Physio-chemical processes active during deformation of plagioclase rich rocks under fluid present conditions: Dissolution and precipitation creep coupled with grain boundary migration and solvent mediate phase transformation

H. Svahnberg, S. Piazolo

1 Department of Geological Sciences, Stockholm University, SE-106 91 Stockholm, Sweden.
2 presently at: GEMOC ARC Key Centre, Department of Earth and Planetary Sciences, Macquarie University, Australia

Abstract

We present microstructural and chemical analyses of chemically zoned and recrystallised plagioclase grains in variably strained samples of a naturally deformed anorthosite-leucogabbro. The recorded microstructures formed in the presence of fluids at mid crustal conditions (T = 550-620 °C and P = 4.5-5.1 kbar). Recrystallised plagioclase grains (average grain size 342 μm) are volumetrically dominant in high strain areas. They are characterised by a random crystallographic orientation and a heterogeneously distributed presence of asymmetric chemical zoning (An$_{80}$ cores and An$_{65}$ rims). This zoning is directly associated with a high abundance of amphibole in the vicinity. Analyses of zoning indicate anisotropic behaviour with a preferred replacement in the $<$010$>$ direction and along the (001) plane. Further recrystallisation of plagioclase is intimately linked to the chemical zoning and is dominantly seen in areas of high finite strain where a second set of new grains ($<$150 μm) formed dominantly by bulging recrystallisation. The lack of CPO as well as the developed asymmetric zoning can be explained by the activity of grain boundary sliding accommodated by dissolution and precipitation creep (DPC). However, two other processes were also active: interface-coupled dissolution and precipitation (icDP) and chemically and strain induced grain boundary migration (CI-SI-GBM). These two processes possibly acted simultaneously in single grains in a two-sided replacement direction. We suggest that during deformation, in high strain areas, stress induced DPC caused grain rotations where geometric incompatibilities caused a deformation enhanced influx and heterogeneous distribution of fluids. This caused local plagioclase replacement with accompanied bulging recrystallisation along with neocrystallisation of other phases resulting in bands with a phase mixture. Still, in these areas deformation was dominated by grain boundary sliding resulting in marked strain partitioning.

Keywords: plagioclase; recrystallisation, fluid-rock interaction; chemically induced grain boundary migration; interface-coupled dissolution and precipitation; electron backscatter diffraction (EBSD).
Introduction

During deformation, rocks commonly recrystallise i.e. the grain boundary network is rearranged (Means 1989). The extent and character of recrystallisation is in the broadest terms dependent on mineralogy, strain, strain rate, and presence and nature of fluids. The mechanisms driving the formation of new grains may be either physical or chemical, or a combination of both (e.g. Stünitz 1998). Dynamic recrystallisation is a physical process assumed to produce new grains without compositional change (e.g. Passchier and Trouw 2005). Grains are formed by either grain boundary migration (bulging recrystallisation) or by subgrain rotation recrystallisation (SGR) and is dominantly driven by elastic strain energy (Yund and Tullis 1991). Subgrain rotation recrystallisation is common at higher temperatures in feldspars where recovery processes become active to prevent dislocation tangling (e.g. Tullis 2002). Grain boundary migration (GBM) is a response to adjust the material to the prevailing conditions where the boundary movement lowers the free energy of the system. Strain induced migration (SIGBM) occurs when neighbouring grains contain different dislocation densities (i.e. stored strain energy) causing the grain with the lowest strain to grow on the expense of the grain with larger internal strain (e.g. Urai et al. 1986; Hirth and Tullis 1992). Other driving energies for GBM are boundary surface energies, impurities and chemical energies (Jessell et al. 2003). As pointed out by several authors there is probably more than one driving force active during deformation (e.g. Stünitz 1998; Piepenbreier and Stöckhert 2001). Brittle fragmentation at lower temperatures is also a physical process leading to new grain formation (e.g. Vernooij et al. 2006) and references therein.

New grains may also be produced by chemical processes such as heterogeneous nucleation (e.g. Kruse and Stünitz 1999), chemically induced grain boundary migration and its similar process liquid film migration (CIGBM and LFM; Hillert and Purdy 1978; Hay and Evans 1987), by dissolution and precipitation creep (DPC; Wintsch and Yi 2002) and by pseudomorphically replacing grains (interface-coupled dissolution and precipitation; e.g. Putnis and Austrheim 2010). Of importance is also the distribution and interfacial energies (cf. Putnis and Austrheim 2010). The distribution of fluids is shown to be affected by the presence of a fluid will have profound effects on the behaviour of minerals during deformation through hydrolytical weakening, which lowers the temperature for onset of effective dislocation creep (Tullis and Yund 1980). With respect to DPC, fluids expand the PT field for dissolution and precipitation creep (DPC) mechanisms (Wintsch and Yi 2002) and may result in changes in deformation mechanism by accelerating reaction softening and ease fluid assisted grain boundary sliding (GBS; e.g. Tullis et al. 1996). As a result of the above, presence and/or influx of fluids may lower the strength of the rock and localize strain.

If fluids enter the system it will have a large impact on new grain formation but also on the strain localisation mechanism (Wintsch and Yi 2002). Disequilibrium conditions will promote replacement processes and nucleation of new phases. Material transport aided by a media (e.g. a fluid) along grain boundaries is several orders of magnitude faster than diffusion through the crystal lattice (e.g. Farver and Yund 1992). Fluids will further enhance reactions and grain boundary mobilities and therefore grain boundary velocities (Urai et al. 1986). Furthermore, the presence of a fluid will have profound effects on the behaviour of minerals during deformation through hydrolytical weakening, which lowers the temperature for onset of effective dislocation creep (Tullis and Yund 1980). With respect to DPC, fluids expand the PT field for dissolution and precipitation creep (DPC) mechanisms (Wintsch and Yi 2002) and may result in changes in deformation mechanism by accelerating reaction softening and ease fluid assisted grain boundary sliding (GBS; e.g. Tullis et al. 1996). As a result of the above, presence and/or influx of fluids may lower the strength of the rock and localize strain.

Of importance is also the distribution and pathways of the fluid media which may be heterogeneously distributed over short distances (micro-scale) and cause various deformation mechanisms to be activated during the same event, even simultaneously (e.g. Reinecke et al. 2000; Fussies et al. 2008; Brander et al. submitted). The distribution of fluids is shown to be affected by deformation leading to wetted and open grain boundaries (Tullis et al. 1996; Reinecke et al. 2000). Furthermore, the fluid distribution is also affected by the presence of different mineral phases (strength, e.g rigid rotation) and interfacial energies (cf. Putnis and Austrheim 2010). Transport of fluids may occur via fractures, along grain boundaries and triple junction channels, but also through interconnected pore systems in reaction products (e.g. Putnis 2009).

Plagioclase is an anisotropic mineral. The rate of diffusion (dissolution) of a grain is affected by the lattice arrangement and a grain may exhibit different diffusion/dissolution rates in different crystal directions due to elastic compliances. This has been shown in dissolution experiments by e.g. Arvidson et al. (2004), Niedermeier et al. (2009) and Hövelmann et al. (2010).

This paper presents detailed microstructural and chemical analysis of a recrystallised plagioclase dominated rock deformed at wet amphibolite facies conditions.
Observations suggest a close link between physical and chemical processes where fluid played a major role. Furthermore, analyses show possible anisotropic diffusion/dissolution rates in different crystallographic directions.

