Metamorphic refinement of quartz under influence of fluids during exhumation with reference to the metamorphic/metasomatic evolution observed in amphibolites – a detailed field, microtectonic and geochemical study from the Bamble sector, South Norway

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Preface

The current PhD thesis is integrated in a larger project entitled "The value chain from mineral deposit to beneficiated product with emphasis on quartz". This thesis is dedicated to studies of quartz formed in a metamorphic environment with emphasis on the trace element evolution of quartz during prograde and retrograde recrystallisation processes. Quartz from quartzites and quartz veins from the Bamble sector was included in the study.

To understand the trace element behaviour in quartz in a metamorphic environment we had to address the more general issue of understanding the fate of quartz during multiple episodes of recrystallisation because we realised that not much was known regarding the behaviour of quartz in a complex shear zone environment such as the Bamble belt. Accordingly, the aim was enhanced to both document quartz purification and to understand more about the trace element behaviour of quartz in general in a metamorphic environment as a function of PT- X_{fluid} conditions. To place the quartz recrystallisation history and trace element evolution in a well constrained geological framework the study also include comprehensive studies of metamorphic petrology and fluid inclusions

Although the results of this thesis does show avenues to the genesis of high purity quartz, it is probably making more significant contributions to the importance of shearzone fluids and fluid-rock interaction processes, particularly in quartzites. The fluid evolution during cooling and exhumation of the Bamble sector is unravelled through fluid inclusion studies along with the construction of a new cooling and uplift path. Moreover the study of mineral equilibria in amphibolite demonstrates the importance of fluids on the composition of hydrous minerals and also suggests a genetic model for the formation of Fe-Cu deposits in the Bamble sector.

A vast amount of data was collected in connection with the thesis work. They are summarised in diagrams in each of the three papers, however, raw data were deliberately omitted from the thesis because of their voluminous character. An electronic file with raw data may be requested from the author or Rune B. Larsen.

Bjørn Eske Sørensen, Trondheim 2007

Oomenita	
Introduction	1
Background	1
Application of High Purity Quartz (HPQ)	3
Trace elements in quartz	3
Geological setting	6
Objectives of the project	10
Architecture of the thesis	12
Main results	13
Quartz recrystallisation during retrogression, implications for rheology and purification	13
Retrograde P-T-Xfluid evolution of the Bamble sector	18
Interaction between volatile bearing minerals and a coexisting fluid	20
Metasomatic evolution of the Bamble sector and formation ore deposits	22
Publications and presentations during PhD work	24
Acknowledgements	25
References	26
Paper 1: Fluid induced multistage recrystallisation microstructures in Quartzites and Quartz veins from th Bamble shear zone complex	e
Paper 2: The fluid evolution of the Froland area in the Bamble sector from peak P-T through cooling and uplif implications for retrograde mineral paragenesis and PT evolution of the Bamble sector	t:
Paper 3: Metasomatic evolution of the Froland amphiboli during cooling and uplift – textural observations and	ites

Introduction

Background

Application of High Purity Quartz (HPQ)

High purity quartz (HPQ) owes its applicability and high demand to current expansions in the communication industry and other actors in the high technology sector. Some agencies forecast a solid 40 % annual growth in the demand for high purity granular quartz and even moderate estimates predicts a >25 % annual increase. By far the largest proportion of HPQ comes from granitic pegmatite in the Spruce Pine district, North Carolina. The quality of quartz from Spruce Pine is steadily decreasing and, having an arid climate with limited water supplies, the processing of quartz is difficult and costly.

The high purity silica glass industries may be divided in to the semi-conductor industry that requires very high chemical purity of HPQ and the lighting and fibre optical industries that accepts somewhat higher concentrations of impurities yet require excellent melting behaviour of HPQ and primarily are concerned with minimal bubble formation in the silica glass melts.

With these requirements in mind, it appears that HPQ at any time should contain very low concentrations of structural impurities and in particular for the lighting and optical fibre industries must have very low contents of fluid inclusions that, due to expansion during melting, will generate bubbles in the silica glass melt.

Trace elements in quartz

Quartz is a framework silicate comprising SiO₄ tetrahedrons that are corner linked in a network. Quartz is the most common SiO₂ polymorph in metamorphic environments. In the quartz structure, tetrahedra of SiO₂ are linked together in spirals (e.g. Heaney, 1994). Spirals are paired in groups that are related by a two fold rotation axis parallel to the c-axis (e.g. Heaney, 1994). Together six spirals produce helixes surrounding open channels running parallel to the c-axis. β -quartz is hexagonal with 6-fold symmetry in the helixes, whereas they have 3-fold symmetry in the trigonal α -quartz (Heaney, 1994). The α -quartz structure is more compact than the β -quartz structure hence is less open to the incorporation of trace elements.

Trace elements in quartz divides into two groups; lattice bound and not lattice bound. The lattice bound trace elements are related to substitutions in the quartz lattice and occurs along with defect in the lattice that do not relate to trace elements: NBOHC (Non Bridging Oxygen Hole Centres) (Griscom, 1985) silanol groups (Weil, 1984) or peroxy radicals and linkages (Friebele et al., 1979).

Substitution for Si⁴⁺ is seldom in quartz because of the small crystal radii (CR¹) and high valence of Si⁴⁺ (0.40 Å Shannon, 1976). However trace amounts may be incorporated during crystal growth and recrystallisation in the cation site of quartz. The ionic potential (charge/ionic radius: Z/CR) and bonding type are the most important factors that control incorporation of trace elements. Al³⁺(CR=0.53 Å), Ga³⁺(CR=0.61 Å), Fe³⁺(CR=0.63 Å), Ge⁴⁺(CR=0.53 Å), Ti⁴⁺(CR=0.56 Å) and P⁵⁺(R=0.31 Å) were reported to substitute for Si⁴⁺ in quartz (see summary in Frondel (1962), Goetze et al.(2001) and Larsen et al.(2000). CR (CN=4) is from Shannon (1976).

Three main substitution modes govern the incorporation of lattice bound trace elements (e.g. Goetze et al., 2001 and Figure 1):

- 1) Single substitution. Corresponds to isoelectronic substitution of Si⁴⁺ by an other tetravalent cation, commonly Ti⁴⁺ or Ge⁴⁺
- Double substitution. Refers to AlPO₄ groups (Beck, 1949; Huttenlocher, 1935). Charge balance is maintained by direct replacement of two Si⁴⁺ atoms by one P⁵⁺ and one Al³⁺ cation.
- 3) Compensated substitution. Occurs when trivalent cations (Al³⁺, Fe³⁺) substitute for Si⁴⁺ to form [(Al, Fe)O₄/M⁺] centres, in which M⁺ represents a charge compensator alkali cation such as H⁺, Li⁺, Na⁺ or K⁺(Frondel, 1962; Goetze et al., 2004; Goetze et al., 2001; Mackey, 1963).

The small size of inter-atomic cavities in quartz prevents large cations from entering the lattice. The elasticity of the lattice hence the available space for trace element incorporation varies as a function of pressure and temperature. Trace elements substituting for Si in the structure are strongly confined to the lattice defects. Trace elements incorporated along the channels running parallel to the c-axis are more mobile, because of the relative weakness of pure ionic bonds compared to ionic-covalent bonds. Accordingly, their abundance may be sensitive to remobilisation processes (Larsen et al., 2004). This has been extensively documented in sweeping experiments (solid state electrolysis). Na⁺ and Li⁺ in channels and lattice defects related to compensated substitution of Si⁴⁺ by Al³⁺ is replaced by Al-OH or Al-hole centres, whereas larger alkali ions (e.g. K⁺) associated with compensated substitution of Al³⁺ for Si⁴⁺ appear to be less mobile, probably because they are too large to migrate along the channels (e.g. Armington, 1991).

