reference direction and pole figures of selected plane poles and crystal directions. The three major texture components are highlighted in color. All highlighting colors correspond to one sample direction in one of the pole figures, except for the porphyroclast twins, which were marked directly in the IQ map. For all highlighting a tolerance angle of 15° has been applied. The texture component of the porphyroclasts was defined based on two aggregations of $m$-poles close to +X (blue) and -X (yellow). The first (red) and second (green) texture components of the recrystallized grains were defined based on the aggregation of $a$-axes close to +X and the aggregation of $\langle 2021 \rangle$ directions close to +Y, respectively. Lastly the twins pertaining to the blue porphyroclast orientation were marked in purple and those pertaining to the yellow orientation in orange. The color highlighting was applied in this order, so that in the case of overlapping orientations the latest applied color is visible.

4.7 Microstructure at 235 °C

The samples deformed at 235 °C show remarkably different microstructures than those deformed at 450 °C. In the samples deformed at 235 °C, the microstructures are dominated by highly strained porphyroclasts with a high density of twins and fine-grained domains, pointing to cataclastic behavior. In the porphyroclasts the main twinning system is $e$-twinning with a subordinate occurrence of $r$-twins and occasional interspersed $f$-twins. The porphyroclasts do not exhibit any shape-preferred orientation. They are mostly bounded by open cracks or by fine-grained material, presumably formed by cataclastic deformation. The $e$-twins are thinner and less curved than those in samples deformed at 450 °C and, especially at high strain, they may show sutured boundaries or trails of smaller bleb-shaped twins (Figs. 10 and 11a). The thickness of the twin lamellae decreases with increasing confining pressure. Porphyroclasts or porphyroclast areas oriented favorably for dislocation glide are pervaded by high- and low-angle grain boundaries with
Figure 10: EBSD inverse pole figure (IPF) map colored with respect to the sample normal (i.e. the torsion axis) of a sample deformed by one rotation at 235 °C and 2 GPa. The map area was located about 600 µm NE from the rotation axis corresponding to a shear strain of ~ 6 and a shear strain rate of ~ 2.1 × 10^{-3} s^{-1}. Despite the similar color in this IPF map the orientation of the primary, secondary and tertiary twins are not identical as illustrated by the unit cell wire frames.

straight traces crossing the entire diameter of the porphyroclasts in a parallel arrangement, where the porphyroclasts show little evidence of internal misorientation apart from the grain boundaries (Fig. 11).

The primary e-twin lamellae in samples deformed at 1 or 2 GPa pressure are typically several µm thick and may be accompanied by thinner secondary and tertiary e-twins and occasionally by r- and f-twins (Fig. 10). The secondary e-twins terminate at the boundaries of the primary twins, and are referred to as stopping twins. They induce additional local deformation inside the primary twins adjacent to their common boundary, as can be inferred from the elevated local misorientation and formation of subgrain boundaries inside the primary twins. At confining pressures > 2 GPa twins are usually 500 - 700 nm wide and rarely are
Figure 11: EBSD inverse pole figure (IPF) maps colored with respect to the sample normal (i.e. the torsion axis) of a sample deformed by 2 rotations at 235 °C and 4 GPa. The maps were located at successively increasing distance from the rotation axis. (a) was taken 0.3 mm NE from the center corresponding to $\gamma \sim 6$ and $\dot{\gamma} \sim 1 \times 10^{-3}$ s$^{-1}$. (b) was taken 1.2 mm S from the center corresponding to $\gamma \sim 25$ and $\dot{\gamma} \sim 4.2 \times 10^{-3}$ s$^{-1}$. The third neighbour kernel average misorientation (KAM) maps are colored using a rainbow color scheme, where blue corresponds to a misorientation angle of 0° and red to the maximum misorientation of 5°. The step size is 130 nm for map (a) and 120 nm for map (b).

wider than 1 µm. The twins may exhibit subgrain boundaries and an elevated point to point misorientation in the EBSD maps. Their boundaries are heavily sutured leading to short twin lamellae or trails of small grains (Fig. 11).

Grains that are not orientated favorably for one slip or twin system exhibit irregu-
lar (sub)grain boundary traces as well as increased lattice distortion (Fig. 11). In these porphyroclasts primary twins are often intersected by other $e$-twins, $r$-twins, regular low or high-angle grain boundaries or thin cracks that likely formed during the pressure release after deformation by HPT (Fig. 11b).

5 Discussion

5.1 The effect of temperature

Deformation at 450 °C proceeds by crystal-plastic dislocation creep and twinning in porphyroclasts and leads to dynamic recrystallization by subgrain rotation. By contrast, the microstructures in samples deformed at 235 °C show no evidence of subgrain rotation recrystallization and are dominated by porphyroclasts separated by cleavage planes and rupture surfaces.

The mechanisms for the removal of accumulated lattice strain in the porphyroclasts differ in samples deformed at 235 and 450 °C. Samples deformed at both temperatures exhibit gradual variation of lattice orientation within the porphyroclasts showing that geometrically necessary dislocations are not only located at subgrain boundaries but are distributed across the grain interior. However, at 450 °C, the dispersed dislocations locally organize into energetically more favorable dislocation arrays finally forming curved low-angle grain boundaries or subgrain boundaries with increasing grain-internal strain. At 235 °C the low-angle boundaries show mostly straight traces and little evidence of recovery. This is due to the fact, that at low temperature thermally activated dislocation climb is extremely sluggish. The low atomic mobility also renders the recrystallization of grains in the outer portions of the porphyroclasts sluggish, and recrystallization is restricted to high strains.

The higher density of $e$-twins in the porphyroclasts in samples deformed at 235 °C than in the porphyroclasts in the samples deformed at 450 °C is due to the considerably lower temperature dependence of the critically resolved shear stress (CRSS) for $e$-twins compared to the CRSS for the slip systems in calcite. The
CRSS for the \( r\{10\overline{1}4\}⟨2021⟩ \) slip systems increases threefold from 10 at 450 °C to 32 at 235 °C and the other notable low-temperature slip system in calcite \( f\{\overline{1}012\}⟨10\overline{1}1⟩ \) has a CRSS of 67 at 235 °C, while the CRSS for \( e \)-twinning is essentially constant in this temperature range (De Bresser and Spiers, 1997). The temperature influence on the twin morphology conforms with the calcite twin morphology geothermometer established by Ferrill (1991) and Burkhard (1993) from observations in naturally deformed calcite rocks. Regardless of the confining pressure, \( e \)-twins observed in porphyroclasts deformed at 450 °C correspond to 'type III' twins in the scheme by Burkhard (1993), which relate to deformation temperatures \( \geq 200 \) °C. By contrast, the \( e \)-twins in porphyroclasts deformed at 235 °C and confining pressures \( \geq 3 \) GPa are either relatively narrow (< 10 µm) and straight or show strongly sutured boundaries and trails of small grains (Fig. 11). According to Burkhard (1993), narrow and straight twins are classified at 'type II' twins, which occur at deformation temperatures between 150 and 300 °C, while severe twin boundary migration resulting in sutured boundaries and trails of small twinned grains is associated with 'type IV' twins, which occur after large deformation at temperatures above 250 °C. At 2 GPa and 235 °C 'type III' twins are observed together with type II twins (Fig. 10). However, 'type III' twins in samples deformed at 235 °C are thinner and exhibit more straight boundaries compared to the 450 °C case.

5.2 The effect of pressure

The high confining pressures during our experiments inhibit brittle processes and suppress macroscopic fracturing, since the nucleation and propagation of cracks must occur against the confining pressure (Poirier, 1985). This allows for deformation to high shear strains of at least 80 without macroscopic sample failure. By contrast, sample failure at comparatively low strain was regularly encountered in earlier torsion experiments on calcite which were performed at lower pressures. Barnhoorn et al. (2004) observed sample failure in torsion experiments at 300 MPa confining pressure by brittle macroscopic fracturing at 500 °C deformation temperature after reaching shear strains of 13 or less. In our experiments, the
suppression of brittle failure leads to the increased activity of other deformation mechanisms, in particular crystal-plastic mechanisms, at high confining pressures. The increased activity of crystal-plastic deformation mechanisms may produce microstructures that are usually associated with higher deformation temperatures. However, high confining pressures in the GPa range also affect atomic movement. Dislocation climb, which is necessary for the formation of subgrains in the highly strained porphyroclasts and for recrystallization by subgrain rotation, requires the supply or removal of atoms to or from the dislocation core. High pressures may have a qualitatively similar effect as low temperatures in impeding atomic motion. This may lead to the pile-up of defects and to the accumulation of high dislocation densities and smaller grain sizes (Poirier, 1985; Zehetbauer et al., 2003). Similar trends are observed in other HPT deformed materials and can be explained by the diminished effect of further pressure increases on the mobility of point defects (Zehetbauer et al., 2003). Hence, confining pressures in the GPa range do not only inhibit fracturing but also impede recovery and dynamic recrystallization facilitated by dislocation creep.

**Pressure induced low temperature characteristics of the microstructure**

Earlier studies established that temperature is an important factor for the size of recrystallized grains in calcite (Pieri et al., 2001a; Barnhoorn et al., 2004). Barnhoorn et al. (2004) found that the size of recrystallized grains decreases from about 4 to 2 μm, when the deformation temperature decreases from 600 to 500 °C in torsionally deformed calcite at 300 MPa confining pressure. A pressure effect on the size of the recrystallized grains has, however, not been reported before. In our study, we do find a substantial influence of the confining pressure on the size of the recrystallized grains (Table 2, Figs. 8a and 12). The \(\langle x_{\text{area}} \rangle\) parameter in the highly strained sample regions \((γ ≥ 30)\) decreases from 2 μm at 2 GPa to about 800 nm at 3-4 GPa. The pressure dependence of the grain size mirrors the pressure dependence of the size of the coherently scattering domains (CSD) and of the dislocation density, as determined from X-ray line profile analysis (Schuster et al., 2017) on HPT deformed calcite (Fig. 12). Similar effects of the confining pres-
Figure 12: The influence of pressure on the microstructural evolution for samples deformed at 450 °C for one rotation. All data points are from measurements taken about 3 mm from the rotation axis except for the grain size at 1.2 GPa, which was taken at a distance of 2.5 mm. The grain sizes of the recrystallized grains given as area weighted crystallite size measured by EBSD (black circle) are from this study. The CSD sizes also given as area weighted crystallite size and dislocation densities are from a previous study on HPT deformed calcite using XPA (Schuster et al., 2017).

Sure on grain size have been found for a variety of materials that were subjected to deformation by HPT (Wetscher et al., 2005; Schafler et al., 2006)). Ferrill et al. (2004) used the width of twins in naturally deformed calcite as a low-temperature geothermometer and found that at deformation temperatures above 200 °C e-twins are typically 1 to 4 µm wide, and they become narrower at lower temperatures. Mechanical twins in samples deformed at 235 °C and 4 GPa in our study are only several 100 nm wide. Thus, twin widths in samples deformed at 235 °C in the GPa range are narrower than twins from deformation at lower confining pressures and correspond to twin widths observed at significantly lower
temperatures. The "low temperature effect" of high confining pressure is also evident from the absence of 'type III' twins in samples deformed at 235 °C and \( \leq 3 \) GPa, even though they occur in natural calcite at 200 °C deformation temperature. The climb of partial dislocations in the twin boundary out of the twin plane is inhibited by the lower mobility of point defects at confining pressure in the GPa range compared to sub-GPa confining pressures.

**Pressure induced high temperature characteristics of the microstructure**

Schmid et al. (1980) investigated the temperature and strain rate dependence of the deformation behavior of Carrara marble during uniaxial compression at 300 MPa confining pressure. They distinguished three different deformation regimes. A low-temperature/high strain rate regime (up to 700 °C and \( 10^{-4} \) s\(^{-1} \)) with twinning as the main deformation mechanism, an intermediate regime (from 700 °C and \( 10^{-5} \) s\(^{-1} \) to 1000 °C and \( 10^{-3} \) s\(^{-1} \)) resulting in core-mantle microstructures and a high-temperature/low strain rate regime with a homogeneous breakup of porphyroclasts. All microstructures in samples deformed at 450 °C correspond to the intermediate or high temperature regime despite the comparatively lower deformation temperature and higher strain rates.

