Research paper

Deciphering fluid inclusions in high-grade rocks

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ABSTRACT

The study of fluid inclusions in high-grade rocks is especially challenging as the host minerals have been normally subjected to deformation, recrystallization and fluid-rock interaction so that primary inclusions, formed at the peak of metamorphism are rare. The larger part of the fluid inclusions found in metamorphic minerals is typically modified during uplift. These late processes may strongly disguise the characteristics of the "original" peak metamorphic fluid. A detailed microstructural analysis of the host minerals, notably quartz, is therefore indispensable for a proper interpretation of fluid inclusions. Cathodoluminescence (CL) techniques combined with trace element analysis of quartz (EPMA, LA-ICPMS) have shown to be very helpful in deciphering the rock-fluid evolution. Whereas high-grade metamorphic quartz may have relatively high contents of trace elements like Ti and Al, low-temperature re-equilibrated quartz typically shows reduced trace element concentrations. The resulting microstructures in CL can be basically distinguished in diffusion patterns (along microfractures and grain boundaries), and secondary quartz formed by dissolution-reprecipitation. Most of these textures are formed during retrograde fluid-controlled processes between ca. 220 and 500 °C, i.e. the range of semi-brittle deformation (greenschist-facies) and can be correlated with the fluid inclusions. In this way modified and re-trapped fluids can be identified, even when there are no optical features observed under the microscope.

1. Introduction

Fluid inclusions in high-grade metamorphic rocks have been studied much later than for other lithologies such as hydrothermal and magmatic rocks, which have been systematically described since the 19th century. Pioneering studies on geological fluids in high-grade rocks dated back to the early 1970's (Touret, 1981, 2001) and awakened a lively interest, which continues until today. The study of fluid inclusions in metamorphic rocks was particularly stimulated by the recognition of their role in stabilizing metamorphic mineral assemblages from autoclave experiments coupled with thermodynamic calculations (e.g. Winkler, 1965). Relic fluids, preserved as inclusions in natural rocks, are the only direct evidence of the role of fluids during metamorphism. However, fluid inclusions in metamorphic rocks are normally strongly modified during retrograde conditions such that the corresponding microtextures are complex. They therefore pose a challenge for unravelling the role of the metamorphic fluid during rock evolution. The fluid inclusion inventory within one rock sample may show a large variation in compositional and density, which must reflect different stages of rock evolution to investigate. In some granulites the fluid inclusions are extremely difficult, consisting only of small, highly transposed inclusions. In other granulites, they are much easier to investigate consisting of relatively large and abundant fluid inclusions in many of the rock-forming minerals. It should be emphasized that since fluid inclusions are a part of the rocks, they must be studied as much as any other rock constituent (Jacques Touret pers. comm.).

Carbonic fluid inclusions are typical for many granulite rocks and were recorded for the first time in the Bamble Sector, southern Norway (Touret, 1971a, b), i.e. within the zone delimited by the orthopyroxene-in isograd. The CO_2 is assumed responsible for the low H_2O activities required for the stabilization of orthopyroxene in these rocks. Following this first discovery, carbonic fluid inclusions were found in many other granulite-facies rocks worldwide. The

number of fluid inclusion studies in granulite rocks rose steadily from <5 to ca. 15 to 35 publications per year in the late 1980's and early 1990's (Fig. 1). In the early 1980's the introduction of Laser Raman micro-spectrometry for geological studies allowed for the fast detection of CO_2 and therewith stimulated the study of micron-scale "gas inclusions" in rocks. The somewhat lower number of studies nowadays can be explained by the general acceptance of CO_2 being the dominant fluid phase in granulite-facies rocks. Still some scepticism persists for a number of geologists who consider a proper interpretation of fluid inclusions in high-grade metamorphic rocks problematic, or at the best "difficult", due to the strongly modified character of the majority of fluid inclusions with only a few (if any at all) preserved unchanged from peak-metamorphic conditions.

In addition to CO_2, high-salinity brines are known as an important constituent of many high-grade metamorphic rocks. These fluids also help to reduce the rock H_2O activity and stabilize "dry" mineral assemblages (Touret, 1985). Brines are found in many granulite-facies rocks along side carbonic inclusions.