Electron Paramagnetic Resonance (EPR) either alone or in combination with spectroscopic methods such as thermoluminescence (TL), cathodoluminescence (CL), infrared and atomic spectroscopy is the most efficient technique to identify point defects in quartz (Goetze and Ploetze, 1997; Goetze et al., 2001; Weil, 1984; Weil, 1993). Spectral CL-analysis in combination with spatially resolved trace element EPMA, SIMS or LA-ICP-MS analysis is an alternative technique to investigate and quantify point defects in quartz (Müller et al., 2003). Our study implement gray scale SEM-CL in combination with LA-ICP-MS and SEM-CL spectroscopy to quantify trace elements in quartz.

 $^{^{1}}$ CR = Crystal radii, states the actual size of the ion when the ion is tied in a lattice structure. The normal ionic radii in unrealistically large, because ions in the lattice share electrons and are partly drawn toward each other.

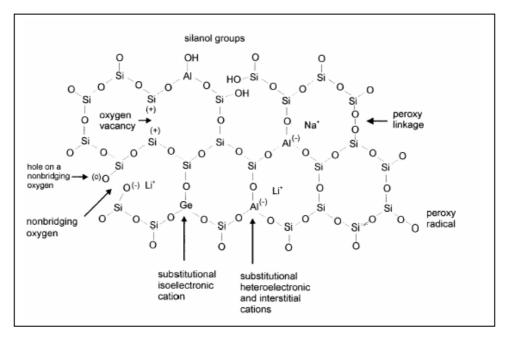


Figure 1: Schematic drawing of the quartz structure showing the most common intrinsic and extrinsic lattice defects. From Goetze et al. (2001). Note that the figure is highly schematic and that the quartz structure is drawn as a simple "ideal high quartz structure" projected along the c-axis as opposed to the true trigonal structure of low quartz.

Several studies document mobilisation of trace elements during recrystallisation. Larsen and co-workers (2004) documented sub solidus alteration of quartz leading to mobilisation of trace element in pegmatite quartz. Armington and Balascio (1984) documented that dislocation and trace element content of quartz was reduced through multiple recrystallisation events at conditions corresponding to the greenshist facies (Figure 2). Several SEM-CL studies document trace element mobilisation associated with textures related to sub solidus processes acting on magmatic quartz.(e.g. Jacamon, 2006; Larsen et al., 2004; Müller et al., 2002) and on vein quartz (Landtwing and Pettke, 2005; Van den Kerkhof et al., 2004).

There is no general correlation between the hand-specimen colour of quartz and the trace element content. Clear apparently inclusion free quartz may be rich in trace elements whereas smoky quartz may have low trace elements contents i.e. <1 ppm. This is because a very small amount of colour centre related defects results in strong colouration of quartz. As an example the smoky colour in smoky quartz is due to ionising radiation from neighbouring minerals (Larsen et al., 1998) and minute concentrations of structurally bound elements in colour centres in the quartz lattice (Larsen et al., 2004). However, other colour variations are signs of high trace element abundance (Larsen et al., 2004). Amethyst owes its purple colour to structurally bound Fe (e.g. Aines and Rossman, 1986; Cohen and Makar, 1984; Cohen and Makar, 1985; Hassan and Cohen, 1974; Lehmann, 1975). Several explanations exist for the colour of rose quartz; structurally bound Fe and Ti (e.g.

Cohen and Makar, 1984; Cohen and Makar, 1985; Hassan and Cohen, 1974), by Al-P substitutions (Maschmeyer and Lehmann, 1983) or due to inclusions of microscopic rose coloured inclusions of dumortierite (e.g. Applin and Hicks, 1987; Goreva et al., 2001). The latter probably account for most occurrences of massive rose quartz (Goreva et al., 2001) and also seem to be the explanation in our study (paper 1, Sørensen and Larsen, 2007a). Most occurrences of blue quartz are explained by light scattering by tiny inclusions (Jayraman, 1939), which are commonly rutile (Postelmann, 1937; Vultée and Lietz, 1956) or ilmenite (Zolensky et al., 1988). The presence of tiny rutile needles explains the blue colour of quartz reported in our study.

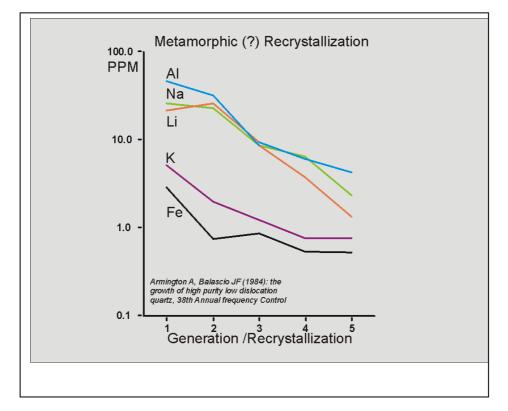


Figure 2: Unpublished experimental data by Armington and Balascio ((Armington and Balascio, 1984)) displaying the effect of multiple recrystallisation events on trace element content of quartz. Modified from Armington (1984). Courtesy Rune B. Larsen.

Geological setting

The rocks included in this study comprise quartzites, amphibolites and calcsilicate lithologies from the Froland area, Bamble sector, South Norway (Figure 3). The Bamble sector is part of the South West Scandinavian domain (SSD) that is divided into a number of segments bounded by regional shear zones and thrusts that formed during the Sveconorwegian orogeny (Ahall and Gower, 1997; Bingen et al., 2002). The Bamble sector is interpreted as the mid-crustal part of a volcanic arc complex (Knudsen and Andersen, 1999). The Bamble sector was accreted to the Telemark terrain during an early Sveconorwegian (1,15-1,10 Ga) event (Bingen et al., 2002; 2001).

Structurally, the Bamble sector comprises a SW to NE linear deformation belt with onshore dimensions of 20-40 km times 140-150 km (Figure 1).

Supracrustal lithologies of amphibolite to granulite facies metasedimentary and metavolcanic rocks dominate the belt and is intruded by numerous mafic stocks and dykes as well as granitiod plutons and pegmatites (Starmer, 1991; Starmer, 1993; Starmer, 1996). The Supracrustal suite was deposited in two inter-orogenic periods of the Gothian orogeny at 1,85-1,7 Ga (Knudsen et al., 1997) and 1,5-1,2 Ga (Bingen et al., 1998) respectively. Recent studies confirmed Sveconorwegian high-grade metamorphic overprint throughout the Bamble sector (Bingen et al., 1998; Bingen and Van-Breemen, 1998; Cosca et al., 1998; Johansson and Kullerud, 1993; Knudsen, 1996; Kullerud and Machado, 1991; Kullerud and Dahlgren, 1993).

Generally, the foliation trends NE-SW in the Bamble belt (Falkum and Petersen, 1980). Based on structural trends, the Bamble sector is divided in two main domains (Falkum and Petersen, 1980):

-The eastern sub-region (main zone) in the coastal area is dominated by intense shear folding with a NE-orientation, most other directions being rotated into parallelism by a dextral strike slip regime. The structural pattern is dominated by tight isoclinal folds and well developed mineral lineations. Older structures are preserved in rigid bodies.