The recrystallized grains in samples deformed at 450 °C exhibit isometric grain shapes except for the regions deformed to shear strains \( \leq 20 \) at pressures \( \leq 2 \) GPa, where grains may have high aspect ratios (Fig. 4b). Barnhoorn et al. (2004) demonstrated that the aspect ratio of recrystallized grains in torsionally deformed calcite decreases with increasing temperature, leading to isometric grains in samples deformed at 1000 K. Studies on HPT processing of metals have shown that the grain shape resulting from dynamic recrystallization can be influenced by the applied confining pressure (Zhilyaev et al., 2003; Hebesberger et al., 2005). Hebesberger et al. (2005) and Zhilyaev et al. (2003) found for copper and nickel, respectively, that HPT processing at pressures up to 2 and 3 GPa, respectively, to limited strains leads to microstructures exhibiting similar elongated grains as in the calcite specimens deformed at pressures up to 2 GPa in this study, whereas higher applied strains lead to microstructures with isometric grain shapes. At
higher confining pressures, recrystallization results in isometric grains already at low strains in both copper and nickel. This indicates a similarity between the dislocation-based recrystallization and recovery mechanisms in calcite and metals. Such similarities have also been revealed in TEM studies by Barber and Wenk (1979) and Barber et al. (2010), who observed the formation of dislocation-cell structures by recovery in calcite deformed at elevated temperatures.

**Pressure influence on recrystallization mechanisms at 450 °C**

In contrast to earlier studies on torsionally deformed calcite at 300 MPa confining pressure and temperatures between 500 and 727 °C (Barnhoorn et al., 2004), we did not find evidence for any significant activity of grain boundary migration recrystallization. The measured grain-size distribution of the recrystallized grains is excellently approximated by a lognormal distribution function in all samples deformed at 450 °C (Equation 2 and Fig. 8). Barnhoorn et al. (2004) found a stable bimodal size distribution of recrystallized grains in calcite that was deformed to shear strains beyond 30 at 300 MPa and 727 °C. They concluded that the bimodal distribution emerges from a balance between grain refinement by subgrain rotation recrystallization and nucleation and growth of new grains due to grain boundary migration. The lack of a second grain size fraction in the samples deformed at 450 °C by HPT in this study indicates that no significant activity of grain nucleation mechanisms such as grain boundary migration occurs.

The morphology of e-twins provides additional evidence for the lack of grain boundary migration at 450 °C. Based on their width and lensoid shape the twins in the porphyroclasts are classified as 'type III' in the scheme of Burkhard (1993). These twins occur in calcite deformed to moderate to high strains at temperatures above 200 °C and in combination with dislocation glide on r− and f− planes (Burkhard, 1993). According to this scheme, 'type IV' twins, which are characterized by thick and patchy lamellae, sutured boundaries and trails of small, elliptically shaped twin domains, are formed, when dynamic recrystallization by grain boundary migration overprints twinning. In our samples, the boundaries of e- and especially of r-twins served as sites, where recrystallization is initiated.
(Fig. 4), but evidence for bulging or grain boundary migration is absent. The lack of 'type IV' twins in our samples suggests that recrystallization by twin boundary migration was rather subordinate or did not occur at all.

The pronounced dispersion of the texture components pertaining to both porphyroclasts and recrystallized grains at 450 °C provides further evidence for the absence of significant grain nucleation by grain boundary migration during recrystallization. Grains pertaining to the dispersed part of the orientation components are rotated away from the ideal orientation for the respective slip system, leading to the activation of other slip systems and higher lattice strain energies. These grains are preferred nucleation sites for new grains, when grain boundary migration contributes significantly to the dynamic recrystallization, leading to sharp texture maxima with only minimal dispersion (Barnhoorn et al., 2004).

5.3 Influence of polymorphic phase transformations

While the pressure influence on the microstructural evolution at 450 °C is monotonic between 2 and 4 GPa, a pressure change from 1.2 to 2 GPa leads to a discontinuity in the development of the deformation microstructures. Between 1.2 to 2 GPa the $\langle x \rangle_{\text{area}}$ parameter of the recrystallized grains increases from about 1.3 to about 2 µm, while it decreases as expected with increasing pressure from 2 to 4 GPa. Recrystallization at 1.2 GPa confining pressure leads to core-mantle microstructures already at distances of about 1 mm from the rotation axis. By contrast, samples deformed at pressures of $\geq 2$ GPa exhibit a more homogeneous break-up of the porphyroclasts at the innermost 2 mm from the rotation axis and core-mantle microstructure only develop at higher strain rates. The occurrence of a transient core-mantle microstructure prior to complete recrystallization was also observed in earlier studies on torsional deformation of calcite at sub-GPa pressures and 1000 - 1200 K (Pieri et al., 2001a,b). Studies on calcite deformed by uniaxial compression showed that the deformation and dynamic recrystallization of calcite by dislocation creep produces core-mantle microstructures, when the deformation occurs at lower temperatures and higher strain rates compared to samples that exhibit a more homogeneous break-up of porphyroclasts (Schmid
et al., 1980; Valcke et al., 2007).

The discontinuity in the pressure dependence of microstructural parameters between 1.2 and 2 GPa was previously observed in a study using X-ray line profile analysis for studying calcite deformed at 450 °C by HPT (Schuster et al., 2017). In this study it was observed that dislocation densities increase and CSD sizes decrease with increasing confining pressure, except for the jump from 1.4 to 2 GPa, where the dislocation density decreases and the CSD size increases. Furthermore, the dislocation density saturates with increasing strain at a distance of ≤ 1 mm from the rotation axis after a sharp initial increase in samples deformed by one rotation at 1 or 1.4 GPa. By contrast, the samples deformed at pressures ≥ 2 GPa for one rotation yielded a more gentle increase of the dislocation density with increasing radial distance. After a maximum at an intermediate radial distance, depending on the confining pressure, the dislocation density even decreases further outwards from the center. At 4 GPa the maximum dislocation density is reached at about 2.5 mm from the rotation axis. The onset of the formation of core-mantle microstructures occurs at the same radial distance in the current study. Interestingly, in our experiments a change in the recrystallization behavior marked by the onset of the formation of core-mantle microstructures occurs at the same radial distance (Fig. 5). Schuster et al. (2017) ascribed the change in the microstructural evolution between confining pressures of 1.4 and 2 GPa to the change from the calcite stability field to the stability field of CaCO$_3$-II, which occurs at a pressure of 1.6 GPa at 450 °C (Kondo et al., 1972). Our observations on the evolution of microstructural parameters of samples deformed at pressures up to 1.4 GPa, i.e. within the calcite stability field, are in line with earlier studies that were performed at lower confining pressures (Pieri et al., 2001a; Barnhoorn et al., 2004). In these studies it was found that a steady state is attained in the textural and microstructural evolution at a shear strain of about 5 - 10. The effect of the calcite to CaCO$_3$-II phase transition could explain the apparent ”high temperature characteristics” of the recrystallization microstructures at confining pressures in the stability field of CaCO$_3$-II as well as the increase in grain and CSD size and the decrease in dislocation density between 1.4 and 2 GPa confining pressure.
This is probably due to the effect that relaxation of the crystal structure after the calcite to CaCO₃-II phase transition leads to a higher mobility of point defects and enhance the activity of thermally activated processes.

5.4 Interpretation of the texture and slip-system analysis

To interpret the texture components and investigate the associated slip systems in samples deformed at 450 °C, we adopt the terminology used by Pieri et al. (2001b) and Barnhoorn et al. (2004) for the description of texture components in deformed calcite. This terminology is based on specifying the lattice plane, which is parallel to the macroscopic shear plane (msp) and the lattice direction, which is parallel to the macroscopic shearing direction (msd). Pieri et al. (2001b) discerned three pairs of conjugate texture components in calcite deformed at 727 °C and 300 MPa in torsion geometry: (i) $\pm r\{10\overline{1}4\} \parallel msp$ and $\{\overline{2}021\} \parallel msd$, which is abbreviated as ($\{r\}\{\overline{2}021\}$), (ii) $\pm r\{10\overline{1}4\} \parallel msp$ and $\mp a\{1\overline{1}0\} \parallel msd$, with abbreviation ($\{r\}\{a\}$), and (iii) $\pm c\{0001\} \parallel msp$ as well as $\mp a\{1\overline{1}0\} \parallel msd$, abbreviated as ($c\{a\}$).

The texture components resulting from crystal-plastic deformation can be related to the active slip and twinning systems through the orientation of the texture component with regard to the macroscopic stress tensor. For a uniaxial-stress setting, Schmid’s law relates the resolved shear stress for a specific slip system to the orientation of the crystal with respect to the stress tensor. Law et al. (1990) modified Schmid’s law for deformation in simple shear geometry. According to Law et al. (1990) the resolved shear stress $\sigma_r$ for a specific slip system in simple shear geometry reads

$$\sigma_r = \tau (\cos \phi_1 \cos \alpha_3 + \cos \phi_3 \cos \alpha_1) = \tau S_{ss}$$

where $\tau$ is the component of the shear stress tensor resolved in the shear direction, $\phi_1$ and $\phi_3$ are the angles the slip system’s Burgers vector encloses with the shear direction and with the shear plane pole, respectively, while $\alpha_1$ is the angle enclosed by the slip-plane normal and the shear direction and $\alpha_3$ is the angle enclosed by the slip-plane normal and the normal to the shear plane. In contrast
to the Schmid factor in the uniaxial case, which varies between 0 and 0.5, the simple shear Schmid factor $S_{ss}$ varies between 0 and 1 (Law et al., 1990). The $S_{ss}$ allows to calculate the resolved shear stress of possible slip systems for given crystallographic and stress orientations. As can be seen from Eq. 4, the $S_{ss} = 1$ for orientations, where the slip plane is parallel to the shear plane and the Burgers vector is parallel to the shear direction. These orientations are referred to as ”easy slip” orientations (Pieri et al., 2001a). In the case of simple shear with a constant deformation path such orientations may remain stable, because successive slip on such a slip system does not lead to lattice rotations (Pieri et al., 2001b). Note that the Schmid factor $S_{ss}$ may be unity also for other orientation relationships between slip systems and shear geometry.

In addition to the texture components themselves, the specific dispersions of the maxima may help to shed light on the activity of different slip system during deformation. Turner and Weiss (1963) have shown that in calcite the rotation axes caused by dislocation glide are perpendicular to the slip direction if only one slip system is active or dominates. Therefore, the rotation axes associated with the rotational dispersion of texture components allow to constrain possible slip systems.

To separate the texture pertaining to porphyroclasts and recrystallized grains, we calculated individual ODFs for the porphyroclast and recrystallized partitions of the map taken 3 mm from the rotation axis in a sample deformed at 4 GPa for 0.25 rotations shown in Fig. 9, where the two partitions were separated by grain size (Fig. 13). To ease visualization of the texture components, the pole figures are provided both as a projection in the XY and YZ plane.
Texture component associated with the porphyroclasts:

The texture component corresponding to the porphyroclasts (Fig. 13b,e) lies in between the ideal orientations \((c\langle a\rangle)\) and \((\{r\langle a\rangle\})\). One \(a\)-axis is perfectly aligned with \(Y\), and the \(c\)-axis maxima lie in the \(XZ\) plane and are rotated by about 10-15° from ± \(Z\). The corresponding \(r\{10\overline{4}\}\) poles also lie in the \(XZ\) plane enclosing an angle of 30-35° with ± \(Z\). A similar texture component was documented by Pieri et al. (2001b) and Barnhoorn et al. (2004) for the recrystallized domains in calcite that was torsionally deformed to high strains at temperatures between 1000 and 1200 K and 300 MPa confining pressure. The texture component documented here shows, however, two notable differences with respect to the texture components reported in the earlier studies.