Geological background

The investigated samples stem from a variably strained amphibolite facies grade anorthosite-leucogabbro unit on Storø, an island located in the Godthåbsfjord in the Nuuk region, southern west Greenland (Fig. 1). The Nuuk region is dominated by rocks of Archaean age (>2.5 Ga.) which according to current models consist of several (amalgamated) terranes displaying a complex geological history (e.g. Nutman et al. 2007 and references therein). Orthogneisses of tonalitic and granodioritic composition (TTG) are the most common units in the region with subordinate amounts of greenstone belts consisting primarily of mafic supracrystals and metasediments (e.g. Friend and Nutman 2005). In the region, anorthosite complexes are commonly associated with greenstone belts and ultramafic units (e.g. Windley and Garde 2009 and references therein).

At present day levels, the anorthosite-leucogabbro on Storø Island is structurally on the top of such a greenstone belt (the Storø greenstone belt; SGB; van Gool et al. 2007) and is positioned within an overturned fold limb in an antiform, in the hanging wall of the Storø shear zone (SSZ, 2630 Ma; Fig. 1). In addition to the anorthosite-leucogabbro, the SGB consists of mafic to felsic supracrustal rocks such as homogeneous and banded amphibolites, quartzites and heterogeneous biotite gneisses, with variable content of garnet, sillimanite and cordierite. Structurally above the SGB are heterogeneous tonalites with ages between 3800 and 3600 Ma, representing the early Archaean Færringehavn terrane (Nutman and Friend 2007; van Gool et al 2007). In the north-northeast, the SGB sequence overlies a tectonic slice of 2800 to 2700 Ma old orthogneisses which have intrusive contacts with the anorthosite-leucogabbro (van Gool et al 2007; Nutman et al. 2007). Tonalitic rocks of ~3000 Ma age (the Akia terrane) occur structurally below the SGB and SSZ to the north-west and are separated from the rest of the island by the Ivinguit fault, which transects Storø on the north-western side of the island (Fig. 1). The SGB is host to a gold mineralisation where the early mineralisation occurred at ca. 2860 Ma (apparently coeval with hydrothermal alteration subsequent to sediment deposition) and was followed by remobilisation at retrograde amphibolite facies conditions at 2635 Ma, possibly related to development of the SSZ (Juul-Pedersen et al., 2007; Knudsen et al. 2007; Nutman et al. 2007). Thus, the syn-metamorphic remobilisation (after peak-metamorphism) resulted in further gold concentration where fluid transport may have occurred over large distances (100 m’s to km’s distances) from SSZ into the hanging wall antiform-synform pair (van Gool et al. 3000 Ma, Nutman et al. 2007).
The different terranes surrounding the SGB are believed to have experienced the final amalgamation between 2650-2600 Ma (cf. Nutman et al. 2007), concurrent with high grade metamorphism of the SGB. Nutman et al. (2007) proposed that the SSZ represent a terrane boundary between two plates. This terrane boundary suture formed at 2650 (D1) causing high pressure assemblage in the lower plate (i.e. only little affecting the upper plate) and followed by a protracted reworking (D2) and exhumation of the boundary only shortly after at 2650-2600 Ma, including development of the SSZ at 2630 Ma. Plagioclase coronas surrounding garnets in some of the garnet bearing amphibolites in the SGB (van Gool et al. 2007) may indicate a decompression related to the inferred exhumation of the SGB.

Noting that the studied anorthosite–leucogabbro possibly experienced earlier deformation events we assume that the intimately associated D1-D2 events are the deformation events responsible for the deformation structures analysed in this contribution. According to thermobarometric investigations by Hollis and Persson (in Hollis 2005), which were carried out on nearby garnet (Grt) + sillimanite (Sil) + biotite (Bt) gneisses and Grt-amphibolites, temperature and pressure reached a range of 550-620°C and 4.5-5.1 kbar, representing the conditions of the central and upper supracrustal package during exhumation. Mineral abbreviations used follow Whitney and Evans (2010).

The studied anorthosite-leucogabbro is ~ 400 meters wide and folded on a regional scale (Fig. 1). Within the unit, slivers of interleaved tonalitic orthogneisses and amphibolites are present. The anorthosite-leucogabbro is characterized by significant strain partitioning ranging from coarse grained anorthosite with preserved igneous textures, to highly strained anorthositic gneiss, characterized by completely or near completely recrystallisation and general fine grain size and strong mylonitic foliation. In the former, amphibole and large plagioclase (Pl) crystals only display minor recrystallisation of rims, whereas in the latter, minerals are commonly segregated into alternating bands dominated by plagioclase and amphiboles resulting in a zebra-striped appearance.

Methods

Mineral chemistry

Mineral chemical compositions were analysed using a JEOL Superprobe JXL 8200 (University of Copenhagen, Denmark) and a Cameca SX50 (Uppsala University, Sweden). For the JEOL superprobe standard online ZAF-correction was performed during acquisition and the analytical conditions used were a 15kV acceleration voltage, 10 nA sample current and 10s counting time for peak and background using a 5 µm beam spot size. Analytical settings for the Cameca were a 20 kV acceleration voltage and 15 nA sample current with a 3 µm beam spot size. Here, analyses were corrected for by a PAP modified-ZAF correction method. The presence, position and symmetry of chemical zoning were additionally documented by backscattered electron imaging (BSE).

Acquisition and analysis of crystallographic orientation

Crystallographic data were collected using the electron backscatter diffraction (EBSD) technique (Adams et al. 1993; Prior et al. 1999). Analyses were performed on thin-sections at Stockholm University using a Philips XL-30 FEG-ESEM equipped with a Nordlys detector and Channel 5 analysis suite from HKL Technology (Oxford instruments). Thin-sections were chemically polished using colloidal silica and left uncoated during analyses. EBSD settings used were a working distance of between 19-21 mm and an accelerating voltage of 20 keV (~0.8 nA). Triclinic bytownite I-1 (Facchinelli et al. 1979) was used as the theoretical Pl match unit. To analyse the crystal orientation differences between a core and rim, the rim structure was transformed and plotted as triclinic labradorite (C-1) using the lattice parameters of Wenk et al. (1980). A step size of between 2 µm and 10 µm, depending on the crystallographic detail needed, was used during automated data collections in a rectangular grid using a beam scan. The raw EBSD data acquired automatically was processed to remove false data and to enhance the continuity of data over the microstructures. Processing of data followed that of Prior et al. (2002) and Bestmann and Prior (2003) in order to exclude introduction of artefacts. Following Piazolo et al. (2006) a grain is denoted “strain free” when the average internal misorientation (along a profile) is < 1°.

Analysis of chemical zoning related to crystal structure in plagioclase

To determine the position of the chemical zoning related to the crystal structure and to the foliation and lineation, i.e. to the stress field, we used information from the collected EBSD data. The Channel 5 software provides a 3-D feature that visualises a box-mineral with the crystallographic a/- b- and c-axis for each analysed point (i.e. for every 2 µm in a map with a step size of 2 µm). We used this 3-D feature in combination with pole figures, backscattered electron images and photomicrographs to deduce the position of the rims on the most likely plane and direction in the bytownite atomic structure (I-1). We assumed a simple shear component in the both the higher and lower strain areas.

Furthermore, to assess if the location and width of the asymmetric zonation could be related to crystallographic orientation of grains we systematically evaluated the position of the asymmetric chemical zoning to crystallographic planes and directions in the Pl structure.