- *The Northern border* constituting a transitional zone 10-15 km wide, is characterized by moderate shear folding where NE-SW trending structures of the Bamble sector are superimposed on former NW-SE trending folds of the Setesdal gneisses. The transition zone commonly shows interference between the two structural events.

The Bamble sector features well preserved granulite facies rocks and distinctive metamorphic zones gradually going from amphibolite facies in north to granulite facies along the coast. Peak metamorphic conditions are well constrained, both in terms of P, T and fluid evolution.

Traditionally the Bamble sector is divided into four coast parallel regions labelled A-D (Field et al., 1980; Lamb et al., 1986; Smalley et al., 1983):

A: Amphibolite facies, as defined by absence of metamorphic orthopyroxene in metabasite.

B: Granulite facies; primarily comprising acid to intermediate host gneisses with a broadly granitic mineralogy, separated from A by an orthopyroxene isograde in metabasites.

C: First occurrence of charnokitic gneiss (K-feldspar, plagioclase, orthopyroxene and quartz).

D: Region within the granulite facies area with low concentrations of potassium and low concentration of LILE, REE and chalcophile elements, especially Au, Sb, As and S.

Earlier studies of the Bamble sector placed the area of highest temperature in the coastal region near Arendal and Tromøy in region D which was thought to be LILE

depleted during peak metamorphism. However recent studies imply that low LILE concentration reflects the origin of the mafic gneisses rather than granulite facies depletion (Knudsen and Andersen, 1999). Furthermore, geothermobarometry show that the temperature in zones C and D are comparable (Harlov, 1992; Harlov, 2000a; Knudsen and Lidwin, 1996; Nijland and Maijer, 1993). Accordingly, zone D is not a separate metamorphic zone (Harlov, 2000b). Geothermobarometry of mineral equilibria imply that the highest temperatures probably were situated inland in a NW-SE oriented thermal dome with peak T at 830°C in the granulite facies area (Zones B and C) and peak T=750-700°C in the so called amphibolite facies area (zone A) (Nijland and Maijer, 1993). Obviously, given these temperatures the entire region was actually exposed to granulite facies metamorphism and the "amphibolite facies area" is a relic name from previous studies.

Metamorphic fluids developed from pure $CO_2 + N_2 \pm CH_4$ inclusions in the granulite facies to mixed H₂O-CO₂ fluids in the amphibolite facies (Touret, 1971; Touret, 1972; Touret, 1985). Some authors suggest a magmatic origin of the CO₂ rich fluids (Knudsen and Lidwin, 1996; Van den Kerkhof et al., 1994). The presence of CO₂ rich fluids during peak granulite facies metamorphism is confirmed by titaniferrous magnetite-ilmenite thermometry and tintaniferous magnetite –ilmenite-orthopyroxene-quartz oxygen barometry, implying that the stable COH-fluid phase at LOGfO₂ = -11 to -14 estimated for the peak PT-conditions (800°C and 7.5 kbar) is CO₂ for both region C and D (Harlov, 2000b).

Given that the structures of the Setesdal district are rotated into the foliations of the Bamble belt, it is inferred that the structures in the Bamble belt comprise the youngest structural event in the evolution of the South Norwegian basement. Following the strike-slip deformation, the Bamble sector was thrust on top of the Setesdal sector. In many places, the main thrust zone follows the Porsgrund Kristiansand fault, but thrusts are also identified to the east of the fault (e.g Touret, 1968). Thrusting probably began in epidote-amphibolite facies and progressed through lower greenshist facies as exhumation proceeded (e.g Touret, 1968). Finally extensional tectonics depressed the SE Bamble block. Evidence of thrusting is indisputable, although the kinematic evolution during thrusting is poorly understood and mostly inferred from, mapping and large scale observation by Starmer (1987; 1991; 1993; 1996) and (e.g. Henderson and Ihlen, 2004).

Thrust related greenshist facies deformation generated quartz mylonites (Morton et al., 1970), mainly comprising quartz and muscovite (Morton et al., 1970). Grain size reduction in the mylonites is considerable i.e. from cm-size to microns-size. Thrust related deformation terminated with brittle deformation, cataclasites and brecciation as exhumation proceeded and the temperatures lowered (e.g Touret, 1968).

Recently, Henderson & Ihlen (2004) documented ductile deformation of synkinematic pegmatites. They infer that thrust related deformation in the Bamble sector was incremental with long periods of ductile deformation interrupted by short periods of high strain rate leading to fracturing and injection of the syntectonic pegmatites.

Using the retrograde P-T path of Nijland et al. (1993b) the uplift and cooling rates were constrained to \sim 3°-8°C/Ma at 725-550°C, and cooling rates of \sim 2°-

4°C/Ma in the interval 550-300°C (Cosca et al., 1998). Initial cooling of the Bamble sector approached isobaric conditions (dP/dT=2bars/°C) from 725-550°C, but was followed by near isothermal uplift (dP/dT=30bars/°C) in the temperature interval 550-300°C (Cosca et al., 1998). Following the relatively fast exhumation path, the Bamble sector experienced near isobaric cooling from 300°C and onwards (Cosca et al., 1998). The very low temperature (<300°C) path is constrained by late prehnite and pumpelyite together with fluid inclusion data (Touret and Olsen, 1985).

Amphibolites are common in the Bamble sector. They feature four expressions (Nijland et al., 1993a):

- 1. Concordant amphibolite bands intercalated with gneisses (Brøgger, 1934; Starmer, 1985).
- 2. Entirely metamorphosed but discordant plutons like the Vimme amphibolite (Nijland, 1989)
- 3. Partly amphibolitised "hyperites" with cores of coronitic gabro, which are increasingly amphibolitised towards their margins (Brickwood and Craig, 1987; Brøgger, 1934; Bugge, 1940).

Nijland (1995) studied the geochemistry of the amphibolites in the Bamble sector and documented that the majority are of an igneous origin. The amphibolites are commonly subjected to significant metasomatic processes affecting the mineralogy (e.g. (Brøgger, 1934; Frodesen, 1968).

The Bamble sector contains abundant coarse grained quartzites that experienced Sweconorwegian high grade metamorphism. This study concerns quartzites from the Nidelva Quartzite Complex close to Blakstad. Static high grade textures with cm-sized quartz grains formed at peak conditions (750°C/6-7 kbar (Nijland and Maijer, 1993)) and are cut by younger localized high-grade shear zones with mm-sized amoeboid quartz grains. Localized retrogression related to the formation of white mica occurs throughout the area, typically related to mm-thin fault zones with adjacent SGR (subgrain rotation recrystallisation) causing a reduction in grain size (50-200 microns).