In our samples, the \(c\)-axes are slightly more closely aligned with \(Z\) than in the previously reported textures. As a consequence, the \(r\{10\overline{4}\}\) poles are rotated further away from \(Z\), which makes \(r\{10\overline{4}\}\langle T2\overline{T}0\rangle\) slip, suggested by Pieri et al. (2001a), less likely to represent the "easy slip" system for this component. None of the known slip systems in calcite is perfectly aligned with this texture component, so that more than one slip system must have been active during deformation produc-
ing this texture component (Barnhoorn et al., 2004). In our previous study where XPA was applied to the same samples $r\{10\bar{1}4\}\langle2021\rangle$ slip was identified as the dominant slip system at the deformation conditions applied in our experiments. According to De Bresser and Spiers (1997) this set of slip systems has the lowest CRSS for the pertinent $P-T$ conditions. In fact, although not perfectly aligned for "easy slip", two of the $r\{10\bar{1}4\}\langle2021\rangle$ slip systems have a high Schmid factor of 0.8 for the given orientation. Barnhoorn et al. (2004) related the misorientation between the two maxima of the texture component between $\{r\langle a\rangle\}$ and $\{c\langle a\rangle\}$ to $f$-twinning, resulting in a misorientation of $78^\circ$ about $\langle02\bar{1}1\rangle$ whereas the misorientation of the porphyroclast component maxima in this study corresponds to a rotation of about $60^\circ$ about a $\langle1T01\rangle$ direction. If the texture components related to the porphyroclasts and those reported by Barnhoorn et al. (2004) resulted from the same process, a relationship with twinning seems unlikely, since this would lead to a distinct crystallographic orientation relationship.

The second difference to the textures reported in the earlier studies lies in the pronounced dispersion of the texture component by rotations around a ${1\bar{1}01}$-pole that is aligned parallel to X (Fig. 13g,h). This dispersion is much more pronounced than in the previous torsion studies at similar applied shear strain (Barnhoorn et al., 2004). If this texture component were due to only a single slip system, the rotational dispersion would suggest the direction close to $\pm X$ to be the rotation axis and Y to be the direction of the respective Burgers vector. The Burgers vectors of the two aforementioned $r\{10\bar{1}4\}\langle2021\rangle$ slip systems deviate up to about $10^\circ$ from the ideal direction normal to the $\{1\bar{1}01\}$-pole. Furthermore, the abundance of subgrain boundaries and lattice rotations within the porphyroclasts (see Fig. 4d) cannot be produced solely by slip on a single slip system. These features rather suggest a more complex intragranular deformation including secondary slip and dislocation climb.

**Texture components associated with the recrystallized grains:** Out of the two texture components associated with the recrystallized grains, the one with the $c$-axis maximum parallel to Z is dominant. This texture component has not been described in any of the earlier studies on torsionally deformed calcite. While the
IPF with respect to X exhibits a well defined maximum around an \(a\)-axis, the orientation distribution in the IPFs with respect to Y and Z are more diffuse (Fig. 13). The inverse pole figure drawn with reference direction Y (Fig. 13e,g), shows an accumulation around \(m\{10\overline{1}0\}\)-poles, which is dispersed out of the basal plane by a rotation about the \(a\)-axis aligned parallel to X.

This texture component would therefore represent an "easy slip" orientation for a \((c)\langle m \rangle\) slip system. Slip on the basal plane has indeed been reported from the deformation of calcite. The corresponding slip direction would, however, be \(\langle a \rangle\) instead of \(\langle m \rangle\). In fact, \(\langle m \rangle\) does not correspond to any known slip direction in calcite. However, for one of the \(r\{10\overline{4}\}\langle \overline{2}021 \rangle\) slip systems the Schmid factor equals 1, and the texture component thus lies in an ideal orientation for slip on a single \(r\{10\overline{4}\}\langle \overline{2}021 \rangle\) slip system. This slip system is also compatible with the dispersion of the texture component. In calcite every \(a\)-axis is perpendicular to one of the three symmetrically equivalent \(\langle \overline{2}021 \rangle\) directions. The \(\langle \overline{2}021 \rangle\) direction is the slip direction for two known slip systems in calcite \(r\{10\overline{4}\}\langle \overline{2}021 \rangle\) and \(f\{1012\}\langle 2201 \rangle\). Experimental studies on the temperature-dependence of the activity of slip systems in calcite have shown that at 450 °C \(r\{10\overline{4}\}\langle \overline{2}021 \rangle\) has a significantly lower CRSS than \(f\{1012\}\langle 2201 \rangle\) and constitutes the dominant slip system (De Bresser and Spiers, 1997). This agrees with the findings in an earlier study using X-ray line profile analysis, where the \(r\{10\overline{4}\}\langle \overline{2}021 \rangle\) slip system was found to be the dominant slip system at the pertinent deformation conditions (Schuster et al., 2017).

The second texture component associated with the recrystallized grains is characterized by a \(c\)-axes maximum that is tilted away from Z by about 45° against the shear direction. This corresponds to the "easy slip" orientation for \(r\{10\overline{4}\}\langle \overline{2}021 \rangle\), with the \(r\{10\overline{4}\}\) pole parallel to Z and the slip direction \(\langle \overline{2}021 \rangle\) parallel to Y (Fig. 13e,g). This texture component has repeatedly been observed in naturally and experimentally deformed calcite (Schmid et al., 1981, 1987; Rutter et al., 1994; Pieri et al., 2001b; Barnhoorn et al., 2004). Schmid et al. (1981) showed that this preferred orientation results from the activity of e-twinning and \(r\{10\overline{4}\}\langle \overline{2}021 \rangle\) glide. This texture component is, however, also observed in re-
crystallized domains in calcite mylonites, which do not show any evidence of
twinning (Schmid et al., 1981; Rutter et al., 1994). Rutter et al. (1994) and Schmid et al. (1987) argued that in this case earlier twinning has been obliterated by later recrystallization. However, in our case this texture component becomes stronger with increasing strain and extent of recrystallization and cannot be observed in the porphyroclasts themselves (Figs. 4, 6 and 13). It is therefore inferred that this texture component is formed by subgrain rotation recrystallization irrespective of the microstructure and texture evolution in the precursor porphyroclasts.

The rotation axis responsible for the dispersion of this component is parallel to the ⟨2021⟩ direction, which is aligned with the shear direction (see Fig. 13c,d,g). This direction is perpendicular to one of the a-axes. This points to the activation of c(0001)⟨T2T0⟩ as a secondary slip system. Note, that this rotational dispersion is most pronounced for the second texture component of the recrystallized grains, but it may also be present in the other texture component of the recrystallized grains (see Fig. 6), which is a common observation especially in regions with extensive recrystallization. This suggests that c(0001)⟨T2T0⟩ is activated as a secondary slip system, when r{10T4}⟨2021⟩ dominates.

In conclusion, despite of some similarities, the texture evolution in our experiments differs markedly from previously observed textures that were generated during torsional deformation of calcite at lower pressure. The saturation texture attained in the course of recrystallization during deformation to high strain at temperatures of 1000 and 1200 K is very similar to the texture of porphyroclasts developed during HPT deformation at 450 °C. This texture component is not shown by the recrystallized grains, and in our experiments becomes successively weaker with increasing extent of recrystallization. Barnhoorn et al. (2004) deformed calcite samples to high strains at 600 °C and produced textures that are quite similar to the textures produced in our experiments. In their experiments a strong texture component formed, which resembles the second texture component of the recrystallized grains in our study. However, whereas in our study the c-axes maximum is tilted from Z by about 45° against the shear direction it is tilted into the shear direction in the study of Barnhoorn et al. (2004).
6 Conclusions

High pressure torsion was employed to investigate the evolution of the microstructure and texture during shear deformation of calcite at 235 °C and 450 °C at very high confining pressures of 1 to 4 GPa. Brittle failure was efficiently suppressed through the high confining pressures. At 450 °C the experimental setup allowed for deformation to shear strains exceeding 80 entirely by crystal-plasticity. We could demonstrate that confining pressures in the GPa range have a significant influence on the microstructural evolution during deformation to high strains and lead to both apparent high temperature and low temperature characteristics. Samples deformed at 450 °C show remnants of heavily twinned porphyroclasts with extensive grain-internal lattice strain and pervasive recrystallization. Based on texture, microstructure and grain size distribution of the recrystallized grains subgrain rotation is identified as the dominant recrystallization mechanism. The size of the recrystallized grains depends, apart from the local strain and strain rate, on the confining pressure. In general, higher pressure leads to smaller grain sizes. This trend is broken only at the calcite to CaCO$_3$-II phase transition at 1.6 GPa, which leads to a sudden increase of the size of the recrystallized grains. This pressure effect also causes the formation of different transient recrystallization microstructures. At 1.4 GPa deformation to intermediate strains produces core-mantle microstructures regardless of the strain rate. By contrast, the microstructural evolution is strain-rate dependent at higher confining pressures. At pressures above about 2 GPa core-mantle microstructures are formed, when strain rates are high, whereas recrystallization is more homogeneously distributed, when strain rates are low. Deformation at 450 °C leads to the development of a pronounced texture, which is independent of the confining pressure. The texture comprises three components one of which is associated with the porphyroclasts, whereas the other two are associated with the recrystallized grains. Both, the texture component associated with the porphyroclasts and those associated with the recrystallized grains are compatible with glide on $\{10\overline{1}4\}$$\langle20\overline{2}1\rangle$. Whereas for the second texture
component of the recrystallized grains, the \( r\{10\bar{1}4\}\langle 20\bar{2}1\rangle \) slip system perfectly matches the "easy slip" condition, this is not the case for the other two texture components. Based on their high Schmid factors, simultaneous slip on two symmetrically equivalent \( r\{10\bar{1}4\}\langle 20\bar{2}1\rangle \) slip systems is inferred for the porphyroclasts. In the case of the first texture component associated with the recrystallized grains, none of the known slip systems of calcite is in "easy slip" orientation, but one of the \( r\{10\bar{1}4\}\langle 20\bar{2}1\rangle \) slip systems exhibits a Schmid factor of 1 and therefore lies in an ideal orientation for slip. The maxima of these texture components are dispersed by lattice rotations caused by dislocation slip on \( r\{10\bar{1}4\}\langle 20\bar{2}1\rangle \) or \( c(0001)/\langle 12\bar{1}0\rangle \).

The samples that were deformed at 235°C show strong intracrystalline deformation in the form of twinning and the formation of deformation lamellae, while intracrystalline recrystallization is strongly retarded as compared to deformation at 450 °C. The twin morphology is pressure dependent. At low pressures up to 2 GPa, thick curved twins similar to the twins in porphyroclasts deformed at 450 °C occur, while at 4 GPa in addition to thick straight twins, a second type of twins with sutured boundaries and trails of small, twinned grains typical for grain boundary migration recrystallization appear.