Grain surface topography

3-D surface topography measurements across rim-core boundaries of zoned Pl grains were performed using a new technique called confocal profilometry. Equipment used was a SENSOFAR Plµ 2300 optical imaging profiler.
with accompanied SensoScan 2.45 software at Stockholm University. Confocal profiometry data are collected by vertical scan of the surface in multiple 100 nm steps. The high numerical aperture (0.95) and a 150x magnification lens allows a lateral and vertical resolution of 10 nm and 1 nm, respectively. In addition surface slopes of up to 71° can be detected. Since the reflectivity of the surface is dependent on its chemical composition the intensity of light detected makes possible to distinguish different solid phases. Before analyses, the surface of the sample was chemically polished using colloidal silica (as for the EBSD analyses, see above) to remove irregularities produced during mechanical polishing.

Results

Thin section description

Ten thin sections representing areas of variable finite strain as determined in the field were examined in transmitted light microscope. Three thin sections were selected for analyses, representing low (86009), medium (86006c) and high strain (86006b), respectively (Fig. 2).

In general, studied samples consist of Pl + hornblende (Hbl) +/- quartz (Qz) +/- Bt +/- clinozoisite (Czo). Accessory phases are ilmenite (Ilm), titanite (Ttn), pyrite (Py) and muscovite (Ms). Titanite occurs as rims around Ilm that also contains exsolution lamellas of Fe-oxide. Pyrite is associated with Ilm and contains exsolution of chalcopyrite (Ccp). Tabular Bt crystals are dominantly aligned with foliation. Clinozoisite is mostly euhedral and intergrown with Bt.

Characteristics vary significantly between samples and are summarised in the following. More detailed analyses of the observed chemical variations and crystallographic characteristics are provided subsequently. The low strain sample (86009) contains large (up to several centimetres) Pl crystals, i.e. porphyroclasts, while smaller grained, recrystallised Pl grains are found as clusters between the large grains and are more sericitised than their equivalents in higher strained counterparts (Fig. 2b and d). Fractures are found inside and across Pl porphyroclasts and recrystallised grains. Asymmetric chemical zoning occur as rims around porphyroclasts, recrystallised grains and along some fractures. The number of recrystallised Pl grains that have chemical zoning increases in the vicinity of amphibole (Amp)-rich horizons and hydrous phases (Fig. 3). Transgranular fractures without chemical zoning commonly contain hydrous minerals phases such as micas. Amphiboles are mainly replaced by randomly oriented Bt (Fig. 2b).

The high strain sample (86006b) is finer grained than its low strain equivalent and exhibits mineral segregation into Pl and Hbl dominated foliation parallel bands. Only a few porphyroclast remnants exist. These are less than 2 mm across and show undulose extinction.
Biotite, Czo, opaque minerals and Ms are mostly found in association with Hbl in Hbl-rich foliation parallel horizons.

The medium strain sample (486006c) shows similar structures as the high strain sample with difference that the porphyroclasts are larger and less deformed.

Detailed microstructural grain analysis: shape, size, boundary characteristics, crystal orientations and chemical composition

**Plagioclase porphyroclasts**

Pl porphyroclast sizes range from millimetres up to several centimetres in diameter, where the larger grains are found...
Paper II

In low strain areas they display growth twins and show a low internal lattice distortion. Fractures are common and found as irregular, transgranular fractures and as crystal lattice bound fractures, following crystal planes (Fig. 4a). Micas decorate parts of the transgranular fractures. The average anorthite (An) content of porphyroclasts in all areas is $\text{An}_{80} \pm \text{An}_{2}$ (Table 1). Chemical zonation (rims of $\text{An}_{65}$) is frequent along lattice bound fractures and is also found at grain boundaries (Fig. 4a). Hüttenlocher intergrowths ($\text{An}_{74}$) with a herring bone structure are found in Pl porphyroclasts. These intergrowths are also found in the recrystallised grains in the lower strain area where they are truncated by rims (chemical zonation) with lower An content (cf. Figs. 8c-d).

At the transition from low to high strain the porphyroclasts display the same features as in low strain, but in addition exhibit migration of twin boundaries (Fig. 4b), substructure and subgrain development and presence of small, recrystallised grains with similar sizes as the subgrains. These substructures are to a large extent confined to twins, as are chemical changes. Still, recrystallised grains dominantly occur at grain boundaries.

Porphyroclasts in high strain areas only display a few fractures. These are mostly late transgranular, i.e. they cut across grain boundaries. These porphyroclasts display an intense development of substructures and recrystallisation (Fig. 4c). The shape of the porphyroclasts is irregular and amoeboidal. Large recrystallised grains grow on the expense of the clast as evidenced by truncation of twins and fractures (Fig. 4c).

**Recrystallised plagioclase**

In general, recrystallised Pl grains exhibit growth twins and low internal deformation. They are cut by thin, late, transgranular fractures without any visible (by BSE) accompanying chemical change. These fractures are decorated with hydrous phases.

For the sake of clarity, we grouped recrystallised plagioclase grains into three groups depending on their size, occurrence and chemistry. Group I consists of large grains, with a size range of 400-1800 $\mu$m and an average size of 720 $\mu$m. These grains are few and only found around and inside highly strained remnants of porphyroclasts in the high strain sample (Figs. 2d and 4c). Grain orientations (n=51) scatter around the host porphyroclast orientation (adjacent and surrounding porphyroclast; Fig. 5a). All

---

**Fig. 4 a-c** Representative Pl porphyroclasts from low-, transition- and high strain area, respectively. Note the increased abundance of microstructures indicative for crystal plastic deformation from low to high strain. a Arrows A and B point to irregular fractures and crystal plane bound fractures, respectively. Note chemical change associated with fractures and grain boundaries (darker gray), 486009. b Twin boundary migration in clast (arrows); 486006b. c Amoeboid-like clast (cl) remnant and group I recrystallised grains; arrow points to truncation of porphyroclast by newly grown grains; 486006b. d Recrystallised grains (group II) in the low strain area, 486009, see text for further details.
Paper II

Group II is the dominant group of recrystallised grains and occurs in all samples. Their shape preferred orientation (SPO) is more pronounced in the high strains areas (Fig. 6) where long axis of grains are subparallel to the foliation. They have a chemical composition of An₈₀ with rims (chemical zoning) of An₆₅ (Table 1). The chemical zoning is asymmetric (Figs. 3, 7 and 8) and only a few of the larger grains display subgrain structures and deformation twins (Figs 7 and 8). Group III grains have a composition of dominantly An₆₅ and are more abundant in the high strain area. For both Group II and III grains crystallographic orientations are random in both low and high strain areas (Figs. 5b-d). Group II commonly have smooth and straight grain boundaries; however, lobate boundaries with increased boundary curvatures are present in high strain areas which are always associated with asymmetric chemical zoning (e.g. Fig. 7b). Grain boundary bulging is observed in both low and high strain samples in group II grains and is closely associated with chemical zonation (Figs 7a, 7e and 8e). The bulges have variable sizes (~50-150 µm) which further correspond to the grain sizes of Group III grains (Figs. 7a, 7e and 10).