There are several compositional and textural types including very pure and coarse-grained quartzite, quartzo-feldspatic gneiss and nodular gneiss/quartzite. The quartzose rocks contain variable amounts of tourmaline. Layers of stratabound tourmaline are locally observed (Nijland et al., 1993c). Black tourmaline frequently occur on the more Al-rich cleavage planes ((Nijland et al., 1993c), this study). Redbrown transparent tourmaline (field colour, orange-red brown in thin section, Dravitic) occurs in layers and lenses in quartz microcline and oligoclase and biotite at Grendal Tjern (Nijland et al., 1993c) and at Trevann (This study). Black tourmaline (field colour, green-brown pleocroic in thin section Schorl-Dravite) also occur as reaction zones bordering quartz veins in quartzites together with biotite and muscovite. In addition black (Schorl rich) and brown (Drawite rich) tourmaline together with biotite defines the foliation in some mylonitic gneisses. Occasionally Rare sedimentary structures occur in the Nidelva Quartzite Complex (NQC), and well documented cases of cross beddings, mud cracks, ripple marks and strongly deformed meta-conglomerates imply a sedimentary origin (Nijland et al., 1993c).

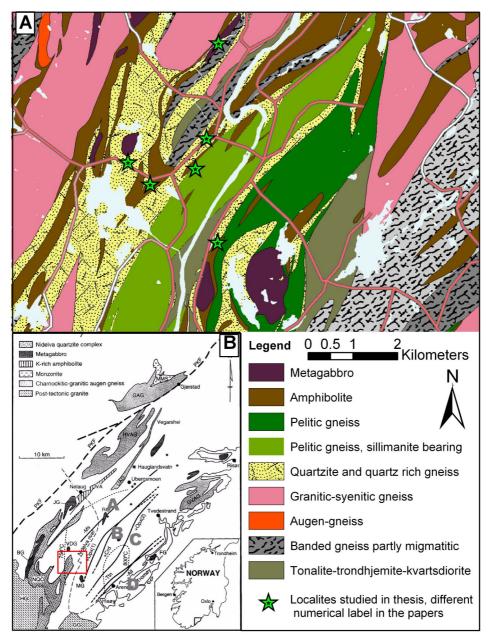


Figure 3: Geological maps. A) Detailed map of the investigated area. Modified from Geological Survey of Norway. N-50 berggrunns kart 16123 Nelaug and 16114 Arendal. Geographic data (roads, lakes and rivers) are added for easy orientation (source: www.geonorge.no). B) Overview map of the Bamble sector displaying the most important rock units (see legend on map). Insert show the position of the Bamble Sector in South Norway. Red square denotes the position of the study area shown in A. From Nijland et al. (1998). Also shown in A are the metamorphic zones in the Bamble sector.

Objectives of the project

The aim of this thesis is to study the evolution of quartz from high T amphibolite facies conditions during multi stage retrogression induced by infiltrating fluids. The high grade quartzites are coarse-grained with cm sized quartz grains. They owe their blue colour to microscopic rutile needles. During the fist field season it was documented that the quartzites featured bleached zones related to recrystallisation along narrow fault zones (mm-dm wide) formed during retrogression.

The results from this study were not expected to directly lead to the discovery of large resources of pure quartz. Instead we focussed on processes underlying quartz recrystallisation and the mobility of trace elements in association with metamorphic recrystallisation. From the fact that several studies had already documented trace element mobilisation through recrystallisation of quartz, we expected that the trace element concentration in the high grade blue quartz, was also lowered by retrograde metamorphic processes.

It was soon realised that the metasomatic processes in quartzites were much more complex than previously thought. Therefore, the main challenge was not to show that trace elements could be mobilised during retrogression, but how it happened. To pin down the important processes it was realised that one ought to improve our understanding of the relation between metamorphic/metasomatic processes and the observed quartz recrystallisation.

Accordingly, three main objectives crystallized from this realization:

1: Document chronology and spatial relationships between quartz recrystallisation in veins, quartzites and quartz rich gneisses in the Froland area.

2: Document how the quartz chemistry related to recrystallisation events.

3: Understand the observed quartz recrystallisation and purification in the context of the regional $P-T-X_{fluid}$ and tectonic evolution.

Although, quartz is the principal target of the present study, it is impossible to study and interpret the chemical alterations of quartz without also including chemical changes of other rock types and minerals to constrain the physiochemical framework.

As the quartzites are intimately associated with amphibolite/metagabbro that underwent the same metamorphic history it was natural to include the amphibolites in constraining the P-T-X conditions. Not least, because the amphibolites were intersected by and altered in association with the quartz veins.

Fluids are imperative in alteration processes and therefore, a fluid inclusion study was included as an important part of the thesis work. Main focus was on fluids that could be related to recrystallisation events in quartz. Calc-silicate rocks that were observed in close association with intense alteration of amphibolites, quartz veins and quartz rich gneisses were included as a supplement to the fluid inclusion study because volatile dependant mineral equilibria in calc-silicates are highly sensitive to changes in P-T and fluid composition.

Based on the defined goals of the project, it was decided to combine a SEM-CL study with Laser ablation induced coupled mass spectroscopy (LA-ICP-MS) study to document the chemical evolution of quartz. To define the physiochemical framework underlying the observed quartz recrystallisation, a fluid inclusion study and metamorphic petrology in amphibolites and calc-silicate rocks in which mineral equilibria are sensitive to fluid composition was also initiated.

Architecture of the thesis

The thesis is comprised of three papers that are intended for journal publication. The version provided in the thesis is a bit longer than they will be at final publication. However it was the desire to include some additional documentation that may be omitted in the final versions. Each paper in the manuscript is written as an independent paper. Because all the papers are strongly tied together there is significant repetition partly because the documentation and interpretation of the results in on paper depends on the results documented in another paper. The essence of the three papers are summarised below:

Paper 1:

Sørensen, B.E. and Larsen R.B. 2007. "Fluid induced multistage recrystallisation microstructures in Quartzites and Quartz veins from the Bamble shear zone complex"

Paper 1 deduces basic principles of infiltration, physiochemical alteration processes and deformation mechanisms in quartzites and in quartz veins from the Froland area, the Bamble sector. SEM-CL is used to define generations of recrystallised quartz. A progressive quartz purification process ending with high purity quartz through recrystallisation is documented through LA-ICP-MS. The study demonstrates how fluids provokes recrystallisation and trace element mobilisation from the quartz lattice and at fluid-absent conditions, quartz is resistant to retrograde recrystallization hence preserving its early high grade metamorphic trace element signature. Retrograde fluid flow is preserved in fluid channel textures intersecting quartz and documented by SEM-CL images as well as changes in the trace element distribution. Quartz recrystallisation is associated with metasomatic processes in the quartzites such as for example the replacement of ilmenite by rutile and replacement of biotite by muscovite. The strong focus of fluid flow along narrow pathways intersecting the quartzites generates mm-scale differences in the rheological properties of the quartz grains with increased ductility and recovery in recrystallised grains. Therefore, the study demonstrates a strong coupling between strain softening, fluid flow and mass transfer in shearzones in quartz rich rocks.

Paper 2:

Sørensen, B.E. and Larsen R.B. 2007. "The fluid evolution of the Froland area in the Bamble sector from peak P-T through cooling and uplift: implications for retrograde mineral paragenesis and PT evolution of the Bamble sector"

Paper 2 comprise a detailed characterisation of the fluid evolution during cooling and uplift though fluid inclusion studies compared with thermodynamic modelling of calc-silicate volatile dependant mineral equilibria. Fluids are documented to be brines throughout the cooling and uplift path. The paper also includes a detailed discussion of the chemical properties of the aggressive brines and their implications for mineral equilibria during cooling and exhumation. The study also document which fluids that were in equilibrium with quartz recrystallisation and purification. The study focussed on fluids that could be related to the quartz SEM-CL textures documented in Paper 1. Had the main purpose of this thesis been to understand calc-silicate equilibria in the Bamble sector fluid inclusions in the calcsilicates would have been in the focus.