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References


Supplementary data

Pole figure data from Fig. 5 projected into the YZ plane (Y west, Z north)

Pole figure data from Fig. 7 projected into the YZ plane (Y west, Z north)
Manuscript III

Intragranular deformation mechanisms in calcite deformed by high-pressure torsion at room temperature

Intragranular deformation mechanisms in calcite deformed by high-pressure torsion at room temperature

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Abstract

Polycrystalline calcite was deformed to high strain at room temperature and confining pressures of 1-4 GPa using high-pressure torsion. The high confining pressure suppresses brittle failure and allows for shear strains $>100$. The post-deformation microstructures show inter- and intragranular cataclastic deformation and a high density of mechanical twins and deformation lamellae in highly strained porphyroclasts. The morphologies of the twins resemble twin morphologies that are typically associated with substantially higher deformation temperatures. Porphyroclasts oriented unfavorably for twinning frequently exhibit two types of deformation lamellae with characteristic crystallographic orientation relationships associated with calcite twins. The misorientation of the first deformation lamella type with respect to the host corresponds to the combination of one $r\{10\bar{1}4\}$ twin operation and one specific $f\{01\bar{2}2\}$ or $e\{01\bar{2}8\}$ twin operation. Boundary sections of this lamella type often split into two separated segments, where one segment corresponds to an incoherent $r\{10\bar{1}4\}$ twin boundary and the other to an $f\{01\bar{2}2\}$ or $e\{01\bar{2}8\}$ twin boundary. The misorientation of the second type of deformation lamellae corresponds to the combination of specific $r\{10\bar{1}4\}$ and $f\{01\bar{2}2\}$ twin operations. The boundary segments of this lamella type may also split into the constituent twin boundaries. Our results show that brittle failure can effectively be suppressed during room temperature deformation of calcite to high strains if confining pressures in the GPa range are applied. At these conditions, the combination of successive twin operations produces hitherto unknown deformation lamellae.
1 Introduction

Mechanical twins are the most conspicuous deformation features in calcite deformed at low temperatures ($T < 300 \, ^\circ C$) or at high strain rates (e.g. $10^{-4} \, s^{-1}$ at 700 °C) (Barber and Wenk, 1979; Schmid et al., 1980; Burkhard, 1993; Lacombe, 2010). Three types of deformation twins occur in calcite (Paterson and Turner, 1970; Barber and Wenk, 1979). For the most common, the so called $e$-twins, the misorientation between twin and host corresponds to a rotation of 180° about the pole of an $e\{01\overline{1}8\}$-plane, resulting in slip along a $\langle 40\overline{4}1 \rangle$ direction, where the twin and the host share the $e$-plane as their common boundary. The other two known deformation twins in calcite are the $r$- and $f$-twins, which show a misorientation between twin and host corresponding to a rotation of 180° about an $r\{10\overline{1}4\}$ and $f\{01\overline{2}2\}$ plane pole, respectively, resulting in slip along a $\langle 20\overline{2}1 \rangle$ and a $\langle 10\overline{1}1 \rangle$ direction, respectively, where the $r$- and $f$-planes constitute the respective twin boundaries. Due to the trigonal symmetry of calcite three symmetrically equivalent twins occur for $e$-, $r$- and $f$- twins (Fig. 1).

Mechanical $e$-twins are common in naturally deformed rocks and can also be produced in experiments (Turner et al., 1954) even by simple means such as by pushing a knife edge into a calcite single crystal (Baumhauer, 1879). The $e$-twins show characteristic morphologies and frequencies (#/mm) depending on deformation conditions such as stress, strain and temperature (Burkhard, 1993; Ferrill et al., 2004). Many of the pioneering studies on mechanical twinning focused on the symmetry relations and dislocation mechanisms of mechanical twins in calcite (see review by Duparc (2017)). More recent studies addressed the relationships between deformation conditions and the morphology (Burkhard, 1993; Ferrill et al., 2004; Rybacki et al., 2013; Covey-Crump et al., 2017) and frequency (Jamison and Spang, 1976; Rowe and Rutter, 1990; Lacombe, 2007) of $e$-twins. The morphology and characteristic size of mechanical calcite twins were calibrated as geothermometers and were used for extracting information on deformation conditions in naturally deformed carbonate rocks (Burkhard, 1993; Ferrill et al., 2004; Lacombe, 2010).
Burkhard (1993) and Ferrill et al. (2004) established a scheme for relating four characteristic ε-twin morphologies to specific deformation conditions. Thin (< 1 μm) and straight twins are referred to as “type I” twins, which are characteristic for deformation at T < 200 °C; wider twins (>> 1 μm) with a moderate lensoid shape constitute “type II” twins, which occur at temperatures between 150-300 °C; wide (>> 1 μm) and curved twins, which taper out towards grain boundaries, are termed “type III” twins and form at T > 200 °C; they are produced during high strain deformation by dislocation creep; “type IV” twins form thick lamellae with irregular and sutured grain boundaries and may be disrupted by the host, giving rise to trails of small twin grains with low aspect ratios. Type IV twins commonly occur in rocks that were deformed to high strain at temperatures above 250 °C and are associated with significant twin boundary recrystallization.
The influence of temperature and applied strain on the morphology of mechanical twins is due to the mechanism of twin propagation. Mechanical twins grow by the movement of partial dislocations that may be generated by dissociation from full dislocations (Hirth and Lothe, 1982). Lamellae of mechanical twins in calcite may grow in length by glide of partial dislocations on the twin plane, where the Burgers vectors are oriented parallel to the shear direction of the twin. The broadening of twins, however, requires that dislocations move out of the glide plane. For dislocations with edge character this can only occur by climb, which is a thermally activated process. The broadening of twin lamellae is thus also regarded as a thermally activated process, which gives rise to the relationship between twin-thickness/morphology and deformation temperature providing the basis for twin morphology geothermometers. Boundary migration, which leads to lamellae with irregular shapes, is driven by the heterogeneity of the lattice defect energy associated with dislocations and vacancies in twin and host grains and is also a thermally activated process (Urai et al., 1986). In contrast to the deformation temperature, the influence of the confining pressure on deformation mechanisms and in particular on twinning in calcite is usually assumed to be negligible (De Bresser, 2002). However, since high confining pressures during deformation suppress both macroscopic material failure as well as recovery, the lattice defect energies produced during deformation increase with higher pressures and thus influence intragranular deformation mechanisms.

In this communication we report on the influence of high confining pressures on the mechanisms of intragranular deformation in polycrystalline calcite deformed to high strains at room temperature. We employed high-pressure torsion (HPT) to perform deformation experiments under confining pressures between 1 and 4 GPa. The high confining pressures suppress crack formation and propagation and allow to perform experiments to high shear strains without brittle sample failure, which occurred at previous low temperature deformation experiments at confining pressure up to 300 MPa (Barnhoorn et al., 2004). Deformation under confining pressures above 1 GPa facilitated the activation of alternative deformation mechanisms leading to previously unreported microstructural elements.
Schaebitz et al. (2015) reported evidence for internal pressures of up to 4 GPa in nanocrystalline calcite deformed at near ambient conditions in landslides, illustrating the importance to investigate the deformation mechanisms of calcite during low temperature and high pressure deformation.

The microstructures of HPT deformed samples were analyzed by electron backscatter diffraction (EBSD) in a scanning electron microscope (SEM). This contribution complements earlier studies by Schuster et al. (2017), where the deformation mechanisms in calcite deformed by HPT were analyzed by means of X-ray line profile analysis (XPA) and Schuster et al. (2019), which investigated the microstructural and textural evolution of calcite deformed by HPT at elevated temperatures by means of EBSD.

2 Materials and methods

2.1 Sample preparation

Sample preparation, HPT-deformation experiments, and microstructure analysis by SEM followed the same procedures as laid out in the previous study on HPT deformation of calcite at elevated temperatures (Schuster et al., 2019). Therefore only a brief description of the methods is given here. The powder samples for the HPT deformation were prepared by crushing a block of Carrara marble of high purity and sieving the resulting powder to obtain the 63-100 µm particle size fraction. To obtain specimens with the necessary dimensions for HPT processing, 110 and 170 mg, respectively, of the calcite powder were subsequently cold pressed into cylindrical discs with 8 and 10 mm diameter, respectively, which corresponds to a sample height of 0.8 mm for samples with no porosity.

2.2 Deformation experiments

The HPT experiments were performed using the HPT device at the Faculty of Physics, University of Vienna. The samples investigated in this study were deformed at room temperature at a twist rate of 0.02 rotations per minute (RPM).
The confining pressure was varied between 1 and 4 GPa. The sample diameter was 8 mm for deformation experiments with confining pressures of at least 1.75 GPa and 10 mm for deformation at lower pressures. The sample thickness was 0.6 mm after deformation. The local shear strain $\gamma$ in the sample increases with increasing radial distance from the rotation axis:

$$\gamma = \frac{2\pi nr}{t},$$

where $n$ is the number of rotations, $r$ is the distance from the rotation axis, and $t$ is the thickness of the sample. The maximum shear strain rate at the sample rim was therefore $1.7 \times 10^{-2} \text{s}^{-1}$ in the 10 mm case and $1.4 \times 10^{-2} \text{s}^{-1}$ in the 8 mm case. Torsion experiments where markers on the bottom and top surfaces of the pellets were used to test for slip at the sample-anvil interface, revealed that no such slip occurred and that the applied torsion was entirely accommodated by deformation within the specimen.

### 2.3 Specimen preparation for EBSD

After the deformation experiments the samples were embedded in epoxy resin. Most samples were analyzed on sections normal to the rotation axis (parallel to the sample’s basal plane). A selection of samples was cut normal to the basal plane through the sample center and subsequently investigated along this section to obtain access to the grain morphology parallel to the rotation axis.

The embedded samples were ground and polished with silicon carbide, diamond- and aluminum oxide-suspensions down to a particle size of 0.05 µm to obtain the surface quality required for EBSD analysis. Despite the sophisticated polishing technique, the surface quality was not sufficient for EBSD analysis of the fine-grained regions between the porphyroclasts. Thus, the EBSD results only refer to the porphyroclasts and their relatively coarse-grained derivatives. To reduce charging effects during the SEM measurements, the samples and epoxy mounts were coated with a thin layer of amorphous carbon. In some cases the epoxy mount was painted with a layer of graphite paste to further decrease sample charging during EBSD data collection.
2.4 EBSD and texture measurements

The EBSD analyses were carried out on the FEI QuantaTM 3D FEG scanning electron microscope at the Laboratory for Scanning Electron Microscopy and Focused Ion Beam Applications of the Faculty of Geosciences, Geography and Astronomy at the University of Vienna. The EBSD data were collected using an EDAX Digiview IV EBSD camera installed at an elevation angle of 5° in the microscope applying the software TSL OIM Data Collection 6.2. The acceleration voltage of the electron beam was at 15 kV. The sample surface was positioned at a working distance of 14 mm, with a 20° angle to the beam incidence direction. An EBSD camera binning of 4×4 was used, while Hough settings of a 140 pixels binned pattern size, a θ step size of 1°, and a 9×9 convolution mask were employed. To index the data, the lattice parameters of calcite were defined as a = 4.99 Å and c = 17.064 Å using the hexagonal unit cell. The maps were collected on a hexagonal grid using step sizes between 80 and 600 nm. The texture of cold-pressed pellets not yet subjected to HPT deformation was measured using an AXS BRUKER D8 diffractometer at the Faculty of Physics at the University of Vienna utilizing Cu Kα1 radiation with a spot size of 0.5 mm.

2.5 Data treatment

The crystal orientation data derived from EBSD analyses were processed using the EDAX OIM analysis software version 7. Before data evaluation, the EBSD raw data were subjected to the clean-up procedures implemented in the EDAX OIM analysis software. After a grain confidence index (CI) standardization procedure, where the CI of equally oriented data points inside an identified grain are changed to the maximum CI value inside that grain, one step of the Neighbor Orientation Correlation procedure was applied. Finally one step of Grain Dilation was used in order to minimize mis- or non-indexed data points, which mainly occur at grain boundaries due to mixed EBSD signals from the two neighbor crystals. This ensured that neighboring grains are in direct contact with one another. After the cleanup procedure, data points with a CI smaller than 0.05 and grains consisting
of only a single data point were excluded from the data evaluation, so that only
grains with a diameter larger than the step size were considered. Grains were
defined as domains with a minimum misorientation angle $\geq 15^\circ$ to neighboring
domains.