Hornblende

Hbl is the second most abundant mineral in the investigated samples and occurs between large Pl porphyroclast in the low strain area (Fig. 2b) and dominantly as elongated grains (up to 1 mm long) aligned with foliation in higher strain areas. Hbl grains from the high strain area (Fig. 2d) other recrystallised grains have an average grain size of 314 µm in the low strain sample (range 42-825 µm; Figs. 2b and 4d) and 240 µm in the high strain sample (range 34-862 µm; Figs. 2d and 3). However, grains with an anorthite content of An₆₅ is only found in grains <150 µm. Therefore (in combination with interpretations from new grain formation, see discussion) we used this grain size as boundary between Group II and III, giving Group II an average grain size of 354 µm (range 154-825 µm; in low strain sample) and 329 µm in the high strain sample (range 151-862 µm) with a total average of 341 µm. Group III grains have an average grain size of 112 µm (range 42-148 µm; low strain sample) and 96 µm in the high strain sample (range 39-149 µm). Group II is the dominant group of recrystallised grains and occur in all samples. Their shape preferred orientation (SPO) is more pronounced in the high strains areas (Fig. 6) where long axis of grains are subparallel to the foliation. They have a chemical composition of An₈₀ with rims (chemical zoning) of An₆₅ (Table 1). The chemical zoning is asymmetric (Figs. 3, 7 and 8) and only a few of the larger grains display subgrain structures and deformation twins (Figs 7 and 8). Group III grains have a composition of dominantly An₆₅ and are more abundant in the high strain area. For both Group II and III grains crystallographic orientations are random in both low and high strain areas (Figs. 5b-d). Group II commonly have smooth and straight grain boundaries; however, lobate boundaries with increased boundary curvatures are present in high strain areas which are always associated with asymmetric chemical zoning (e.g. Fig. 7b). Grain boundary bulging is observed in both low and high strain samples in group II grains and is closely associated with chemical zonation (Figs 7a, 7e and 8e). The bulges have variable sizes (~50-150 µm) which further correspond to the grain sizes of Group III grains (Figs. 7a, 7e and 10).

Hornblende

Hbl is the second most abundant mineral in the investigated samples and occurs between large Pl porphyroclast in the low strain area (Fig. 2b) and dominantly as elongated grains (up to 1 mm long) aligned with foliation in higher strain areas. Hbl grains from the high strain area (Fig. 2d)

other recrystallised grains have an average grain size of 314 µm in the low strain sample (range 42-825 µm; Figs. 2b and 4d) and 240 µm in the high strain sample (range 34-862 µm; Figs. 2d and 3). However, grains with an anorthite content of An₆₅ is only found in grains <150 µm. Therefore (in combination with interpretations from new grain formation, see discussion) we used this grain size as boundary between Group II and III, giving Group II an average grain size of 354 µm (range 154-825 µm; in low strain sample) and 329 µm in the high strain sample (range 151-862 µm) with a total average of 341 µm. Group III grains have an average grain size of 112 µm (range 42-148 µm; low strain sample) and 96 µm in the high strain sample (range 39-149 µm). Group II is the dominant group of recrystallised grains and occur in all samples. Their shape preferred orientation (SPO) is more pronounced in the high strains areas (Fig. 6) where long axis of grains are subparallel to the foliation. They have a chemical composition of An₈₀ with rims (chemical zoning) of An₆₅ (Table 1). The chemical zoning is asymmetric (Figs. 3, 7 and 8) and only a few of the larger grains display subgrain structures and deformation twins (Figs 7 and 8). Group III grains have a composition of dominantly An₆₅ and are more abundant in the high strain area. For both Group II and III grains crystallographic orientations are random in both low and high strain areas (Figs. 5b-d). Group II commonly have smooth and straight grain boundaries; however, lobate boundaries with increased boundary curvatures are present in high strain areas which are always associated with asymmetric chemical zoning (e.g. Fig. 7b). Grain boundary bulging is observed in both low and high strain samples in group II grains and is closely associated with chemical zonation (Figs 7a, 7e and 8e). The bulges have variable sizes (~50-150 µm) which further correspond to the grain sizes of Group III grains (Figs. 7a, 7e and 10).

Hornblende

Hbl is the second most abundant mineral in the investigated samples and occurs between large Pl porphyroclast in the low strain area (Fig. 2b) and dominantly as elongated grains (up to 1 mm long) aligned with foliation in higher strain areas. Hbl grains from the high strain area (Fig. 2d)

other recrystallised grains have an average grain size of 314 µm in the low strain sample (range 42-825 µm; Figs. 2b and 4d) and 240 µm in the high strain sample (range 34-862 µm; Figs. 2d and 3). However, grains with an anorthite content of An₆₅ is only found in grains <150 µm. Therefore (in combination with interpretations from new grain formation, see discussion) we used this grain size as boundary between Group II and III, giving Group II an average grain size of 354 µm (range 154-825 µm; in low strain sample) and 329 µm in the high strain sample (range 151-862 µm) with a total average of 341 µm. Group III grains have an average grain size of 112 µm (range 42-148 µm; low strain sample) and 96 µm in the high strain sample (range 39-149 µm).
Paper II

display a CPO with the (100) plane aligned with foliation and the <001> axis with lineation (Fig. 5e). Hbl is also found in layers with a phase mixture of Pl + Hbl + Qz (Fig. 3c) and with an average grain size of 190 µm and aspect ratio of 2.27. Some grains are strained with an apparent bending of the crystallographic lattice from edge to edge in elongation. Subgrain walls (up to 8°) are seen perpendicular to the grains long axis. Some are also observed along long axis parallel grain boundaries. Hydrous (e.g. Ms and Bt) and opaque phases are commonly seen in Hbl-rich bands (Fig. 7d).

**Quartz**

Quartz is less abundant than Hbl and Pl and mostly occurs in layers with a mixture of Pl and Hbl (Fig. 3d). Grains are up to 800 µm large but more frequently less than 200 µm, with an average of 130 µm. They commonly have

---

Fig. 7 Photomicrographs showing Pl rim and grain boundary structures from a high strain area. **a** Asymmetric rims, bulging and cannibalism. Note angle between twins in core and rim. Solid arrow point at position where an old grain will be separated into two smaller grains, retaining the old grain chemistry. **b** Lobate and facetted grain boundaries. **c** Indentation between grain i and ii with development of subgrain boundary (sgb) and a chemical change from An80 (core) to An65 (rim). Note grain size differences. **d** Plane polarised micrograph of representative Amp-rich horizon with spatially related opaques, and hydrous phases. **e** Pinning of Pl bulge between Amp grains. **f** Misorientation profile, a-b, showing a low angle grain boundary (6°) across the pinned bulge in (e). 3-D representation of mineral orientation is shown for some selected grains. Photos are XY. Dotted lines are boundaries between core and rims. Stippled line is a low angle boundary and stippled arrows infer growth / dissolution directions.
smooth grain boundaries and an average aspect ratio of 1.97 in high strain areas. Grains commonly show undulose extinction and some subgrain boundaries. Grains (n=36) from the high strain sample (Fig. 2d) indicate random grain orientations (not shown).

Characteristics of plagioclase chemical zoning

Recrystallised grains of group II exhibit asymmetric chemical zonation in form of rims of lower Ca content than the grain core (An$_{80}$ and An$_{65}$ respectively; e.g. Figs. 8 and 9; Table 1). In group I, grains and porphyroclasts
only rarely show chemical zoning. Several characteristic features are associated with chemical zoning in form of rims:

a) sharp compositional change from rim to core (e.g. Fig. 9),
b) smooth and sharp boundaries towards the adjacent grain and grain cores, respectively (Figs. 7 and 8).
c) commonly developed on more than one side of a grain, along two-grain boundaries as well as in triple junctions (cf. Fig. 3).
d) some rim areas exhibit visible porosity (Fig. 8d).
e) bulging structures and associated pinning features with or without a bridging subgrain boundary (e.g. Figs 7a and 7e-f respectively; cf. Halfpenny et al. 2006), where the bulge size is comparable to the group III smaller grains (e.g. Figs. 7 and 10).
f) microstructures similar to the so-called cannibalism structures observed by Menard and Spear (1996; Figs. 7-10).
g) higher internal misorientations in rims than in cores (i.e. more deformed; Fig. 10d); this is most pronounced in high strain areas.
h) faceted grain edges where a rim with straight grain boundaries cuts growth twins of the neighbouring grain (e.g. in Figs. 7b and 8a).
i) in the high strain areas, an increased curvature where rims are (i.e. lobate size boundaries; e.g. Fig. 7b).
j) in low strain areas (Fig. 8e), zig-zag shaped core - rim boundaries where at the 1 μm scale no micro-fractures could be identified. The zig-zag step coincides with twin boundaries.
k) crystallographic orientation is consistent across core-rim boundary (Fig. 8e). However, in the high strain sample (486006b), some rims show a slight misalignment with respect to the core (Fig. 7a).
l) zig-zag shaped grain boundary between two Pl grains (Fig. 10b).