Paper 3:

Sørensen, B.E, Larsen R.B. and Austrheim, H. 2007. "Metasomatic evolution of the Froland amphibolites during cooling and uplift – textural observations and geochemical evolution of hydrous minerals"

Paper 3 comprises a detailed study of alteration processes in amphibolites. The study focuses on the chemistry of amphiboles as a function P, T and the composition of the co-existing fluids. Amphibole and biotite undergo a co-genetic evolution both becoming more Mg-rich during cooling and exhumation. The chemical changes in biotite and amphibole reflects the interaction with the brines present throughout cooling and uplift. A relationship between element depletion in amphibolites and formation of Fe-Cu sulphides is observed.

As earlier stated the papers are strongly tied together. In conjunction with each other they deduce the metamorphic and metasomatic evolution of the area and put the observed quartz recrystallisation and purification into a physiochemical framework. The locality numbering varies between the papers because samples from different localities are included in each paper, accordingly a locality termed"1" in one of the papers may have a different number in the next paper. This was done because the papers are supposed to be independent research papers and the numbering logically relate to the context of the single papers and not the thesis as a whole.

In the next section the most important results that are deduced from the three papers are summarised.

Main results

Quartz recrystallisation during retrogression, implications for rheology and purification

Four main quartz types are documented in quartzites, quartz veins and quartz in leocosomes through SEM-CL (Paper 1, Sørensen and Larsen, 2007a) (Figure 4):

Qz1: Bright islands demarcated by darker cracks. Typically they are partially luminescence quenched. The bright islands in Qz1 relate to the high grade

history of the area, but the cracking relates to retrogression and formation of Qz2 (next). Qz1 is richer in B, Al and Ti than the other types.

- Qz2: Light grey, sometimes featuring weak oscillatory zonation. Qz2 has brighter cores and darker rims approaching the luminescence of Qz3. The formation of the island texture in Qz1 and Qz2 are probably related, since Qz2 and the cracks in Qz1 has the same luminescence. Qz2 has low Al contents (<50 ppm) but variable Ti contents in quartz veins in amphibolite (210-10 ppm) due to inclusions of rutile needles and more consistent values in quartzites (peak value 32 ppm).
- Qz3: Dark grey diffuse fluid channel texture, which follows grain boundaries or intersects grains. Qz3 relates to alteration of biotite to muscovite and SGR (Sub-Grain rotation Recrystallisation) in narrow fault zones. Qz3 has Ti< 5 ppm and Al contents below 10 ppm (≈LOD) and low B content (paper1, Sørensen and Larsen, 2007a). Therefore, the recrystallisation path documented by SEM-CL, lead to the formation of high purity quartz, represented by Qz3.
- Qz4. Narrow cracks and pods of black quartz, intersecting the other types. Trace elements were not measured because Qz4 was too fine-grained

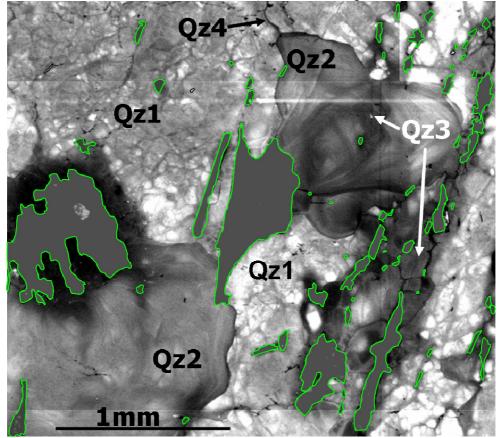


Figure 4: Definition of quartz types. SEM-CL image displays mica and quartz. Mica grains are given a green outline and uniform grey colour to enhance the quartz textures comprised by quartz types Qz1, Qz2, Qz3 and Qz4. See text for discussion.

The complex textures in quartz are explained by to major pulses of fluid in a genetic model related to deformation processes (Figure 5):

- 1. Homogeneous trace element rich quartz forms at high grade conditions under relatively dry conditions.
- 2. Introduction of aqueous fluids under differential stress induced brecciation. Quartz dissolved during brecciation precipitates as Qz2, Qz1 is the brecciated old grains. Fluid inclusion studies (paper 2 Sørensen and Larsen, 2007b) document that Qz2 formed with a mixture of low salinity CO₂-rich H₂O-CO₂ and H₂O-CO₂-NaCl-KCl brines with eutectic salinity (FIA2 see next section) . Qz2 coexist with rutile and rutile quartz thermometry (Wark and Watson, 2006) on the typical Ti content in Qz2 in quartzites gives a formation temperature of 626°C in agreement with interpretation made from phase equilibria in calc-silicate rocks for the early stages of retrogression at 7kb, 626-640°C (Paper 2, Sørensen and Larsen, 2007b). Thus Qz2 formed during isobaric cooling of the Bamble sector. This agrees well with the decussate texture (static) in the alteration assemblages related to Qz2-rich quartz veins intersecting amphibolites (paper1, Sørensen and Larsen, 2007a).
- Renewed deformation induces cracking. Infiltrating aqueous fluids move 3. along the cracks causing recrystallisation (Qz3), but also promoting crack mobility. The recrystallised quartz (Qz3) behaves more plastic than Qz1 and Qz2 and deform by SGR (subgrain rotation recrystallisation). Continuous fluid flow through the more fine-grained Qz3 domains increase recovery rates and reduce strain hardening. Crack propagation and recrystallisation still continue and the amount of Oz3 increase. Fluid composition in equilibrium with Oz3 is approximated by .the H₂O-NaCl-CaCl₂ system with 25 wt% NaCl and 6 wt% CaCl₂ (FIA3)(paper 2, Sørensen and Larsen, 2007b). Textural observations demonstrate that not only was the quartz purified from structurally incorporated trace elements during the influx in FIA3, but rutile needles were also removed providing quartz that was also pure on the bulk scale (paper 2, Sørensen and Larsen, 2007b). The observation that Qz3 formed in relation with thrust related deformation in combination with the isochore of the fluid inclusions in Qz3 suggest formation conditions at 300-400°C, 4-6 kb. Exhumation occurred near the brittle-ductile transition as also suggested by the mix of plastic and cataclastic textures (paper 1, Sørensen and Larsen, 2007a). Qz1 experienced considerable strain hardening due to accumulation of dislocations as evidenced by increased SEM-intensity towards deformation zones comprising Qz3 (paper 1, Sørensen and Larsen, 2007a), see Figure 4.

The relation between fluid infiltration, recrystallisation and change in rheology of quartz is supported by experiment in which the strength of quartz is an order of magnitude lower at water saturated than at dry conditions in experiments (e.g. Kronenberg, 1994). However, we suggest that other structural properties of the quartz may be equally as important as H_2O related defects. The presence of trace elements and other defects in the quartz structure may serve as obstacles for dislocation moves during deformation hence decrease the efficiency of both dislocation climb (recovery) and dislocation glide (plastic slip)

Grain boundary geometry is affected by the different defect structure of the quartz types. GBAR (Grain Bounday Area Reduction) facilitated straight boundaries and triple junctions between Qz2 grains whereas Qz2-Qz1 boundaries are lobate-interlobate with textures documenting consumption of Qz1 by Qz2 during GBM (high temperature Grain Boundary migration) (paper 1, Sørensen and Larsen, 2007a). The possibility exists that SEM-CL could be a vital tool to improve the understanding of the little understood GBM process in quartz tectonites (paper 1, Sørensen and Larsen, 2007a). In addition it is suspected that the trace elements may also contribute to the grain boundary migration processes.