The color coding of twin and deformation lamella boundaries in the inverse
pole figure (IPF) maps was defined by the misorientation relationship between the
twin or lamella and the host. The twin misorientations were defined by a $180^\circ$
rotation about the respective pole of the twinning plane. The tolerance angle for
the misorientation relationships was set to $10^\circ$. The relatively high tolerance angle
is required to include most relevant boundary segments, as the high lattice strain
in the porphyroclasts leads to a significant deviation from the ideal misorientation
relationships, in particular in the case of early twins, which were exposed to high
shear strains after their formation. In addition, since mechanical twins in calcite
are coherent twins, i.e. the boundary plane coincides with the twin plane, the ori-
etentation of the twin plane traces in both the host and twin were manually compared
to the orientation of the boundary trace. General low- and high-angle boundaries
with misorientation angles of $2^\circ - 15^\circ$, and larger than $15^\circ$, respectively, are plotted
as thin lines colored green and blue, respectively (Fig. 4). Boundaries with mis-
orientations corresponding to $e$-, $r$-, and $f$-twins are plotted as thick lines colored
white, green and blue, respectively. Specific misorientations between deformation
lamellae and host are plotted as thick lines and colored purple for misorientations
 corres-ponding to a rotation of $35^\circ$ about an $a$-axis, and cyan for misorientations
 corresponding to a rotation of $76^\circ$ about an $f$-plane pole. For IPF maps where
the color coding deviates from this scheme, the change is described in the corre-
sponding figure caption. The orientation color code of the IPF maps (Fig. 4) was
applied with respect to the sample normal direction, i.e. normal to the pellet sur-
face. The symmetry relationships pertaining to twins and deformation lamellae
were analyzed with the Matlab Toolbox MTEX 4.4 (Bachmann et al., 2010).
Figure 2: Reflected light microscope images of samples before and after HPT-processing. (a) Cold pressed powder before HPT-processing. (b) Central region of sample 'C-3-rt-1' deformed for one rotation at 3 GPa pressure. The image was taken at a distance of 1 mm from the sample center corresponding to $\gamma \simeq 10$ and $\dot{\gamma} \simeq 3.5 \times 10^{-3} \text{ s}^{-1}$. The internal reflections in (a) correspond to surface roughness and internal porosity of the pressed powder sample which was fully eliminated during HPT treatment (b).

Figure 3: Cross polarized light microscope images (a,b) and secondary electron image taken with an Everhart-Thornley SED (c) showing a region near the rim of sample 'C-4-RT-1q'. The dark grain in the center of (a) is a porphyroclast, which is shown in a close-up in (b). Abundant inter- and intragranular cracks, deformation lamellae and undulous extinction in the porphyroclasts are present in all samples investigated in this study. The bright regions in (c) are due to charging effects around cracks. The sample 'C-4-RT-1q' was deformed under 4 GPa for 1 rotation and the images were taken at a distance of 3 mm from the sample center, corresponding to $\gamma \simeq 31$ and $\dot{\gamma} \simeq 1 \times 10^{-2} \text{ s}^{-1}$.

3 Results

The room temperature HPT deformation experiments of the compacted calcite powder produced solid pellets. No traces of any CaCO$_3$ polymorph other than
calcite could be detected by ex-situ X-ray and electron diffraction analysis. Optical and scanning electron microscopy of the post-deformation microstructures reveals evidence of both, cataclastic and crystal-plastic deformation. The samples are pervaded by numerous inter- and intragranular cracks (Figs. 2 and 3). The cracks supposedly result from both brittle deformation during HPT-processing as well as from fracturing during unloading after the HPT experiments. The microstructures are characterized by the presence of larger porphyroclasts of similar size as the initial grain size surrounded by smaller sized porphyroclast remnants. The boundaries between neighboring porphyroclast remnants are constituted either by twin boundaries or cracks. The sample volume between the porphyroclasts is comprised of a fine-grained matrix (Figs. 3 and 5). The samples do not exhibit any significant bulk texture.

The EBSD analysis reveals a large number of \( e \)-, \( r \)-, and \( f \)-twins and deformation lamellae in the porphyroclasts (Figs. 4, 5 and 6). The deformation lamellae show characteristic shape orientations and lattice misorientations with the host that are related to the crystallographic orientation relationships (COR) of mechanical twins. At low shear strain (\(< 10\)) the twins and lamellae in 2D sections have high aspect ratios and straight twin boundary segments. With increasing strain the twin and lamella boundaries tend to become sutured and the twins and lamellae either exhibit irregular shapes, or are disrupted so that trails of small, irregularly shaped crystals with twin orientation relationships to the host form (Fig. 7).

The type and the density of twins and deformation lamellae in a porphyroclast depend on the crystallographic orientation of the porphyroclast relative to the local orientation of the shear stress. Porphyroclasts oriented favorably for \( e \)-twinning are characterized by predominant primary and secondary \( e \)-twins and exhibit only a low density of other twins or lamellae (Fig. 4). The primary \( e \)-twins have rather straight twin boundaries and are several \( \mu m \) wide. The secondary twins, present within both, the host and the primary twins, are thinner and exhibit sutured boundaries or consist of trails of smaller grains, particularly within the host. These characteristics point to the activity of twin boundary migration. The primary twins show clear signs of broadening and subsequent merging of neigh-
Figure 4: EBSD IPF map of sample 'C-4-RT-1q' showing predominant ε-twinning. The sample was deformed for 1 rotation at 4 GPa. The EBSD map was taken at a distance of 1 mm from the sample center corresponding to $\dot{\gamma} \approx 10$ and $\gamma \approx 3.5 \times 10^{-3}$ s$^{-1}$. (b) is a close-up of (a) showing the features associated with twin boundary migration in detail. The stark color alterations in the secondary twins (green/blue) on the right side of (a) are an artefact of color coding and do not represent significant orientation changes. The EBSD scan step size was 120 nm. For the definition of twin and lamella boundaries see the data treatment subsection. The orientation color code of the IPF map relates to the normal of the sample surface.

boring twins, where the former boundary between the two twin individuals can often be traced by low-angle boundaries or "terminal points" of secondary twins inside the primary twins. However, continued deformation may also lead to the elimination of earlier twins by grain boundary migration. Fig. 4b shows the rem-
nant of such a primary twin with a broad internal secondary twin consumed by the host through grain boundary migration. In addition to $e$-twins, trails of $r$-twin grains are found in the primary twins (running W to E on the left hand side of Fig. 4a).

Porphyroclasts oriented unfavorably for $e$-twinning exhibit complex microstructures comprising $r$- and $f$-wins and two types of deformation lamellae (Figs. 5 and 6). The two types of deformation lamellae have a fixed COR with the host and constitute a prominent feature of the microstructures investigated in this study (see also Figs. 5 and 7). The lamellae running SE to NW in Fig. 6b are characterized by a misorientation with respect to the host, which corresponds to a rotation of about 30 - 40° about an $a$-axis. They are referred to as $a$-type lamellae. Such $a$-type lamellae were observed in more than 50 % of the porphyroclasts investigated in this study. The misorientation of the $a$-type lamellae with respect to the host does not correspond to any of the known twin laws in calcite and neither can it be described in terms of a single 180° rotation about a plane pole or direction in calcite with reasonably low Miller indices ($< 30$). The observed misorientation of the $a$-type lamellae can, however, be constructed by successively applying the rotations corresponding to the misorientations of either specific $e$- and $r$-twin boundaries or $f$- and $r$-twin boundaries. In particular, two successive rotations of 180° about an $e$- and an $r$-plane pole, which both lie on a great circle with the $c$-axis in the stereographic projection lead to a rotation of 142° about the negative $a$-axis that is normal to the plane defined by the specific $e$- and $r$-plane poles (Fig. 8a). Since the $a$-axes are 2-fold rotation axes this rotation is symmetrically equivalent to a rotation of 38.2° about the respective positive $a$-axis. The misorientation of the lamellae can thus be produced by the combination of one $e$- and one $r$-twin boundary. Three combinations of $e$- and $r$-twin boundaries are conceivable, namely $e(01\bar{T}8)$ and $r(0\bar{T}14)$, $e(1\bar{T}08)$ and $r(\bar{T}104)$ as well as $e(\bar{T}018)$ and $r(10\bar{T}4)$ (Fig. 1). However, the misorientation between the $a$-type lamellae and the host can also be constructed by successive rotations of 180° about an $r$- and an $f$-plane pole, which both lie on a great circle together with the $c$-axis in the stereographic projection (Fig. 8b). The combination of these two rotations leads
Figure 5: EBSD IPF map (a) and two close-ups (b), (c) of sample ‘8IIb’ deformed under 4 GPa for 0.25 rotations at a distance of 1 mm from the sample center, corresponding to $\gamma \simeq 2.5$ and $\dot{\gamma} \simeq 3.5 \times 10^{-3} \text{s}^{-1}$. (b) Close-up marked in (a) showing the boundary types between $a$- and $f$-type lamellae. (c) Close-up marked in (a) showing the boundary between parallel $a$- and $f$-type lamellae split into two $r$-twin boundaries. In addition to the boundary color coding described in 2.5, the boundaries between the $a$- and $f$-type lamellae (see text) corresponding to a rotation of $52^\circ$ about an $\{21\overline{1}3\}$ pole and $83^\circ$ about an $\{1126\}$ pole are colored dark green and yellow, respectively. The EBSD scan step size was 160 nm. For the orientation color key see Fig. 4.
Figure 6: EBSD IPF map of sample ‘8IIb’ (a), and close-up (b) showing the high density of twins and deformation lamellae in a porphyroclast. (b) shows \( a \)-type boundaries split into \( r \)- and \( f \)-twin boundaries and the interference of \( a \)- and \( f \)-type lamellae. The sample was deformed under 4 GPa for 0.25 rotations. The map was taken at 3 mm distance from the sample center, corresponding to \( \gamma \simeq 8 \) and \( \dot{\gamma} \simeq 1 \times 10^{-2} \text{ s}^{-1} \). In addition to the boundary color coding described in 2.5, the boundaries between \( a \)- and \( f \)-type lamellae (see text) with a misorientation corresponding to a rotation of 52° about an \( \{2\overline{1}3\} \) pole are colored dark green. The EBSD scan step size was 110 nm. For the orientation color key see Fig. 4.

to a rotation of 145° about the negative \( a \)-axis normal to the plane defined by the specific \( r \)- and \( f \)-plane poles. This rotation therefore produces a misorientation of 35.5° about the corresponding positive \( a \)-axis. Accordingly, three combinations of \( r \)- and \( f \)-twin boundaries can produce the observed lamella misorientation: \( f(0\overline{1}\overline{2}) \) and \( r(0\overline{1}4) \), \( f(1\overline{1}02) \) and \( r(1\overline{1}4) \) as well as \( f(\overline{1}0\overline{1}2) \) and \( r(10\overline{1}4) \). The successive application of the reverse order of the twinning rotations (i.e. first 180° about \( r \) followed by 180° about \( e \) and first 180° about \( f \) followed by 180° about \( r \)) leads to the inverse misorientations: 38.2° and 35.5°, respectively, about the negative \( a \)-axis.

The shape orientation of the lamellae is controlled by the crystallographic orientation of the host. The boundary plane traces of \( a \)-type lamellae always lie normal to the \( a\{2\overline{1}10\} \) plane orientation that is common to both the lamellae and the host (i.e. parallel to the projection of the \( a \)-axis that serves as the rotation axis of the lamella host misorientation), both in EBSD sections normal to the HPT
Occasionally, segments of the boundaries between \textit{a-type} lamellae and the host porphyroclast split up into two spatially separated boundaries, thus creating sub-lamellae between the host and the \textit{a-type} lamellae. Both new boundary segments of the sub-lamellae correspond to specific misorientations with respect to the host and the \textit{a-type} lamellae (Figs. 6 and 7). The misorientation across one of the new boundary segments corresponds to the misorientation of an \textit{r}-twin and the misorientation across the other boundary segment corresponds consequently either to the misorientation of an \textit{e}- or an \textit{f}-twin, resulting in the same combined
Figure 8: (a-c) Misorientation relationships between host and *a*-type (a,b) and *f*-type (c) lamellae shown in upper hemisphere stereographic projections using antipodal symmetry of one *a*-axis and the *c*-axis. The original positions of the *c* and *a*<sub>3</sub> axes are marked in red. The color scheme follows the boundary coloring in the IPF maps: *r*-, *f*-, and *e*-plane poles and rotations are colored in green, blue, and black, respectively. The small symbols trace the rotations in 20° intervals and the arrows show the sense of rotation. Rotation axes are marked with the symbol ×. The symbol ′ next to the rotated *a*– and *c*-axes marks the number of rotations performed. The grid spacing is 15°. (a) successive rotations of 180° about *e*([018]) and *r*(1014) leading to a rotation of 142° about *a*[1210]. (b) successive rotations of 180° about *r*(1014) and *f*(1012) leading to a rotation of 145° about *a*[1210]. (c) successive rotations of 180° about *f*(012) and *r*(1014) leading to a rotation of 101° about [2021]. (d) Schematic sketch of an *a*-type lamella and corresponding sub-lamellae using the same color scheme as in (a-c). The lamella interior color code indicates the misorientation with regard to the host and follows the color code used for grain boundaries.

misorientation between lamella and porphyroclast host across the split boundary segments as in the unsplit *a*-type boundary segments. Some *a*-type lamellae exhibit both a split into *r*– and *f*–, and into *r*– and *e*– boundaries (Fig. 7b). The sequence of split boundaries is not random. In the case where the *a*-type boundary splits into *r*– and *f*-twin boundaries, the *r*-twin boundary separates the *a*-type lamella from the sub-lamella and the *f*-twin boundary separates the sub-lamella from the host. When the *a*-type boundary splits into *r*– and *e*-twin boundaries, the *r*-twin boundary separates the sub-lamella from the host and the *e*-twin boundary separates the sub-lamella from the *a*-type lamella (Figs. 6 and 7). However, unlike the boundaries of regular mechanical *e*–, *r*–, and *f*-twins, the boundary segment traces of split deformation lamellae do not follow twin planes and thus the twin boundaries constitute incoherent twin boundaries.
Though in many cases a-type boundary segments split into two parallel twin boundaries, they may also have differently orientated traces. So may a-type lamellae be cross cut by r-twin boundaries, which produce lamella sections with f-twin misorientation relative to the host between two a-type lamella sections (Fig. 6). The f-twin lamella sections extend parallel to the a-type lamella sections and may occur repeatedly along one a-type lamella. In the case of more irregular grain shapes, one or both of the split a-type boundaries may show highly curved, irregular trace geometry in the 2D section. Occasionally, the boundary segments appear to be highly mobile, in particular in regions deformed to high shear strains (Fig. 7b,c).