In principal, possible external factors that may influence the thickness and location of these rims are finite strain, orientation of the stress axes and grain elongation, location of grain with respect to other phases and crystallographic orientation of boundaries and rims. Here, we investigate all but the last two crystallography related factors which are dealt with separately below. Measurements of ~100 grains each from low and high strain areas, show that the average rim thickness is higher in the low strain area (Table 2). In low strain areas, the position of rims is not related to the orientation of foliation, whereas in high strain areas thickest rims nearly exclusively occur in the elongation direction i.e. subparallel to foliation (Table 2 and Fig. 6b). Thus, in high strain zones, grain boundaries which are at low angles to the foliation only rarely exhibit chemical zonation. In low strain areas, rims are seen in 85 % of the recrystallized grains while in high strain areas 75 % of grains show rims. There is a positive correlation between the amount of rims and the presence of hydrous phases (cf. Fig. 3).

Chemical zoning related to crystallography.

The external factors mentioned above do only to a limited extent explain the presence and the location of chemical zonation; for example, some grains with a distinct SPO sometimes lack and sometimes show a pronounced chemical zoning in the extension direction (Figs. 3 and 7-10). This indicates that other factors must have been important. Therefore, we investigate if there is a direct link between crystal orientation and presence and extent of chemical zoning. Detailed measurements from a low and a high strain area respectively are presented in table 3. We have only considered the three principal crystallographic axes but do not exclude the presence of other dominant and less dominant crystallographic planes and directions. Thus, any consistency in position of the thickest rim to specific crystal planes and directions would imply anisotropic behaviour due to differences in elastic compliances, i.e. the resistant to adjust or dissolve and replace the crystal lattice in a given crystal direction (e.g.

<table>
<thead>
<tr>
<th>Table 1 Chemical analyses of plagioclase</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>SiO2</td>
</tr>
<tr>
<td>TiO2</td>
</tr>
<tr>
<td>Al2O3</td>
</tr>
<tr>
<td>FeO</td>
</tr>
<tr>
<td>MnO</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Na2O</td>
</tr>
<tr>
<td>K2O</td>
</tr>
<tr>
<td>Total</td>
</tr>
</tbody>
</table>

Mol %

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>An</td>
<td>80.27</td>
<td>80.20</td>
</tr>
<tr>
<td>Ab</td>
<td>19.68</td>
<td>19.80</td>
</tr>
<tr>
<td>Or</td>
<td>0.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Nr. of analyses

11  61  30

An = Ca*100/(Ca+Na+K), Ab = Na*100/(Ca+Na+K), Or = K*100/(Ca+Na+K)
Results show that ~60% of the thickest rims occur along the (001) plane and ~61% in the <010> direction (i.e. on the (010) crystal face, however not always along the (001) plane). We note that when grains are randomly oriented it is difficult to separate between e.g. the (100) and (001) plane, when these planes are at a large angle to the foliation. The results therefore only indicate the most likely plane and direction and do not present a full set of combined planes and directions.

Uncertainties with the results are that when there is more than one grain orientation that contains a zonation, the thickest rim might be influenced by the strain energy from the neighbouring grains which may inhibit the size of the zonation on the easiest direction. We have not taken into consideration the crystal orientation of the adjacent grain, i.e. our measurements represent the surface direction most prone to the process responsible for the chemical zoning. Pole figures with data from the core (bytownite, I-1) and the rim (labradorite, C-1) from grains with a zig-zag shaped interface boundary show only a minor deviation in orientation between the two, which is expected even with strict epitaxial growth, considering the change in lattice parameters.

Interpretation and discussion

In the following, we concentrate on several issues important to the physio-chemical processes observed in the samples investigated. We are primarily interested in the formation of chemical zoning in Group II and Group III of recrystallized grains. Results show that these rims to a significant extent are related to the deformation history of the sample pointing to the interaction of chemical and physical processes at mid crustal levels. First we discuss briefly the mechanisms of initial grain size reduction, i.e. recrystallisation of group I and II. Since group III grains are intimately linked to chemical changes, that is, they exhibit the rim composition, we discuss their formation in more detail. This directly leads us into the discussion of the origin of chemical zoning, concentrating on the responsible mechanisms and resultant microstructures. Then we assess the influence of crystallographic orientations and fluid distribution on the extent and dominance of the described mechanisms. Finally, we put the deciphered deformation history into the regional context of the samples investigated and finish with the implications for the deformation and chemical modification of Pl rich rocks at wet mid crustal conditions.

Mechanisms of recrystallisation

The three different groups of recrystallized grains can be directly linked to two successive events (D1 and D2) of recrystallisation (i.e. grain size reduction) where group I recrystallized in an early event and group II in a subsequent. Considering that recrystallised grains of group I in some cases still show an orientation relationship with their inferred host (Fig. 5a) we suggest that these were formed by a host controlled recrystallisation process such as subgrain rotation recrystallisation or bulging recrystallisation (e.g. Kruse et al. 2001). However, we also observe that grains seem to have nucleated in these strained porphyroclasts, and subsequently replaced parts of the host grain (Fig. 4c), suggesting heterogeneous nucleation (e.g. Jeřábek, 2007; Brander et al. submitted).

Grains of group II show random CPO and occur both in the low and high strain areas. Substructures such as low angle boundary walls and subgrains are near absent and chemical zonation is common. Subgrain rotation recrystallisation is not a feasible mechanism as we would expect from a noticeable host related crystallography and development of CPO. In areas dominated by Group II grains (e.g. Fig. 3a), grain boundaries are polygonal suggesting that the grains attained energetically stable configuration; bulging recrystallisation is therefore not a feasible mechanism. We suggest that also here nucleation was the dominant grain size reducing process. In contrast to low strain areas dominated by Group II, lobes and bulges are common in the high strain area and are of similar size as the Group III grains (<150 µm). For the formation of Group III grains we suggest three possible processes:

1) Bulging recrystallisation.
Table 2  
<table>
<thead>
<tr>
<th>Measurement of plagioclase rims</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Tot. nr of measured grains</td>
</tr>
<tr>
<td>Average grain aspect ratio</td>
</tr>
<tr>
<td>% has no rim</td>
</tr>
<tr>
<td>% thickest rim in grain elongation</td>
</tr>
<tr>
<td>Rim thicknesses $f$ (µm)</td>
</tr>
<tr>
<td>Average rim thickness $f$ (µm)</td>
</tr>
<tr>
<td>Rim lengths $f$ (µm)</td>
</tr>
<tr>
<td>Average rim length $f$ (µm)</td>
</tr>
<tr>
<td>Length/ Thickness (average) $l/t$</td>
</tr>
</tbody>
</table>

2) Left-over-grains by incomplete consumption during grain boundary migration

3) To a minor extent: Development of subgrains and subgrain rotation inside rims.