For more than two decades, fluid phase petrology, i.e. the study of fluid inclusions and related microtextures, has made good use of cathodoluminescence (CL) techniques in order to visualize fluid-induced textures, which cannot be observed otherwise (e.g. van den Kerkhof and Hein, 2001). In the present paper we give an overview and a guideline for fluid inclusion studies in quartz from high-grade metamorphic rocks, from microscopic observations including detailed fluid inclusion mapping to microthermometry, CL and trace element analysis.

2. Carbonic fluid inclusions in granulite rocks

Fluid inclusions in granulite-facies rocks are almost always preserved in quartz as the host mineral. Some granulite-facies rocks also show carbonic inclusions in other minerals like garnet, plagioclase, pyroxene, apatite, and zircon, besides fluid inclusions in quartz. Examples are the Doddabetta charnockite complex, Southwest India (Touret and Hansteen, 1988), the East African charnockites (Coolen, 1980; Herms and Schenk, 1998), Victoria Land, Antarctica (van den Kerkhof et al., 1998) and Varberg charnockite, SW Sweden (Harlov et al., 2013). The reason that carbonic inclusions are sometimes preserved in all the rock-forming minerals and in other cases only in quartz only, has not been fully explained so far, but suggests a high CO_2 activity during the growth of these minerals. Comparison between examples from the literature suggests that igneous charnockites tend to contain fluid inclusions in more than one rock-forming mineral (e.g. garnet, plagioclase, and quartz), whereas metamorphic charnockites normally have fluid inclusions in quartz only. However, there are exceptions and the distinguishing features between igneous vs. metamorphic charnockites have not been completely resolved (Touret and Huizenga, 2012).

The first studies of carbonic inclusions in metamorphic rocks already demonstrated large variations in fluid inclusion densities on the micron scale (e.g. Touret, 1971a, b). Normally few high-density CO_2 inclusions (>1 g/cm^3), originating from the peak-metamorphic conditions, are preserved and the majority of inclusions show densities down to the critical density of CO_2 (0.47 g/cm^3), or lower. Inclusions with highest density often show primary characteristics, i.e. they are isolated, or part of a cluster, as a group of inclusions formed by partial fluid re-trapping during uplift. However, fluid inclusions with the highest density are earliest only in the case of decompression paths, not always in the case for HT-granulites. Inclusion geochronology should be exclusively deduced from the inclusion morphology, i.e. the relation with the host mineral, and then the density evolution can be discussed in the light of this timing. We will see in the present study that the
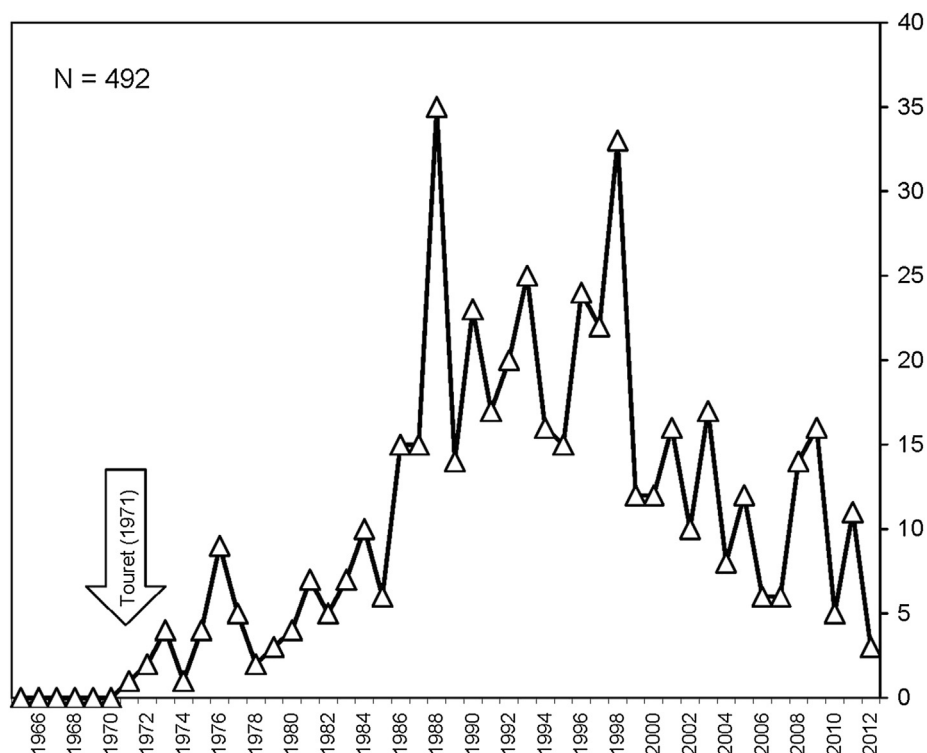