Often deformation lamellae or trails of small grains with misorientations corresponding to r- or f-twins extend parallel to a-type lamellae. Similarly, lamellae that show predominantly twin misorientations with respect to the host, but also comprise a-type sub-lamellae can be aligned with a-type lamellae (Figs. 5 and 7a,d). However, the boundary trace orientations of these incoherent twins differ from those of regular calcite twins. The incoherence of the apparent r- or f-twins with the host indicates that the deformation lamellae with twin misorientation with the host do not develop as regular mechanical twins, but originate from precursor a-type lamellae.

Due to the defined sequence and spatial arrangement of split boundaries (r inside and f outside for r-f splits and e inside and r outside for r-e splits), the split character determines, which type of incoherent twin can form from an a-type lamella. The combination of two $180^\circ$ rotations about the same or antiparallel axis leads to the original orientation. Therefore, the movement of the inner twin boundaries within a lamella may lead to partial or complete annihilation of those boundaries, resulting in twin lamellae corresponding to the outer twin type. Accordingly, r-f splits lead to incoherent f-twins and r-e splits lead to incoherent r-twins (Fig. 7a, d). One apparent contradiction to this rule is the set of incoherent r-twins in the central and left parts of Fig. 6a resulting from r-f splits. However, the pink domain in the center originated from a-type lamellae, which consumed the host domain (orange) in the center of the map presumably by grain boundary
migration. Therefore, the remaining incoherent twins in this domain are \( r \)- instead of \( f \)-twins.

The second and less common type of deformation lamellae observed in this study exhibits a misorientation with respect to the host that corresponds to a rotation of 76° about an \( f \)-plane pole (Fig. 6b). The lamellae are referred to as \( f \)-type lamellae, accordingly. As in the case of \( a \)-type boundaries, this misorientation can be obtained by the combination of two mechanical twins. The misorientation across the \( f \)-type lamella boundary is the result of the successive rotations associated with one \( f \)- and one \( r \)-twin operation. In contrast to the \( a \)-type boundaries, the corresponding \( r \)- and \( f \)-plane poles do not lie on the same great circle as the \( c \)-axis in the stereographic projection (Fig. 1). For example, the successive rotations of 180° about \( f(1\bar{T}02) \) and \( r(0\bar{T}14) \) result in a rotation of 101° about \([0\bar{2}2\bar{1}]\), which is symmetrically equivalent to a rotation of 76° about \( f(\bar{T}012) \) (Fig. 8c). The misorientation of 76° about an \( f \)-plane pole can be produced by rotating first about the \( r \)- and subsequently about the \( f \)-plane pole or vice versa. In the case where the \( r \)-twin operation is applied first, the misorientation axis of the \( f \)-type lamella is identical or antiparallel to the rotation axis of the subsequent \( f \)-twin. The axes are parallel, when a rotation about \( r(\bar{T}104) \) is followed by a rotation about \( f(01\bar{T}2) \), a rotation about \( r(0\bar{T}14) \) is followed by a rotation about \( f(\bar{T}012) \), or a rotation about \( r(10\bar{T}4) \) is followed by a rotation about \( f(1\bar{T}02) \). The axes are antiparallel, when a rotation about \( r(\bar{T}104) \) is followed by a rotation about \( f(\bar{T}012) \), a rotation about \( r(0\bar{T}14) \) is followed by a rotation about \( f(1\bar{T}02) \), or a rotation about \( r(10\bar{T}4) \) is followed by a rotation about \( f(01\bar{T}2) \). When the \( f \)-twin operation is applied first, the misorientation axis is identical or antiparallel to the \( f \)-plane pole that is not the rotation axis of the \( f \)-twin operation and also does not lie on a great circle with the \( c \)-axis and the rotation axis of the corresponding \( r \)-twin operation. So is the misorientation axis for an \( f(01\bar{T}2)/r(10\bar{T}4) \) lamella \( f(1\bar{T}02) \), while for an \( f(01\bar{T}2)/r(\bar{T}104) \) lamella it is \((10\bar{T}2)\).

As in the case of \( a \)-type lamellae, the shape preferred orientation of the \( f \)-type lamellae is controlled by the crystallographic orientation of the host. For \( f \)-type lamellae, the boundary traces lie parallel to one \( f \)-plane in both the host and the
lamella as in the case of a coherent f-twin. Similar to the a-type boundary segments, f-type boundary segments occasionally split into two spatially separated boundaries, where, analogous to the a-type boundaries, the misorientation of one boundary segment amounts to the misorientation of one f-twin boundary and the other segment to a corresponding r-twin boundary (Fig. 5c).

Two a- and f-type lamellae may be adjoined, so that they share a common boundary (Figs. 5 and 6). We observed two different types of boundaries between the lamellae in this study, depending on the angle at which the lamellae connect. Considering that the shape orientation of an a-type lamella is normal to one of the a-planes both in the host and the lamella, and the boundary of an f-type lamella coincides with an f-plane shared by the host and the lamella, f- and a-type lamellae may be parallel in a host, since every a-plane pole is perpendicular to one f-plane pole (e.g. $a(2\overline{1}0)$ is normal to $f(01\overline{2})$). In fact composite lamellae that consist of a- and f-type lamellae may be oriented parallel and joined along the lamellae tips (Figs. 5c and 7d). The boundary between the two lamellae is then characterized by a misorientation resulting in a rotation of $83^\circ$ about an $\{1\overline{1}26\}$ pole. This misorientation also corresponds to the misorientation resulting from the combination of two twin boundaries, namely two different r-twin boundaries (e.g. one $r(10\overline{1}4)$ and one $r(0\overline{1}14)$ twin boundary). This boundary may also split into the two constituent r-twin boundaries (Fig. 5c). The domain between these different incoherent r-twin boundaries corresponds to a coherent f-twin with regard to the host.

When the a- and f-type lamellae connect at a high angle, the misorientation between the lamellae corresponds to a rotation of $52^\circ$ about a $\{2\overline{1}3\}$ pole (Fig. 5b and 6). This misorientation is produced by the combination of the misorientations of one f- and one e-twin boundary, where the corresponding poles do not lie on the same great circle as the c-axis (e.g. $f(01\overline{1}2)$ and $e(\overline{0}18)$). Fig. 5 features one f-type lamella that is connected to two a-type lamellae at two different angles. The misorientation between the two a-type lamellae is $64^\circ$ about an $\{010\overline{1}7\}$ pole. This misorientation can therefore be constructed by combining the misorientations of two a-type boundaries rotated about different a-axes.
or the two types of boundaries between $a$- and $f$-type domains. The successive application of misorientations corresponding to $r(0\overline{1}14)$-, $r(10\overline{1}4)$-, $e(01\overline{1}8)$- and $f(1\overline{1}02)$ twin boundaries then leads to the required misorientation.

The porphyroclasts contain only relatively few low-angle grain boundaries and no subgrains, though the lattice is severely strained. The lattice strain is evident from the high lattice misorientation in the porphyroclast hosts and the deformation lamellae and twins. The lattice strain in porphyroclasts may lead to a cumulative misorientation of more than $1^\circ$ per $\mu$m over distances $> 10$ $\mu$m, without the formation of low-angle boundaries. Porphyroclasts with low densities of twins and deformation lamellae may, however, exhibit long and straight low-angle grain boundaries with misorientation angles typically below $5^\circ$ (Fig. 9a). These low-angle boundaries become patchier at higher strains, but still largely retain their straight traces (Fig. 9b). Grains with unfavorable crystallographic orientation for twinning in regions deformed to high shear strains may show irregularly arranged low-angle grain boundaries with constant misorientation angles (Fig. 5).

4 Discussion

4.1 Effect of pressure on the microstructural evolution

The apparent high-temperature twin morphology and the observation of previously unreported deformation lamellae in calcite deformed to high strains by HPT demonstrate that employing a high confining pressure in the GPa range has a significant effect on the deformation behavior of calcite at room temperature. Through the application of confining pressures in excess of 1 GPa macroscopic brittle failure of the sample during deformation at room temperature is prevented even at shear strains exceeding 40. The formation and propagation of cracks is largely suppressed, because the excess volume that is associated with defects must be generated against the high hydrostatic pressure (Poirier, 1985; Zehetbauer et al., 2003). Thus, HPT allows to perform deformation experiments to much higher strains at low temperatures than would be possible by torsional de-
Figure 9: EBSD IPF maps showing low angle grain boundaries in porphyroclasts with low twin and lamella densities at low (a) and high shear strain (b). (a) IPF map of sample ‘C-1-RT-1b’ deformed under 1 GPa for 1 rotation. EBSD map taken at a distance of 2 mm from the sample center, corresponding to $\gamma \simeq 20$ and $\dot{\gamma} \simeq 7 \times 10^{-3}$ s$^{-1}$. (b) IPF map of sample ‘C-4-RT-1q’ deformed under 4 GPa for 1 rotation. EBSD map taken at a distance of 3 mm from the sample center, corresponding to $\gamma \simeq 30$ and $\dot{\gamma} \simeq 1 \times 10^{-2}$ s$^{-1}$. Low angle grain boundaries are colored yellow (2-5°) and black (5-15°). The EBSD scan step size for was 100 nm for (a) and 120 nm for (b). For the orientation color key see Fig. 4.

formation of calcite at confining pressures of 300 MPa, where sample failure usually occurs at shear strains of 13 or less even at 500 °C (Barnhoorn et al., 2004). Therefore, a markedly higher fraction of the applied strain is accommodated by an increase in lattice strain at confining pressures in the GPa range. This leads to the activation of alternative deformation mechanisms compared to experiments performed at lower confining pressures.

In contrast to HPT experiments performed at 235 and 450 °C, where the variation of the confining pressure between 1 and 4 GPa significantly affects microstructural parameters such as the morphology of mechanical twins (Schuster et al., 2019), increasing the confining pressure beyond 1 GPa at room temperature does not result in significant changes in the microstructural evolution during deformation. On the microscopic level, high confining pressures reduce the mobility of point defects. Therefore, the activity of recovery and dynamic recrystallization,
which requires dislocation climb, is greatly diminished at pressures in the GPa range as compared to deformation at ambient or low confining pressures. While this effect leads to apparent low temperature characteristics of the microstructures in calcite deformed at elevated temperatures (Schuster et al., 2019), the effect is negligible at room temperature, since the mobility of point defects is already limited at the low homologous temperatures of 0.16 - 0.18 at pressures between 1 and 4 GPa (Suito et al., 2001). The additional effect of high confining pressures on the mobility of point defects is minute.