The 1st process, bulging recrystallisation, is evident in e.g. Figs. 7a, 7e and 10, where the bulges may or may not show a bridging subgrain boundary (cf. Halfpenny et al. 2006). Boundary migration resulting in bulging recrystallisation is a low temperature GBM feature when it is linked to a strain induced process (Hirth and Tullis 1992; Tullis 2002; Stipp and Kunze 2002; 2008). Driving forces for strain enhanced bulging may however be enhanced if a chemical driving potential is added to the process (Stünitz 1998; Baxter and DePaolo 2004) as observed in metal systems (diffusion induced recrystallisation (DIR); e.g. Yoon 1995). A bridging subgrain boundary seen in Fig. 7e may be explained by a rotation of the host grain and pinning of the bulge between other grains during deformation, due to dislocations built-up at the bulge neck (Fig. 10). This process also explains the same lower anorthite content of some of the smaller grains (<150 µm) as that of the documented rims. In the 2nd process, left-over-grains are developed when a grain with the higher anorthite content is partly consumed by a growing grain with a lower An content. This explains why some of the smaller grains in the 2nd group do not show a lower anorthite content than the core composition of An$_{90}$. The 3rd process, where a subgrain is developed and presumably rotated (as seen by low angle boundaries and “off-setting” twins), is only rarely seen and then occurs in rims (Fig. 10). The restriction to rims may suggest that only those dislocations were able to build up sufficiently to cause subgrain rotation. Potentially, hydrolytical weakening introduced due to the chemical changes in the rim lower the activation energy for dislocation creep (e.g. Tullis and Yund 1980) and enabled subgrain rotation to operate.

From the above, it is evident that Group III grains are only developed directly or indirectly related to chemical changes. The grains adjacent to chemical zoning dominantly show a low internal distortion, that is not consistent with a solely strain induced GBM (e.g. Urai et al. 1986). However, the fact that lobate and bulging structures are more frequent in the high strain areas, even though rims are thicker in the low strain area, indicate that both driving forces (i.e. strain energy and chemical energy) were significant. The random CPO of Group III grains (Fig. 5d) is explained by sustaining the orientation of the random porphyroclasts but also by subsequent rotation by fluid-induced grain boundary sliding.

In summary, we suggest that the grain size reducing processes resulted in a near random orientation of grains as random CPO is seen in both low and high strain areas and in all grains apart from some possibly shielded Group I grains. During subsequent deformation none of the groups developed a significant CPO (Fig. 5). A random CPO, as is seen among the recrystallised grains, would not be erased by annealing (Piazolo et al. 2010).

Origin of chemical zoning and associated grain characteristics

Combined microstructural and chemical analyses indicate that the character and extent of chemical modifications is directly but not exclusively related to finite strain and the kinematic axes orientation. An increase in SPO is directly linked to a higher abundance of asymmetric chemical rims in the direction of elongation, which is in turn subparallel to foliation (Fig. 6). In the high strain areas, rims become more asymmetric resulting in a high percentage of grain boundaries without rims which are dominantly orientation subparallel to foliation (e.g. Figs. 3b-c and Table 2). At the same time, as mentioned above grain boundaries become increasingly irregular and show bulging microstructures with increasing amount of chemical zonation and strain (e.g. compare Fig. 3a with 3b-c). Let us now evaluate different processes that could be responsible for the chemical zoning and compare expected resulting patterns to those we observe. Alternatives are a) lattice diffusion; b) dissolution precipitation creep (DPC); c) chemically induced grain boundary migration (CIGBM) and/or the related liquid film migration (LFM); and d) grain-inward replacement, i.e. interface-coupled dissolution and precipitation (icDP) a variety of the so-called solvent mediated phase transformation (O’Neil and Taylor 1967; Putnis 2002; Putnis and Putnis 2007; Engvik et al. 2008; Putnis 2009; Hövelmann et al. 2010; Putnis and Austrheim 2010).

Let us first look at a) volume lattice diffusion: In principal lattice diffusion can result in chemical zoning, however this process would result in a smooth chemical change across the chemical zoning. That pattern of chemical change is not consistent with the chemical profile in Fig. 9 that show a distinct step between rim and core compositions. In addition, volume diffusion is too slow to account for the large rims in these samples (Table 2; Yund 1986; Yund and Snow 1989; Yund and Tullis 1991). The second alternative (b) is dissolution and precipitation creep. This process is strongly dependent on the orientation of the stress axis, where material at boundaries perpendicular to σ1 dissolves while material is added on boundaries perpendicular to σ3. Statistically, rim distributions in high strain zones show this relationship which will directly result in an increase in SPO as observed (Fig. 6). This process would go hand in hand with grain boundary sliding as shown by Ford et al. (2002) enhancing the random CPO observed. However, stress is not the only controlling factor since several elongated grains do not
contain their rims in the extensional position but instead show zonation towards the shortening direction (Figs. 3 and 9). Furthermore, the fact that rims are less well defined in their orientation in low strain areas (Fig. 6b) points to the activity of another process.

In the most general sense, grain boundary migration (c) refers to the migration of boundaries in order to attain a lower energy state (Jessell 2003 and references therein). Main driving forces can be strain energy, chemical energy and surface energy. We suggest that the migration is primarily driven by chemical differences. This type of grain boundary migration is termed CIGBM (e.g. Hillert and Purdy 1978; Balluffi and Cahn 1981; Hay and Evans 1987; Stünitz 1998). This mechanism has also been directly associated with dissolution and precipitation creep (Baxter and DePaolo 2004). In the latter model, during CIGBM atoms are dissolved in the consumed grain and transported along the grain boundary (grain boundary diffusion) and precipitated on the advancing grain, leaving a new grain composition in its wake. The presence of a solute along the grain boundary thus accelerates the boundary migration (Evans et al. 1986). A process called liquid film migration (LFM) is intimately coupled to the CIGBM process where it is assumed to be the thickness of the fluid/solute film that governs which process is active (cf. discussion in Hay and Evans 1987). A thick fluid film is in favour for the LFM mechanism while CIGBM is active when less fluid/solvent is available. Since we cannot deduce the amount of fluids (i.e. thickness of the solute/liquid film) that were present at the grain boundaries and that the dominant driving force is the same for CIGBM and LFM we include LFM in the CIGBM terminology. In our samples, some of the characteristic features for CIGBM are observed. These include zig-zag shaped chemical boundaries (Fig. 10) and facetted grains (Figs. 7b and 8a). The observed (and also characteristic) lobate and bulging boundaries are in accordance with an increased boundary curvature meaning that boundary tension forces are not governing the migration (Hay and Evans 1987). However, since some of the grains in high strain areas do show evidence
for plastic behaviour such as slight bending of twins (Figs. 8a) we also assume that strain energy was an additional driving force. However, no boundaries are found with lobate or bulging structures without the chemical zonation, indicating that the chemical driving force for GBM played a dominant role. At the same time, fluid presence would enhance mobilities and allow grain boundaries to migrate faster. Microstructural observations such as Pl grains (the rim of An$_{65}$) growing into other Pl grains (core of An$_{80}$) and cutting through twins (Figs. 7a and 8a), as well as the bulging recrystallisation mechanism for group III grains, support the activity of CIGBM. The interface-coupled dissolution and precipitation mechanism (d) is a solvent mediated phase transformation assumed to be a common mineral replacement process in the presence of fluids (e.g. Putnis 2002). The process may be pseudomorphic and the precipitation is intimately coupled with the dissolution so that the replaced grain is mimicked on the nano-scale. In the process the most soluble surface reacts with the solute (possibly a grain boundary fluid) resulting in an ionic exchange favoured by lowering the Gibbs free energy. However, as lattice parameters change along a solid solution series some structural changes are to be expected. Characteristic features for the icDP mechanism are (after Putnis 2009):

- Sharp chemical interface (reaction front)
- Development of porosity in the product phase (assumed interconnected)
- Preservation of crystallographic orientation
- Preservation of external morphology
- Reaction induced fracture ahead of the reaction front if large increase or decrease in solid molar volume.