Our results also demonstrate that quartz trace elements not only are structurally incorporated, but also exist as microscopic inclusions (paper 1, Sørensen and Larsen, 2007a). A common example is rutile needles that are common in quartz types Qz1 and Qz2. They occur at two scales: in Qz1 they are comprised by crystallographically oriented needles only visible at 500 times magnification whereas in Qz2 are represented by coarser needles visible at 100 times magnification. In Qz2 in quartz veins in amphibolite the rutile needles are crystallographically oriented. The needles in Qz2 are inferred to have formed as intergrowths, whereas the needles in Qz1 are interpreted as exsolutions. The presence of rutile needles in Oz2 affects the measured Ti content, giving a wide Ti range in Qz2 in amphibolite, where the needles were to abundant to be completely avoided. In Qz2 in quartzites, rutile needles were less abundant and could be avoided. This resulted in a Systematic Ti content characterised by a peak value at 32 ppm. The peak is asymmetric with a shoulder towards lower values probably reflecting partial recrystallisation towards Qz3. We did not find systematic variations in the Al content of guartz although high values measured during statistical analysis reveal that all quartz types have peaks close to the detection limit at 10 ppm. High values are inferred to be a result of sub microscopic inclusions of dumortierite Al_{6.5-7}(BO₃)(SiO₄)₃(O, OH)₃ as suggested by a strong correlation between B and Al. B content also reflect dumortierite inclusions. Qz3 has trace element contents close to or below the detection limits i.e. it has a very well defined chemical signature. In addition Qz3 almost has the same chemistry in both amphibolite and quartz veins and in quartz-muscovite veins, except for phosphorous which apparently is higher in the quartz-scapolite veins than in the quartzites.

The generally low trace element contents in Qz3 reflect quartz that is low in both trace elements associated with micro inclusions and structurally incorporated trace elements. The fine grain size of Qz3 and the localised nature of retrograde recrystallisation pose a challenge to the industrial applications because of the demand of bulk qualities. Three options are possible for the applications of quartz purified through metamorphic processes:

1: Quartz with a quality which was already close to the industrial standards, such as pegmatite quartz may be further refined through metamorphic processes.

2: Fine grained quartz bearing rocks with quartz of good quality may be crushed down and the quartz may be separated. This procedure requires aggregation after mineral separation. No technology is currently available for this at a commercial scale. 3: Multistage pervasive greenshist alteration under fluid saturated conditions may provide more homogeneous quartz qualities. Because fluids are expelled during high grade metamorphism and only locally reintroduced during retrogression quartz recrystallisation only occurs at localised scale. Prograde metamorphism of fluid saturated rocks to the greenshist grade is more promising in providing an environment in which fluids were constantly present facilitating more homogeneous quartz recrystallisation.

Fluid composition and growth rate may impose a control on the quartz chemistry. This study demonstrates that H₂O rich fluids facilitated the destabilisation of rutile thus preventing rutile quartz intergrowth. We do not report systematics in the structurally incorporated Al. In our study trace elements in quartz systematically decrease with decreasing temperature. This however, is not always the case because fluid properties impose an important control on the composition of quartz. As an example Al will be higher in quartz formed with a high pH fluid because of the association of Al with OH groups and the Al concentration in guartz will also be function of the Al-content of the fluid(Miyoshi et al., 2005). Studies of magmatic quartz display similar results suggesting that Al is buffered by the Al in the quartz forming environment (Jacamon and Larsen in (Jacamon, 2006)). Thus the trace elements cannot be directly associated with variations in PT-conditions. In our case a drop in PT conditions is probably responsible for the progressive drop in the Ti content of quartz during cooling and exhumation. This is in good agreement with recent experimental calibrations which predicts that the Ti content of quartz in equilibrium with rutile decreases with temperature (Wark and Watson, 2006).

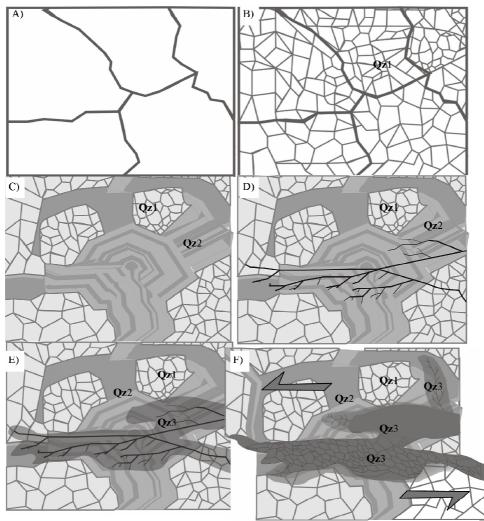


Figure 5: Pattern of recrystallisation as revealed by SEM-CL and optical microscopy. A) Homogeneous quartz at high grade conditions. B) Introduction of aqueous fluids under differential stress induces brecciation. C) Quartz dissolved during brecciation precipitates as Qz2, Qz1 is the brecciated old grains. D) Renewed deformation induce cracking E) Infiltrating aqueous fluids move along the cracks causing recrystallisation (Qz3), but also promoting crack mobility F) The recrystallised quartz (Qz3) behaves more plastic than Qz1 and Qz2 and deform by SGR (subgrain rotation recrystallisation). Continuous fluid flow through the more fine-grained Qz3 domains increase recovery rates and reduce strain hardening. Crack propagation and recrystallisation still continue and the amount of Qz3 increase.

Retrograde P-T-X_{fluid} evolution of the Bamble sector

Fluid inclusion studies document a high salinity of about 30 wt% NaCl equivalent throughout cooling and uplift by four fluid inclusion assemblages (paper 2, Sørensen and Larsen, 2007b):

FIA1. Found in quartz (Qz1) in garnet quartz symplectites, intersecting garnet amphibolite. Texturally correlated with high grade metamorphism of the area and comprising nearly pure CO_2 -fluids co-existing with eutectic melts formed by partial melting of amphibolite. In agreement with studies of Fe-Ti oxides in the granulite facies area around Tromøy (2000b), CO_2 is the stable carbonic species at the ambient oxygen fugacities.

FIA2. Found in quartz (Qz2) in en echelon veins intersecting amphibolite. The earliest retrograde fluid and comprise mixtures of two fluid types: 1) low salinity CO_2 -rich H_2O-CO_2 fluids, 2) H_2O-CO_2 -NaCl-KCl brines with near eutectic compositions and low in CO_2 . Thermodynamic modelling does not allow type 1 and 2 inclusions to be the result of in situ phase separation. Rather they represent fluid mixing of fluids derived from separate reservoirs.