Figure 1. Graphic presentation of the number of publications on fluid inclusions in granulite-facies rocks as obtained from the GeoRef data base (American Geosciences Institute). Total number of items = 492, from the first publication (Touret, 1971a, b) until 2012.

highest-density inclusions are not always easy to recognize from petrological observations and may be "hidden" in between other re-equilibrated inclusions of varying density.

In granulites with carbonic fluid inclusions preserved in more than one rock-forming mineral, high-grade metamorphic inclusions are typically characterized by negative crystal shapes, e.g. hexagonal shapes for quartz (Fig. 2). These inclusions are arranged in diffuse tracks and swarms, and are rarely isolated (e.g. Coolen, 1980; Herms and Schenk, 1998). On the other hand, granulites, which developed carbonic inclusions only in quartz, almost never contain inclusions with a negative crystal shape. In the latter case, early-formed high-density carbonic inclusions are much more difficult to identify.

Homogenization temperatures (or fluid densities) are often graphically presented as bar plots, which may show one, two or more frequency maxima corresponding to episodes of massive CO_2 re-trapping during uplift and never under peak-metamorphic conditions. Touret (1987) earlier preferred curves, which have the advantage of illustrating perturbations (dissymmetric histograms). However, any statistical treatment of the Th distribution has shown to be of limited use so far. The "mean" CO_2 density appeared to be normally not representative for the peak of metamorphism. Peak-

Figure 2. Primary high-density carbonic fluid inclusions $\pm N_2$ in quartz from a granulite-facies rock showing a negative crystal shape. Example from a biotite-garnet gneiss from the Furua Granulite Complex, Tanzania (sample: C. Coolen). The lowest Th_{CO_2} of these inclusions is ca. −46 °C. (a) View parallel to the quartz c-axis; (b) view perpendicular to the quartz c-axis.

metamorphic fluid inclusions are rare and one of the main tasks of studying metamorphic fluid inclusions is the identification of these "exceptions". In this respect the decompression re-equilibration experiments of Vityk and Bodnar (1995, 1998) showed that fluid inclusions never equally adjusted to the change in pressure-temperature. His conclusion, that a part of the inclusion always survives the changing P-T conditions, provided a solid base and optimism for the interpretation of natural fluid inclusions. It confirms observations made for natural samples that high-density fluid inclusions are almost always present, even when sometimes difficult and time-consuming to find.

3. Fluid phase petrography

3.1. Primary and secondary inclusions

Primary fluid inclusions in high-grade metamorphic rock have been identified as high-density, isolated carbonic inclusions, e.g. in the Bamble area, southern Norway (Touret, 1971a, b; van den Kerkhof et al., 2004), Furua Granulite Complex, southern Tanzania (Coolen, 1980), southern India (Santosh and Tsunogae, 2003), and East Antarctica (Tsunogae et al., 2002). In these examples, nitrogen has sometimes been found as an additional fluid component, resulting in high-density CO_2-N_2 inclusions (e.g. Kooi et al., 1998). In other cases, like the charnockitic rocks of Söndrum, SW Sweden, low-salinity aqueous-carbonic inclusions could be identified as the earliest, peak-metamorphic fluid (Harlov et al., 2006). These also show regular shapes, whereas the carbonic inclusions, which make up the majority of fluid inclusions, must have formed by the uptake of the H_2O into the melt during partial melting of the granitic host rock. During this process of H_2O-loss the fluid phase becomes enriched in CO_2. This process is in accordance with observations made for rocks which show typical restite reactions, including melt formation (Touret and Dietvorst, 1983).