In the studied sample, chemical profiles show an apparent step function in Ca and Na content across core-rim boundary (Fig. 9) and is therefore consistent with characteristic (i). Volume or lattice diffusion is only effective in Pl at high temperatures (Tullis 2002) and is not consistent with a sharp compositional step function and would produce a concentric chemical zoning pattern which stands in contrast to the observed asymmetric chemical zoning (e.g. Steffen and Selverstone 2006). (ii) Confocal profilometry analyses in this study indicate a higher amount of voids in the rim (product phase) than in the core and this may represent the relict porosity that is expected in the product phase during icDP (Fig. 8d; e.g. Engvik et al. 2008; Niedermaier et al. 2009; Hövelmann et al. 2010). Characteristic (iii) is fulfilled by the preservation of crystallographic orientation and therefore optical continuity (Fig. 8f). Minor crystallographic changes can be explained by the change in lattice parameters in the Pl solid solution series. Preservation of external morphology (iv) is difficult to assess in this study due to the grain boundary mobility of boundaries with a chemical zoning. We do not observe characteristic (v) since there is not a large difference in molar volume (<1 %). Furthermore, during icDP chemical zonation may also occur along fractures (Hövelmann et al. 2010) and that is observed in both clasts and recrystallised grains (Figs. 4a and 8e). The above described and discussed features strongly indicate that in our samples, the fluid induced grain replacement mechanism icDP occurred, in both low and high strain samples.

Since the chemical and microstructural features of the chemical zonation are indicative for both icDP and CIGBM, and sometimes are presumably found in the same grain (e.g. Fig. 8a) we suggest that the replacement may occur at two fronts from the same starting point (Fig. 11), where:

- deformation enhanced fluid distribution promotes fluid influx along grain boundaries and triple junctions,
- dissolution starts on the grain with the most soluble surface (i.e. crystallographically and chemically controlled). When the thin fluid film is supersaturated precipitation occurs and coupled with the dissolution follow the reaction front into the grain (Grain 1). The interface-coupled dissolution and precipitation has now produced a product (An65) more stable with the incoming fluid.
- now, as the product is less soluble than the adjacent Pl of An$_{80}$ (Grain 2) dissolution may start on this grain too if grain orientation permits (i.e. coherency strains). However, the solution will now precipitate on the product of Grain 1, which will advance (grow) into the Grain 2 in the wake of the reaction front. However, since porosity is developed in the product from the initial starting point (line) during icDP fluids may continue to reach the first reaction front (inside Grain 1), simultaneously driving icDP and CIGBM. Thus, a consequence of the simultaneous reaction fronts may

### Table 3: Position of thickest rim related to crystallography

<table>
<thead>
<tr>
<th>Parallel to</th>
<th>High strain</th>
<th>Low strain</th>
<th>Tot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>30</td>
<td>59</td>
<td>62</td>
</tr>
<tr>
<td>(010)</td>
<td>7</td>
<td>14</td>
<td>13</td>
</tr>
<tr>
<td>(100)</td>
<td>14</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>Tot.</td>
<td>51</td>
<td>100</td>
<td>52</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parallel to</th>
<th>High strain</th>
<th>Low strain</th>
<th>Tot.</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;001&gt;</td>
<td>5</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>&lt;010&gt;</td>
<td>33</td>
<td>65</td>
<td>68</td>
</tr>
<tr>
<td>&lt;100&gt;</td>
<td>13</td>
<td>25</td>
<td>29</td>
</tr>
<tr>
<td>Tot.</td>
<td>51</td>
<td>100</td>
<td>52</td>
</tr>
</tbody>
</table>
be an enhanced growth rate limited by the availability of fluids and its local chemical composition.

Migration and replacement directions - anisotropy of plagioclase

There is a two-fold influence of anisotropy related to crystallography in our studied samples involving a) the rate of dissolution important to icDP and b) the rate of grain boundary migration important to CIGBM.

The direction upon which grain boundaries will migrate or dissolve is dependent on external and internal factors. Externally, a strong stress field will support growth in the extension direction and inhibit growth and/or replacement normal to the principal stress axis (e.g. Wintsch and Yi, 2002). The presence of different rim thickness around a grain will also be a result of a heterogeneous fluid-solid-ratio in a sample i.e. the thickness of the fluid film will most certainly be variable around the grain (Huang et al. 1986; Reinecke et al. 2000; Hövelmann et al. 2010).

Internally, the atomic structure will have an effect of replacement (dissolution/migration) direction. The feldspar structure consists of a framework of Al-Si tetrahedrons with interstitial cations (Ca, Na and K). Dissolution studies of feldspars have shown that it is easier to break Al-O bonds than Si-O bonds (Xiao and Lasaga 1994; Oelkers and Schott 1995), hence the crystal lattice configuration should show an anisotropy in dissolution rates as the structure is weaker at Al-O bonding dominating directions (Arvidson et al. 2004). Arvidson et al. (2004) found in experiments of albite dissolution that dissolution rates were faster normal to the (010) surface than to the (001) surface. They also performed dissolution tests on anorthite crystals but only on the (010) surface which however showed an even faster dissolution rates than on the (010) albite surface (although no (001) surface to compare with). The atomic structure, apart from the ease of breaking certain bonds, displays different elastic constants in different directions. Experiments on triclinic albite by Brown et al. (2006) showed that the (001) and the (010) surfaces have the highest constants (179.5 and 183.5, respectively) that can be compared to e.g. (100) with a constant of 69.9. Coherency strain differences along different crystallographic directions are shown to promote growth and or diffusion in different crystal directions. The initiation of migration and the direction of migration occur towards the grain with the surface of the highest coherency strain energy e.g. Lee et al. (1993). Lee et al. (1994) further showed that when the coherency strain energies between two neighboring grains are similar the migration direction may be determined by grain boundary impurities- Twining in plagioclase might also be an extra internal factor influencing the dissolution rates. Albite twins may act as obstacles leading to slower dissolution of the (001) surface than on the (010) surface as indicated in experiments by Arvidson et al. (2004). Our measurements of position of thickest rim to the three principal axis show that the rim is dominantly positioned on the (010) surface (Table 3). Rims on neighbour grains are not always observed nor are bulges into neighbouring grain indicating that either fluid flow was minimised or that the coherency strain in the neighbour grain prevented growth. This indicates that the results dominantly show the preferred dissolution direction and that replacement starts inwards (icDP) since that’s the easiest direction i.e. towards the highest elastic constant (e.g. Lee et al. 1993).

Our observations confirm previous studies and suggestions (e.g. Heidelbach et al. 2000; Arvidson et al. 2004; Niedermeier et al. 2009; Hövelmann et al. 2010) that there is a crystallographic control on growth and dissolution directions in Pl feldspars namely in the <010> direction and along the (001) plane. There is therefore a resistant for chemically induced boundary migration in certain directions depending on the orientation of the neighbouring grains. However, here we have evaluated rim positions only in relation to the three principal
Physio-chemical processes in deforming mid crustal plag- rich rocks: The role of fluids.

Before discussing the influence of fluid on the active processes at mid crustal condition, it should be noted, that under the low/intermediate grade conditions, crystal plastic deformation of the initial Pl was not effective.