FIA3. Found in recrystallised quartz (Qz3) in quartz-scapolite veins and in quartzbiotite-tourmaline gneiss in zones where biotite is partly replaced by chlorite and muscovite. Comprise LVS inclusions of aqueous brines and no carbonic fluids. The most important salts are NaCl (average 25 wt %) and CaCl₂ (average 6 wt%). The salinity is near constant and LV to L homogenisation occurs in a narrow range around 129 °C altogether giving dense brines following a steeply inclined isochore. FIA4. Primary LV inclusions found in growth zones in calcite and in epidote in vug assemblages in calc-silicate rock. Comprises aqueous CaCl₂ (31-36 wt%) brines with no carbonic fluids. The degree of fill is high giving dense fluids following a steeply inclined isochore in P-T space. The final melting of antarcticite varies systematically along growth zones in calcite. Epidote grains are zoned with Xcz (71) in cores and Xcz(65) in rims. Amphibole display similar evolution with actinolite replacing tremolite in a fracture pattern recognised in backscatter images. FIA4 Fluid inclusions are only found in epidote cores. Fluid inclusions in the epidote cores correlate with fluid inclusions with the higher antarcticite melting temperatures in calcite, and with higher initial melting temperatures.

The salinity of the fluids has significant effects on the PT-position of dehydration and decarbonation reactions and was accounted for in phase diagram calculations of calc-silicate rocks observed in this study (paper 2, Sørensen and Larsen, 2007b) and in assemblages reported by Nijland and co-workers (1993b) using PERPLEX (Connolly, 1990; Connolly and Petrini, 2002).

The interpretation of the constructed phase diagrams lead to a redefinition of the cooling and uplift PT- X_{fluid} path of the Froland area (paper 2, Sørensen and Larsen, 2007b) (Figure 6). The retrograde fluids may partially be superimposed upon the PT-evolution of the Froland area (Figure 6). More details in (Sørensen and Larsen, 2007b, paper 2).

In summary, the cooling and uplift path begins by simultaneous formation of tremolite + sanidine and tremolite + sanidine + calcite assemblages at c. $626-636^{\circ}C$ and 7 kb (Figure 6). The next stage agree with MII (ky + chl + ms) and MIII (ma +crn) of (Nijland et al., 1993b) (Figure 6). The pressure is uncertain although a path may be extended from this stage to the isochore of FIA3. Because the fluid inclusions in FIA3 are well preserved showing no evidence of post entrapment modification the exhumation path can not deviate more than 2 kb from the FIA3 isochore (Figure 6). The last part of the cooling and exhumation path is constrained by MV at 2-3 kb and 175-280°C (Nijland et al., 1993b; Touret, 1985) The PT-path

preserves the main characteristics of the path published by Nijland et al.(1993b), but the uplift is shifted 100°C toward lower temperatures and is in better agreement with the dominance of cataclastic microstructures in thrust related structures. A shift between potassic and sodic-calcic alteration occurred between FIA2 and FIA3. The Shift between MII and MIII of Nijland et al.(1993b) probably correlate with the shift in alteration types (Figure 6).

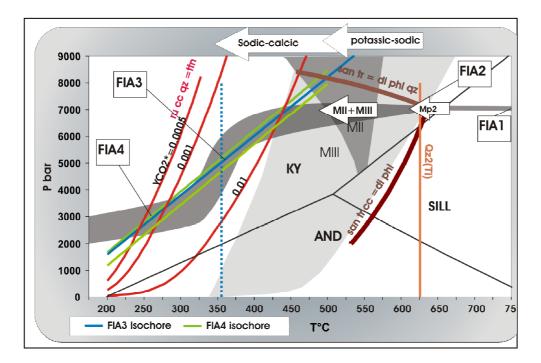


Figure 6: Tentative PT-Xfluid path of the study area, with possible implication for the uplift path of the Bamble sector. The PT-X_{fluid} path is assembled using a combination of mineral paragenetic and fluid inclusions data. Because fluid inclusions and mineral parageneses that are simple enough to be portrayed quantitatively in PT-space are not always present in "real life" the PT-path rely on textural correlations between assemblages in one rock type and fluid inclusions found in other rock types. Arrows on the top of the diagram indicate condition when alteration changed from potassic-sodic to sodic-calcic. From Sørensen (2007b, paper 2). For a more detailed discussion of the derivation of the PT-path see Sørensen (2007b, paper 2). Reactions are written such that the high temperature assemblage is to the right of the = sign. YCO2* denote the CO₂ content compared to H₂O in a fluid with 30 wt% NaCl relative to H₂O.

Interaction between volatile bearing minerals and a coexisting fluid

Paper 3 (Sørensen et al., 2007) document the complex interaction between hydrous minerals and a brine fluid during cooling and exhumation. Primary focus is on the chemistry of amphiboles, but chemistry of apatite, biotite and scapolite is also included.

Based on field and thin section observations the alteration of the amphibolites divides into three main alteration stages: Alt1 potassic alteration with biotite stable, Alt2 potassic alteration with K-feldspar stabilised over biotite and Alt3 scapolitisation. The most commonly observed alteration comprises overgrowth rims on amphibole associated with the introduction of biotite. The amphibole rims display a wide colour range from deep blue green to pale green reflecting a chemical variation from ferrotschermakite rich in Al and Fe to actinolite (XMg=0.9). Amphibole rims also commonly display outward zoning toward more Mg and Si and decreasing Fe, Al^{IV}, Al^{VI}, Cl., Ti, K and Na. Fe, Al, K and Na are positively correlated with Cl whereas Mg and Si are negatively correlated.

Coexisting biotite display a similar chemical zonation of Mg and Fe, but Al does not show as clear a zonation as in amphibole. Neither biotite nor amphibole contain detectable amounts of F, but display a variable Cl-content. The Cl-contents of coexisting biotite and amphibole are correlated in a trend which does not give a 1:1 correlation. In the most Cl rich compositions amphibole is richer in Cl than coexisting biotite whereas the opposite is the case at low Cl contents. A similar observation is seen in the Fe-content. A plot of KdFe biotite vs. amphibole results in a linear trend with a non zero intercepts. We interpret the linear trend to reflect chemical equilibrium between the coexisting biotite and amphibole.

The compositional changes reflect the complex interaction between brine fluids and hydrous minerals during cooling and uplift, where the Fe and Mg contents of the silicates were changed. Accordingly, the brine fluids partly control the composition of Fe-Mg silicates. Hence the models arguing that the Cl content of biotite is a function of the Fe/Mg ratio of the mineral, fluid composition and PTconditions (Munoz, 1992; Munoz and Swenson, 1981) can not explain the Froland amphiboles and biotites. Rather we find that the composition of the halogen bearing Fe-Mg silicates is partially controlled by the aqueous fluid composition along with P and T. Two models may explain the biotite and amphibole chemical zonation:

Model 1: zoning reflects interactions with a fluid of varying composition at fixed P and T. This model explains the compositional zoning observed by Kullerud and co-workers (1995; 1996; 1999), but cannot fully explain the compositional zoning observed in our study because the fluid salinity is constant.

Model 2: compositional zoning reflects interaction with a fluid having constant halogen contents during gradually changing PT-conditions.

Model 2 is preferred in the current study because fluid inclusion studies document constant salinities of the fluid during cooling and exhumation (Sørensen and Larsen, 2007b). This is in good agreement with the non zero intercept in the KdFe plot of amphibole inferred to indicate different temperature at each data point.