At room temperature, calcite transforms to CaCO$_3$-II at 1.7 GPa with further transformations to CaCO$_3$-IIIb at 1.9 GPa and to CaCO$_3$-III at 3.3 GPa (Bridgman, 1938; Merrill and Bassett, 1975; Merlini et al., 2012). The absence of a significant effect of pressure variations between 1 and 4 GPa on the microstructural evolution shows that the stability fields of high pressure polymorphs do not have any discernible effect on the nucleation and propagation of mechanical twins and the $a$- and $f$-type lamellae. Since the presence of $a$- and $f$-type boundaries, as well as the branching into their constituent twin boundaries are observed at pressures above and below the transition between the stability fields of calcite and CaCO$_3$-II, their occurrence cannot be explained by effects of different crystal structures during deformation or back transformation of the high pressure polymorphs to calcite after the pressure release.

4.2 Morphology of e-twins

Our findings on the morphologies of mechanical e-twins differ from those reported in earlier studies on both naturally and experimentally deformed calcite rocks. The twins conform to morphologies typical for substantially higher deformation temperatures according to the twin morphology geothermometer introduced by Ferrill (1991), Burkhard (1993) and Ferrill et al. (2004), where only thin twins ($< 1 \mu m$) should occur in calcite deformed at room temperature and increased shear strain should lead to the nucleation of new twins instead of broadening of existing twins, resulting in a high density of thin twins (Ferrill et al., 2004). The primary e-twins in HPT deformed calcite are significantly thicker than 1 $\mu m$
and have moderate lensoid shape, which indicates some boundary mobility (Fig. 4). These $e$-twins are classified as type II twins in the scheme of Burkhard (1993), which are expected to occur only at deformation temperatures above 150 °C. For producing thick, lens-shaped deformation twins, it is necessary that the glissile partial dislocations that propagate the twin can move out of their glide plane by climb or cross-slip (Hirth and Lothe, 1982) (Fig. 10). In particular, the climb of edge dislocations requires that point defects are appreciably mobile. Motohashi et al. (1976) found that edge $e\{01\bar{T}8\}\langle0\bar{4}41\rangle$ twin dislocations have lower line energies than the corresponding screw dislocations. A prevalence of edge twin dislocations compared to screw dislocations was also observed in TEM investigations on deformed calcite (Braillon and Serughetti, 1976). Our results indicate that even though it is a thermally activated process necessitating dislocation climb, substantial twin broadening occurs during deformation at room-temperature, if confining pressures in excess of 1 GPa are applied. This suggests that particularly high lattice strain produced during the deformation provides a sufficiently strong driving force that can overcome the sluggish twin boundary motion kinetics and leads to twin broadening even at room temperature.

Figure 10: Twin formation and propagation by glide of partial dislocations with their Burgers vector parallel to the shear direction (sd) of the twin. The twin plane is the glide plane of the dislocations. Twin broadening occurs by climb of the partial dislocations. Modified after Hirth and Lothe (1982).

The strongly sutured boundaries of secondary twins inside both the host and the primary twins demonstrate significant recrystallization by twin boundary migration, where the secondary twins are consumed by the host and by the primary twins, respectively. In the scheme of Burkhard (1993), such twins are classified as type IV twins, which occur at deformation temperatures exceeding 250 °C. However, a study by Kennedy and White (2001) on twin microstructures in car-
bonate rocks deformed at low-grade conditions demonstrated that migration and bulging of calcite $e$-twin boundaries may already occur at temperatures between $150 - 250 \, ^\circ\text{C}$. The authors suggested that twin boundary migration recrystallization was driven by the high lattice strain arising from dislocation pileups at twin boundaries. Heterogeneously distributed lattice strain is the most significant driving force for grain boundary migration in heavily deformed materials (Urai et al., 1986). Our results indicate, that very high lattice strain, which is inferred from the intense intragranular fracturing during decompression after the HPT experiments and by dislocation densities of $1 - 2 \times 10^{15} \, \text{m}^{-2}$ (Schuster et al., 2017) can induce twin boundary migration recrystallization in calcite even at room temperature. In this manner, apparent high temperature twin morphologies showing significant twin broadening and twin boundary migration may be generated at room temperature and the influence of high confining pressures cannot be neglected when twin morphologies are used as a geothermometer for naturally deformed calcite bearing rocks.

Though thin primary $e$-twins (type I) were not observed in our study, we cannot exclude the formation of such twins during the initial stages of deformation, since we observed the annihilation of twin lamellae of several $\mu\text{m}$ thickness through twin boundary migration (Fig. 4b). The stability of twin and lamella boundaries varies with the boundary type. The effects of recrystallization on the shape of grain boundaries is usually much more pronounced in the case of $r$-twins, both coherent and incoherent, than for $e$- or $f$-twins or for $a$-type boundaries.

### 4.3 Deformation lamellae

The prevalence and apparent stability of $a$-type boundaries in the microstructures investigated in this study point to a low-energy grain boundary structure, which may have general relevance for microstructures of deformed calcite. In fact, several studies on both experimentally and naturally deformed calcite rocks reported a significant number of grain boundaries with $a$-type misorientation or misorientations about an $a$-axis with a misorientation angle of up to about $40^\circ$ as a result of different recrystallization mechanisms (Bestmann and Prior, 2003; Rogowitz
et al., 2014; Schuster et al., 2019).

In Schuster et al. (2019), this boundary misorientation angle was found between isometric grains formed by subgrain rotation recrystallization in samples deformed by HPT at 450 °C. Although most boundaries between recrystallized grains show random misorientations, the $a$-type boundaries constitute a marked accumulation in misorientation space. Even though remnants of $e$- and $r$-twins, obliterated by recrystallization, can be observed in the vicinity of the $a$-type boundaries, there is no evidence for the twin boundary splitting observed in the current study.

Rogowitz et al. (2014) found evidence for dynamic recrystallization of calcite in natural ultramylonitic shear zones in Syros, Greece, where recrystallization occurs by grain boundary bulging and subsequent overprinting by dislocation glide and grain boundary sliding. The recrystallized shear zones exhibit $a$-type grain boundaries with a significantly higher frequency than in a random misorientation distribution, where the relative frequency of these boundaries increases with the strain rate (A. Rogowitz, personal communication, March 8, 2017).

Bestmann and Prior (2003) studied recrystallization mechanisms in a natural shear zone within calcite marble on Thassos Island, Greece. They reported the formation of recrystallized grains and subgrains by dislocation creep and subgrain rotation recrystallization in twinned porphyroclasts. In one of the microstructures they found that intragranular deformation and nucleation of grains and subgrains proceeds, apart from $e$-twinning, by lattice rotations about an $a$-axis, where the rotation angles are concentrated at low angles. Some more heavily deformed domains show misorientation angles $>30^\circ$, which conform with the misorientations of the $a$-type boundaries found in the current study.

The examples of $a$-type boundaries occurring under a wide range of deformation conditions in calcite demonstrate that they can be produced by different deformation and recrystallization mechanisms. The apparent stability and frequency of these grain boundaries may therefore influence the texture and microstructure development during deformation in a range of deformation conditions in both natural and experimental settings.
5 Conclusions

HPT-processing of compacted calcite powder at room temperature under confining pressures between 1 and 4 GPa produces solid cylindrical pellets that show microstructures associated with cataclastic deformation and extensive twinning as well as the accumulation of substantial lattice strain in the porphyroclasts. The resulting microstructures are characterized by large porphyroclast remnants with pervasive mechanical twins and deformation lamellae.

Results from electron backscatter diffraction indicate the activity of twin boundary migration, a phenomenon that was previously observed only at markedly higher deformation temperatures in calcite. We infer that the high lattice strain accumulated during HPT deformation at confining pressures in the GPa range provides a sufficiently strong driving force that can overcome the sluggish low-temperature kinetics of twin boundary migration. Furthermore, the primary twins are significantly broader than the twins observed after room temperature deformation at sub-GPa confining pressures in the studies, that where used to calibrate calcite twin morphology geothermometers. Thus, high confining pressures cannot be neglected when calcite twin morphologies are used as geothermometers.

In addition to pronounced mechanical twinning on e- and to lesser degree on r- and f-planes, a substantial quantity of two distinct types of deformation lamellae form during high-pressure torsion processing. These a- and f-type lamellae have specific crystallographic orientation relationships with the host. The misorientation of these lamellae with the host results from the combination of two different twin operations. The correlation between deformation lamellae and related twin boundaries manifests itself in the frequently observed separation of lamella boundary sections into the two corresponding twin boundaries.

The deformation lamella boundaries and their split boundary segments appear to be highly mobile, leading to irregular grain morphologies. The combined effects of lamella boundary separation and boundary mobility can lead to trails of incoherent apparent f- or r-twins.

The new experimental data set extends the knowledge on intragranular defor-
formation mechanisms in calcite to deformation to high shear strains at room temperature and high confining pressure. The effect of confining pressures above 1 GPa on the microstructural evolution of calcite during deformation to high shear strains supposes that high confining pressure could significantly contribute to the deformation behavior of carbonate rocks.

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Contribution to the manuscripts

• Manuscript I
  Microstructure of calcite deformed by high-pressure torsion: an X-ray line profile study
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  Schuster, R. 65% Study concept, devising and performing deformation experiments, sample preparation, devising the diffraction experiments, beamtime proposal for ALS measurements, performing the diffraction experiments at DESY, data analysis and evaluation, results interpretation, manuscript preparation
  Schafler, E. 5% Providing the HPT apparatus and synchrotron beamtime at DESY
  Schell, N. 5% Supervising diffraction experiments at DESY
  Kunz, M. 10% Performing diffraction experiments at ALS
  Abart, R. 15% Manuscript preparation

• Manuscript II
  Microstructure of calcite deformed by high-pressure torsion: an EBSD study
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Schuster, R. 70% Study concept, devising and performing deformation experiments, sample preparation, EBSD measurements, data analysis and evaluation, results interpretation, manuscript preparation

Schafler, E. 5% Providing the HPT apparatus

Habler, G. 10% EBSD measurements

Abart, R. 15% Manuscript preparation

• Manuscript III

Intragranular deformation mechanisms in calcite deformed by High Pressure Torsion at room temperature

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Schafler, E. 5% Providing the HPT apparatus

Habler, G. 10% EBSD measurements

Abart, R. 15% Manuscript preparation
Summary and Conclusions

In the scope of this Ph.D. thesis the deformation behavior of calcite deformed to high shear strains at confining pressures in the GPa range and temperatures between room temperature and 450 °C was investigated. The deformation experiments were performed with a HPT apparatus, which was adapted for rock mechanics experiments. The deformation behavior was studied by means of ex-situ microstructure and texture analysis. The main analytical techniques used for the microstructural analysis were synchrotron based XPA and SEM based EBSD analysis. The texture analyses were performed with X-ray diffraction and EBSD. XPA allowed to extract the evolution of key microstructural parameters such as the dominant slip system, the dislocation density and the CSD size with strain and strain rate at varying $P$-$T$ conditions. The influence of varying $P$-$T$ conditions on deformation and recrystallization mechanisms was investigated with EBSD, leading to new insights into various microstructural properties, such as characteristic grain size reduction during recrystallization, texture evolution and twin morphology.

7.1 Implementation of HPT processing for rock deformation experiments

The successful adaption and application of HPT for deformation experiments on calcite demonstrates the viability of HPT for rock mechanics experiments. HPT allows to extend the $P$-$T$ range of well constrained high-strain torsional deformation experiments to a higher pressure range than previously achieved in the Earth sciences. This does not only facilitate the investigation of the influence of confining pressures in the GPa range on the deformation behavior and microstructural and textural evolution during deformation, but also enables to perform deformation experiments at low temperatures to higher strains without experiencing brittle sample failure compared to previous studies at sub-GPa confining pressures (Barnhoorn et al., 2004). The microstructure analysis reveals that the suppression of macroscopic brittle fracturing and the inhibition of the mobil-
ity of point defects lead to significant changes in the evolution of the deformation and recrystallization microstructures compared to experiments performed at lower confining pressures. Additionally, the suppression of brittle deformation leads to the development of previously unreported microstructural features at room temperature. Thus, our results show that HPT is a useful technique to gain new insights into potential deformation mechanisms in brittle rocks or rocks deformed under high lithostatic pressure conditions.