In our samples we see a direct relationship between phase distribution, i.e. monomineralic versus polymineralic areas, and chemical changes in Pl grains (Fig. 3a-b). Furthermore, high strain zones with increased number of small grains are predominately polymineralic and show significant amounts of asymmetric chemical zoning and related grain boundary migration and recrystallisation (Fig. 3c). Computer modelling by Ford et al. (2002) showed that (during compression) samples with differences in grain size and irregular grain shapes promoted significant grain rotations by grain boundary diffusion creep (DPC), while monomineralic samples with regular hexagonal grains showed no rotations. Accordingly, we suggest that strain localised in polymineralic areas as monomineralic areas could not accommodate strain sufficiently and little or no grain rotation occurred, hence no fluid pathways were produced. In contrast, in the polymineralic areas grain boundary diffusion and dissolution was enhanced at boundaries of unlike phases (Renard et al, 2001). In addition, the lack of coherence at these boundaries allowed grain boundary sliding to occur. Both processes resulted in physical grain rotations which assisted fluid influx along the grain boundaries and triple junctions. The presence of aqueous fluids is evidenced by hydrous phases such as Czo and Ms and by the fluid induced mechanisms. These hydrous phases are mostly found associated with amphibole rich horizons in polymineralic areas (along with Ttn and opaque minerals such as Ilm; Figs. 2d and 7d). These amphiboles show subgrain boundaries and a well developed CPO (Fig. 5e) consisting of large grains with a high aspect ratio (2.2). Plagioclase and less amounts of quartz are the dominating phases surrounding the amphiboles and they display random CPOs. This relationship with phases and CPOs is an indication that rigid amphiboles rotated in a softer matrix (e.g. Baratoux et al. 2005; Diaz Aspíroz et al. 2007) and produced voids and/ or open grain boundaries during dynamic wetting, i.e. creating fluid channels and high diffusivity pathways. These above features are also indicative for an open system.

This externally derived fluid had several effects:

a) since it was not in chemical equilibrium with the existing Pl it reacted and partially replaced Pl.,

b) at the same time it increased the effectiveness of dissolution and precipitation creep resulting in higher aspect ratios of grains and asymmetric chemical zonation rims and effective accommodation of grain boundary sliding

c) it helped to decrease the coherence i.e. friction along grain boundaries and thus enabled easy grain rotations allowing grain boundary sliding to be effective

d) it increased the mobility of grain boundaries enabling significant CI-SI-GBM and bulging recrystallisation

e) in areas of replacement hydrolytical weakening allowed some crystal plastic deformation to be active.

The link between physical processes such as grain rotations, grain boundary sliding and crystal plastic deformation and chemical processes such as replacement reactions and dissolution and precipitation is highly dependent on the influx of fluid, its composition and its continuous or limited availability. The fact that some Pl-rich horizons contain an abundance of Pl with zonation mixed with hydrous phases while some do not e.g. close to relict porphyroclast pressure shadows and horizons with few hornblende e.g. box (1) in Fig. 2d ) indicate that the fluid distribution is heterogeneous and enhanced by deformation. This interpretation is in line with previous work, which showed that a deformation-enhanced fluid distribution is important in promoting a change in deformation mechanisms, strength and bulk transport in Pl aggregates (Tullis et al., 1996). Furthermore, Reinecke et al. (2000) suggested that a heterogeneous distribution of CI-GBM in Calcite aggregates may be linked to a heterogeneous grain-scale fluid distribution. In addition, externally derived fluids have been shown to be common at mid crustal levels and are likely to play a significant role in the activity and rates of chemical and physical processes (e.g. Wintsch and Yi 2002; Putnis 2009).

Regional context of samples and their deformation and chemical reaction history

As outlined above, according to regional metamorphic studies, two main deformation events D1 and D2 can be distinguished in the area. The first major event D1 was initiated during terrane amalgamation at mid to lower crustal levels (Juil-Pedersen et al. 2007; van Gool et al. 2007). In our sample, this event can be directly linked to the main recrystallisation event forming Group I and II grains at higher T than during D2 and little fluid influx. It has been proposed by Nutman et al. (2007) that after D1, deformation continued including decompression and subsequent large scale folding and localized shearing. The observed Hüttlenlocher intergrowths in Group I and II recrystallised grains can be related to the proposed exhumation process. Following Grove et al. (1986) arguments, such exsolution features may indicate spinodal decomposition during regional metamorphism as the result of a pressure drop during the inferred initial exhumation during early stages of D2. The regional, large scale folding event (D2) is in our samples seen as the second
recrystallisation event with significant fluid influx. Both deformation conditions and fluid influx is in line with the regionally observed increased fluid flow and large scale shearing (Hollis 2005; van Gool 2007). During this event externally derived, reactive fluids together with differential stress induced DPC, GBS, icDP and strain and chemically induced GBM. Grain size reduction due to bulging recrystallisation of fluid enhanced fast migrating boundaries generated Group III grains. Intracrystalline deformation of Hbl during D2 are consistent with the regionally derived amphibolite facies conditions of D2 at 450°-600°C and 4-6 kbar (e.g. Biermann and van Roermund 1983).

Conclusions

This study shows that the deformation of plagioclase in an anorthosite-leucogabbro deformed during exhumation at wet amphibolite facies conditions (T ~ 550-620°C and P ~ 4.5-5.1 kbar) is strongly governed by the feedback between physical and chemical processes.

During deformation, external fluid influx is promoted by grain rotations caused by heterogeneities in grain size, mineral phases and grain shape during incipient dissolution precipitation creep (DPC). Thus, fluid presence and distribution is deformation enhanced. Several processes operate simultaneously and grain boundary sliding is accommodated by DPC and grain boundary migration. Grain boundary migration is faster in fluid present conditions and is both strain and chemically induced. Chemical induced grain boundary migration is driven by the disequilibrium of the incoming, externally derived fluid with the composition of bytownite plagioclase present in the rock. Furthermore, this disequilibrium causes solvent mediated phase transformations to occur, which transform the bytownite plagioclase to labradorite composition (An65). In low strain areas, interface-coupled dissolution and precipitation (icDP) and chemically induced grain boundary migration (CIGBM) are dominant, and possibly occurred in a two-front system, resulting in an enhanced rim growth rate. In high strain areas, grain boundary sliding and dissolution precipitation creep are dominant mechanisms, while GBM is still effective as it is both strain and chemically induced. The latter allowed bulging recrystallisation to be effective. Replacement by icDP is here active to a minor extent. Thus, DPC is coupled with CIGBM and icDP by enhancing fluid influx and therefore serves as a link between physical and chemical processes.

Furthermore, Pl (bytownite, An65) indicate a marked anisotropy with regard to reaction i.e. dissolution and coupled precipitation rates, where reaction is fastest along the (001) plane in the <010> direction i.e. on the (010) cleavage plane.

Acknowledgement

The Geological Survey of Denmark and Greenland (GEUS) is acknowledged for financing of fieldwork, logistics and thin sections. Knut and Alice Wallenberg foundation is acknowledge for funding the EBSD facility at the Department of Geological Sciences, Stockholm University. Marianne Ahlbom (Stockholm University) is acknowledged for helpful assistance with the SEM and EBSD analyses and José Godinho for introduction to and guidance during confocal profilometry measurements. We are grateful to the Nordic Mineralogical Network (Minnet) for partly financing the electron microprobe analyses (EPMA) and to Alfons Berger (University of Copenhagen) and Hans Harryson (Uppsala University) for assistance with the EPMA analyses.

References

in deformed-then-annealed material: Observations from experimentally deformed synthetic rocksalt. Tectonophysics 427:55-71


NaSi-CaAl in plagioclase. J Geophys Res 94:10662-10668