The difference in Cl, Fe and Al -contents of coexisting amphibole and biotite also probably reflect changes in the temperature and the different effects of the temperature upon the amphibole and biotite structures. Cl-incorporation increases the cell volume of amphibole and, therefore, it is expected that the Cl concentration is positively correlated with the temperature. Local ordering between Fe, Cl and K have been documented in amphibole (Oberti et al., 1993). This together with the observation that Al in amphibole increases more than in biotite with increasing temperature facilitate higher Fe content in amphibole suggest that the change in KdFe and Cl content between amphibole and biotite is a function of temperature fluctuations. Accordingly, increasing temperature would cause increasing Fe in amphibole hence less Fe in biotite. This again would affect the Cl ratio amongst coexisting amphibole and biotite because Cl is attracted to Fe in the amphibole lattice.

Apatite features a halogen evolution that is the opposite of that in amphibole and biotite. Whereas F was not detected in the studied amphibole and biotite, apatite displays an evolution from Cl-OH apatite in the garnet quartz symplectites toward increasingly F-rich apatite parallel with amphiboles and biotites becoming Mg-rich and Cl poor. However, most hydrothermal apatite is F-rich due to the high partitioning of F in favour of apatite. The log(aHCl/aH2O)/log(aHf/aH2O) of Zhu and Sverjensky (1991) show that only small amounts of F (log(aF/aH₂O = 10^{-6}) in the fluid would suffice to give F-apatite fractions of 0.9 in a 5 molal Cl- solution at 300°C. The stability field of F-apatite increase with decreasing temperature (Zhu and Sverjensky, 1991) Hence F-enrichment in the Froland-apatite most likely reflect dropping temperature and not F-enrichment in the fluid.

From our textural observations we infer that scapolite was late in the mineral assemblage. Although scapolite coexisted with CO₂-free fluids, scapolite formula recalculation show that scapolite was meionite rich hence contained significant

 CO_3 and HCO_3 . Accordingly, CO_2 did not come from the fluid. Textural observations imply that scapolitisation depended on the presence of calcite near plagioclase. Similar observations were done by Visser and co-workers (1999). Therefore, we suggest that scapolite formed by a reaction involving calcite as also suggested by Visser et al. (1999):

cc + NaCl + pl = scp

The strongly variable composition is mostly a function of local chemical variations particularly in the amount of calcite, the composition of the replaced plagioclases and the Ca/Na ratio of the coexisting fluid. Given that the fluids maintained constant compositions (paper 2, Sørensen and Larsen, 2007b) it was primarily the local rock composition governed by plagioclase and calcite that buffered the scapolite composition.

Metasomatic evolution of the Bamble sector and formation ore deposits

The observation that both amphibole and biotite become increasingly Mg rich during cooling and exhumation in combination with the observation that commonly the loss of Fe cannot be explained by other phases leads us to conclude that Fe was mobilised.

This is illustrated by mesoscale observations (hand specimen scale) and is particularly well illustrated by alteration patterns surrounding plagioclase-calcite veins: The central zone1 is enriched in ilmenite, Ca CO_2 Fe and sulphur; this is followed by a zone free of biotite mainly comprising plagioclase and amphibole, followed by an amphibole free zone mainly comprising biotite and plagioclase. This local scale observation may possibly reflect what is going on at a larger scale in the Bamble sector. I.e. Fe and other elements are removed from the amphibolites which become increasingly Mg-rich and redeposited elsewhere giving rise to the numerous small Fe-Cu oxide/sulphide deposits scattered throughout the Bamble sector. This was also suggested by Brøgger (1934) for the breccia related deposits at Langøy in relation to the mafic rock that was altered by scapolitisation and albitisation processes and as a general genetic model by Korneliussen et al.(2000).

Genetic models of ore deposits will benefit from an increased understanding of the interaction of fluids with silicates in the wall rocks because fluid-rock interaction in the wall rock probably explain many element enrichments leading to ore formation. Bearing this in mind we find it peculiar that many studies of ore deposits use the (Munoz, 1992; Munoz and Swenson, 1981) models to calculate halogen activities in ore forming fluids because the model assumes that crystal chemical constraint are in control of the halogen contents of biotite and amphibole. Rather we suggest that the fluid phase pose a partial control on the mineral chemistry and that fluid rock interaction leads to changes in mineral and fluid composition in order to obtain equilibrium conditions. As parameters such as pressure, temperature, fluid composition and fluid-rock ratios changes the equilibrium also changes.

In our study the mineralogical changes are induced by fluid rock interaction with a fluid of constant salinity during cooling and exhumation, but different models explain similar mineral zonation elsewhere.

However, the understanding of the architecture and tectono-metamorphic evolution of the Bamble Sector remain fragmentary. Partially because the importance of massive pulses of highly saline fluids were not fully appreciated. Our study concerns a rather limited portion of the Bamble Sector, however, it is one of the few studies that documents the importance of highly saline aqueous fluids and demonstrates the implications for the mineralogy and metasomatic processes on micro as well as macro scale. Studies by Cameron (1993a; 1993b) and Cameron and co-workers (1993) document the mobilisation of Au and other chalcophile elements during high grade metamorphism and retrogression in the Bamble Sector through analysis of the whole rock chemistry. Their results document how chalcophile elements are depleted through amphibolitisation of coronitic gabbro at high f_{02} (Cameron et al., 1993) and reintroduced in retrograde veins focussed at higher crustal levels near the brittle-ductile transition (Cameron, 1993b).

Our work document details on the mineralogical, $PT-X_{fluid}$ and metasomatic evolution of the Bamble sector. Although they represent a rather limited geographical area they confirm the main concept of the ore genetic model proposed by Cameron and co-workers. Further work should, on a much finer scale than done in this study, focus on the mineralogical evolution during cooling and uplift and compare that with the whole rock chemistry. In addition the study of fluid inclusions associated with the ore-forming process in amphibolite and in calc-silicates (Sørensen, 2006 unpublished data) will allow tighter constrains of the PT-

 $X_{\mbox{\scriptsize fluid}}$ evolution associated with element mobilisation and re-deposition of ore deposits.

Publications and presentations during PhD work

- Sørensen, B.E. and Larsen, R.B., 2007. Paper1 Fluid induced multistage recrystallisation microstructures in Quartzites and Quartz veins from the Bamble shear zone complex (in my PhD thesis)
- Sørensen, B.E. and Larsen, R.B., 2007. Paper2: The fluid evolution of the Froland area in the Bamble sector from peak P-T through cooling and uplift: implications for retrograde mineral paragenesis and PT evolution of the Bamble sector.(in my PhD thesis)
- Sørensen, B.E., Larsen, R.B. and Austrheim, H., 2007. Paper3: Metasomatic evolution of the Froland amphibolites during cooling and uplift - textural observations and geochemical evolution of hydrous minerals. (in my PhD thesis)
- Sørensen, Bjørn Eske. Quantitative interpretation of fluid dependant mineral equilibria in complex calc-silicate rocks. . In: Proceedings, 6th Annual Conference for Doctoral Candidates. NTNU: The Organization for Doctoral Candidates of Applied Earth Sciences (DIGOP) 2006. ISBN 82-92319-06-9.
- Larsen, Rune Berg; Ihlen, Peter; Jacamon, Francois Pierre; Müller, Axel; Sørensen, Bjørn Eske (2005). IGNEOUS REFINEMENT OF QUARTZ RAW-MATERIALS. GSA Abstracts with Programs 2005;37(7)
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- Bjørn Eske Sørensen (2005). Fluid inclusions: Their significance, analysis and interpretation in metamorphic rocks. Detailed report focussing on thermodynamic interpretation of microthermometry data. 95 p.

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