7.2 Synthesis of XPA and EBSD analysis

The study demonstrates that the combination of XPA and electron microscopy provides a powerful research method for microstructure analysis in the Earth sciences, allowing for an in-depth investigation and better statistical reliability than in the case of only electron microscopy analysis. XPA enables the fast sampling of large sample volumes and permits to extract important microstructural parameters with good statistical reliability for a large number of strain and strain rate states at different $P$-$T$ conditions (chapter 3/Schuster et al. (2017)). In this study, XPA was performed using the whole profile fitting technique, where the complete shape of each Bragg profile is considered and theoretical profiles accounting for strain and size broadening are fitted to the measured Bragg profiles. Sophisticated XPA techniques in the form of whole profile fitting have heretofore only sparsely been used in the Earth sciences. One application of XPA in the Earth sciences was the in-situ investigation of dislocation activity in metastable high pressure minerals (Cordier et al., 2004). Chapter 3/Schuster et al. (2017) demonstrated that XPA is also a powerful technique for ex-situ microstructure studies of highly deformed materials in the Earth sciences. It allowed to determine the influence of the stability fields of high pressure CaCO$_3$ polymorphs on the evolution of key microstructural parameters such as the dislocation densities, the size distribution of the CSDs, the temperature dependence of the pressure influence, and the formation of saturation microstructures with a good strain and strain rate state resolution.

On the other hand, selective EBSD measurements provided additional and valuable insights into the local crystal orientation and misorientation relationships, the local microstructure including grain and subgrain boundary networks, and grain shapes. It allowed for instance to characterize the development of a pronounced texture in samples deformed at 450 °C and its relationship to the recrystallization process and the temperature, pressure, and strain dependence of twin intensity and morphology (chapter 4/Schuster et al. (2019), chapter 3/Schuster et al. (2018)). Additionally, the characterization of the
7.3. TEMPERATURE INFLUENCE

recrystallization process at high temperatures (chapter 4, Schuster et al. (2019)) and its pressure dependence were resolved. Thus, the combination of the two methods provides an exhaustive picture of the microstructural evolution and allows for a more complete characterization of the deformation microstructures and a deeper understanding of the mechanisms and processes responsible for the microstructure and texture development.

7.3 Temperature influence

XPA and EBSD analysis revealed the significant influence of temperature variations on the deformation behavior of calcite deformed by HPT. Deformation at room temperature, 235 °C, and 450 °C leads to distinctly different deformation microstructures and textures. At room temperature, the microstructure consists of large porphyroclast remnants of similar size as the initial grain size surrounded by a fine grained matrix. The porphyroclasts are marked by twin and deformation lamellae and exhibit pronounced lattice strain. Some regions show the formation of straight and parallel low angle boundaries, but no evidence for subgrain formation can be observed. The fine grained matrix results from cataclastic deformation on the grain edges. XPA reveals a monotonic increase of dislocation density and a monotonic decrease of CSD size with increasing distance from the rotation axis in each sample. The paucity of crystal-plastic deformation and recrystallization leads to an essentially random texture.

By contrast, deformation at 450 °C leads to pronounced grain internal crystal-plastic deformation with subsequent recovery and dynamic recrystallization by subgrain rotation. The microstructures observed by EBSD consist of porphyroclast remnants and a matrix of smaller recrystallized grains. The volume share of recrystallized grains increases with increasing applied strain, leading to a homogeneous distribution of recrystallized grains at high shear strains. The porphyroclast remnants exhibit thick and curved twins and subgrains at the grain edges.

The microstructures in samples deformed at 235 °C exhibit evidence for both brittle and crystal-plastic deformation. The porphyroclasts are characterized by pronounced mechanical twinning and the formation of deformation lamellae, with only subordinate recrystallization compared to the 450 °C case. The porphyroclasts are surrounded by fine grained regions that presumably formed by cataclastic processes.
7.4 Influence of pressure induced structural phase transformations on the microstructural evolution

Both XPA and EBSD investigations revealed changes in the microstructural evolution during deformation, when the phase boundary between calcite and the high pressure polymorphs is crossed. In general, XPA showed that specimens deformed in the calcite stability field close to the transformation pressure exhibit a higher dislocation density and a smaller CSD size than those deformed in the stability field of the high pressure polymorph just beyond the transformation pressure to calcite. While this effect is small at room temperature, leading to a decrease in the dislocation density of less than 10% and an increase in the CSD size by 10-20 % it becomes more pronounced at higher temperatures.

The specimens deformed at 450 °C also show a significant qualitative change in the evolution of dislocation density and the recrystallization process, resulting in a markedly later onset of a steady-state deformation stage, when the boundary between the stability fields of calcite and CaCO$_3$-II is crossed. In the calcite stability field the dislocation density reaches a stable value at shear strains $\simeq 5$, in agreement with the findings in earlier experimental deformation studies on calcite, that reported a saturation of the mechanical stress at similar shear strains (Pieri et al., 2001a, b; Barnhoorn et al., 2004). However, the specimens deformed in the CaCO$_3$-II stability field for one rotation do not exhibit a saturation of the dislocation density, despite the high applied shear strain of $\simeq 40$ at the sample edge. In fact the dislocation density increases with distance from the rotation axis in the innermost 2-3 mm before it decreases again for larger distances. Only in samples deformed for at least 2 rotations does the dislocation density reach a saturation value.

This atypical strain rate dependence of the dislocation density can be explained by the strain rate dependence of the dynamic recrystallization process in the CaCO$_3$-II stability field at 450 °C. The EBSD analysis showed that in the CaCO$_3$-II stability field the dynamic recrystallization in regions close to the sample edge and therefore deformed at high strain rates leads to a typical core-mantle microstructure, where large porphyroclasts are surrounded by a matrix of recrystallized grains. The porphyroclasts exhibit a low density of low-angle boundaries in the interior and subgrains of similar size as the recrystallized grains close to the grain boundaries. On the other hand, recrystallization in regions deformed at lower strain rates exhibit a more homogeneous break-up of the porphyroclasts, where the porphyroclasts show large subgrains across the whole grain at
low strains. With further strain these subgrain boundaries evolve to high-angle grain boundaries. By contrast, the specimens deformed in the calcite stability field develop transient core-mantle microstructures regardless of the strain rate. Both recrystallization processes lead eventually to the same microstructure exhibiting a homogeneous distribution of small \((\langle x \rangle_{\text{area}} = 0.7-2 \, \mu\text{m})\) recrystallized grains.

Both types of recrystallization progress have been previously observed in deformed calcite. Schmid et al. (1980) studied the influence of temperature and strain rate on the deformation behavior of Carrara marble and distinguished three regimes according to rheological and microstructural observations. At the highest temperatures and slowest strain rates, recrystallization leads to a homogeneous break-up of porphyroclasts as in the slow strain rate regions of the specimens deformed in the CaCO\(_3\)-II stability field in the pertinent study. In the intermediate temperature and strain rate regime in Schmid et al. (1980), recrystallization leads to core-mantle microstructures as in the calcite stability field and the high strain rate regions in the CaCO\(_3\)-II stability field. Thus, the microstructural evolution in specimens deformed in the CaCO\(_3\)-II stability field resembles the microstructural development in specimens deformed at higher temperatures compared to the samples deformed in the calcite stability field.

Furthermore, the specimens deformed in the CaCO\(_3\)-II stability field close to the boundary to the calcite stability field exhibit markedly larger CSD and recrystallized grain sizes compared to the specimens deformed in the calcite stability field close to the transformation pressure. The high temperature microstructures in the CaCO\(_3\)-II stability field, the larger CSD and recrystallized grain sizes, and the lower dislocation densities in the low pressure region of the CaCO\(_3\)-II stability field indicate easier crystal plastic deformation compared to samples deformed in the high pressure region of the calcite stability field and point to a more relaxed crystal structure.

7.5 Effect of confining pressure variations on the microstructural evolution

Variation of the confining pressure does not only affect the microstructural evolution when the boundary between the stability fields of two polymorphs is crossed. Microstructural parameters such as dislocation density, CSD size, twin morphology, and recrystallized grain size may vary markedly with changing pressure conditions within the investigated CaCO\(_3\) stability fields. This is in contrast to earlier studies investigating the rheology and microstructure of calcite deformed at confining pressures between 100 and 600 MPa,
7.6. PRESSURE INDUCED DEVELOPMENT OF ALTERNATIVE DEFORMATION MECHANISMS AT ROOM TEMPERATURE

which found only a small pressure effect (De Bresser, 2002).

The XPA evaluations in chapter 3 (Schuster et al., 2017) document that within a given polymorph stability field a higher confining pressure leads to higher dislocation densities and smaller CSD sizes at all temperatures, where the pressure effect is highest at 450 °C and smallest at room temperature. EBSD analyses of the microstructures in samples deformed at 450 °C reveal that the recrystallized grain size decreases with increasing pressure in the CaCO$_3$-II stability field from about 2 µm in regions deformed to high strains at 2 GPa to about 800 nm in regions deformed to high strains at 3-4 GPa (chapter 4, Schuster et al., 2019). The width of mechanical twins in porphyroclasts in samples deformed at 235 °C decreases with increasing pressure and twin boundary migration intensifies at higher confining pressures.

The pressure effect decreases with lower temperatures but also with increasing pressure. For example, the CSD size decreases by about 30 %, when the pressure changes from 3 to 4 GPa at 450 °C but is constant for pressures above 3 GPa at 235 °C.

The reason for the influence of high confining pressures on the microstructural evolution during deformation is twofold. Firstly, the high confining pressure suppresses the formation and propagation of macroscopic cracks, thereby leading to the accumulation of lattice strain and the activation of alternative deformation mechanisms. Secondly, high confining pressure causes a change of the unit cell volume and a variation of the elastic constants (Poirier, 1985). This in turn influences dislocation nucleation and dislocation creep, in particular climb. The nucleation of dislocations is moderately inhibited due to the expansion inherent to dislocation nucleation. Higher confining pressure therefore leads to an increase in the work that must be performed during dislocation nucleation (Poirier, 1985). In addition, the mobility of point defects during deformation is markedly inhibited by high confining pressure (Poirier, 1985; Zehetbauer et al., 2003). The low mobility of point defects suppresses dislocation climb, which necessitates the presence of point defects at the dislocation cores.

7.6 Pressure induced development of alternative deformation mechanisms at room temperature

Microstructure analysis of samples deformed at room temperature revealed extensive evidence for the activity of previously unreported deformation mechanisms (chapter 5, Schuster et al., 2018). EBSD data showed that porphyroclasts favorably oriented for e-twinning exhibit a high density of e-twin lamellae in agreement with earlier studies.
performed at lower confining pressures \cite{Ferrill2004}. However, while mechanical twins produced at room temperature and sub-GPa confining pressures are thin ($< 1 \mu m$) and straight and exhibit smooth boundaries, the mechanical $e$-twins resulting from room temperature HPT deformation may be several $\mu m$ thick and slightly curved and both host and primary twins typically exhibit thinner secondary twins. Furthermore, the strongly sutured twin boundaries give evidence for significant twin boundary migration activity.

The high confining pressure also leads to the formation of two types of deformation lamellae with characteristic misorientation relationships with the host porphyroclasts in samples deformed at room temperature. The lamellae have not been reported in previous studies on the deformation behavior of calcite, yet occur often and with high densities in porphyroclasts oriented unfavorably for $e$-twinning in samples deformed by HPT. The characteristic misorientations of the lamellae can be traced to the CORs of mechanical twins, where the misorientation of both lamella types result from combinations of the rotations associated with two specific twin operations. The connection between the lamellae misorientations and the twin operations is also revealed by the splitting of segments of the lamellae boundaries into two twin boundaries that exhibit the misorientations pertaining to the two twin operations.
Bibliography


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