Under high-grade metamorphic conditions two immiscible fluid phases coexist for a wide range of bulk fluid compositions. Therefore, it is thought that many salt-bearing aqueous fluid inclusions formed simultaneously with the carbonic ones (CO_2 with up to 50 mol% H_2O, and very low salt concentration). The latter inclusions show only small H_2O volume fractions under the microscope at room temperature and are recognized as "carbonic". Experiments by Shmulovish et al. (1994) and Zhang and Frantz (1989) showed that bulk fluids with a $CO_2/(CO_2+H_2O)$ ratio of >0.3 and salt concentrations of even less than 10 wt.% must plot in the two-phase field under high-grade conditions. During uplift the aqueous inclusions tend to strongly re-equilibrate due to their steep isochores. These fluids may be largely retrapped as secondary inclusions. The expansion of the immiscibility field on the lowering of pressure may result in the further "unmixing" of the aqueous-carbonic fluids during retrogression.

Secondary fluid inclusions make up the large majority of fluid inclusions in granulites. Carbonic inclusions are typically better preserved and may, in part, originate from an early metamorphic stage. On the other hand, the aqueous inclusions are normally secondary in character with only a few exceptions. Swanenberg (1980) distinguished between clusters and trail-bound secondary fluid inclusions, which was very useful also for later studies. These textures can be observed for carbonic as well as for aqueous inclusions. Clusters are defined as spatially dispersed groups of fluid inclusions, which occupy a specific volume of the host mineral. They are also sometimes referred to as decrepitation clusters as they are thought to form as a result of fluid re-trapping after leakage due to internal fluid overpressure ("explosion") during uplift. The process of fluid re-trapping is still not well understood. So far, attempts at generating "explosion" clusters in experiments
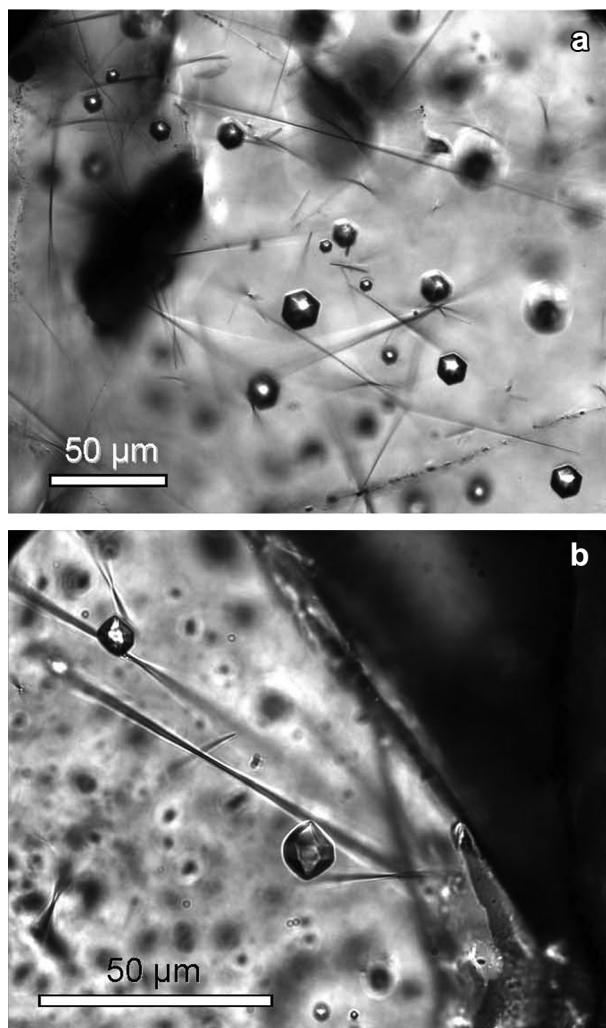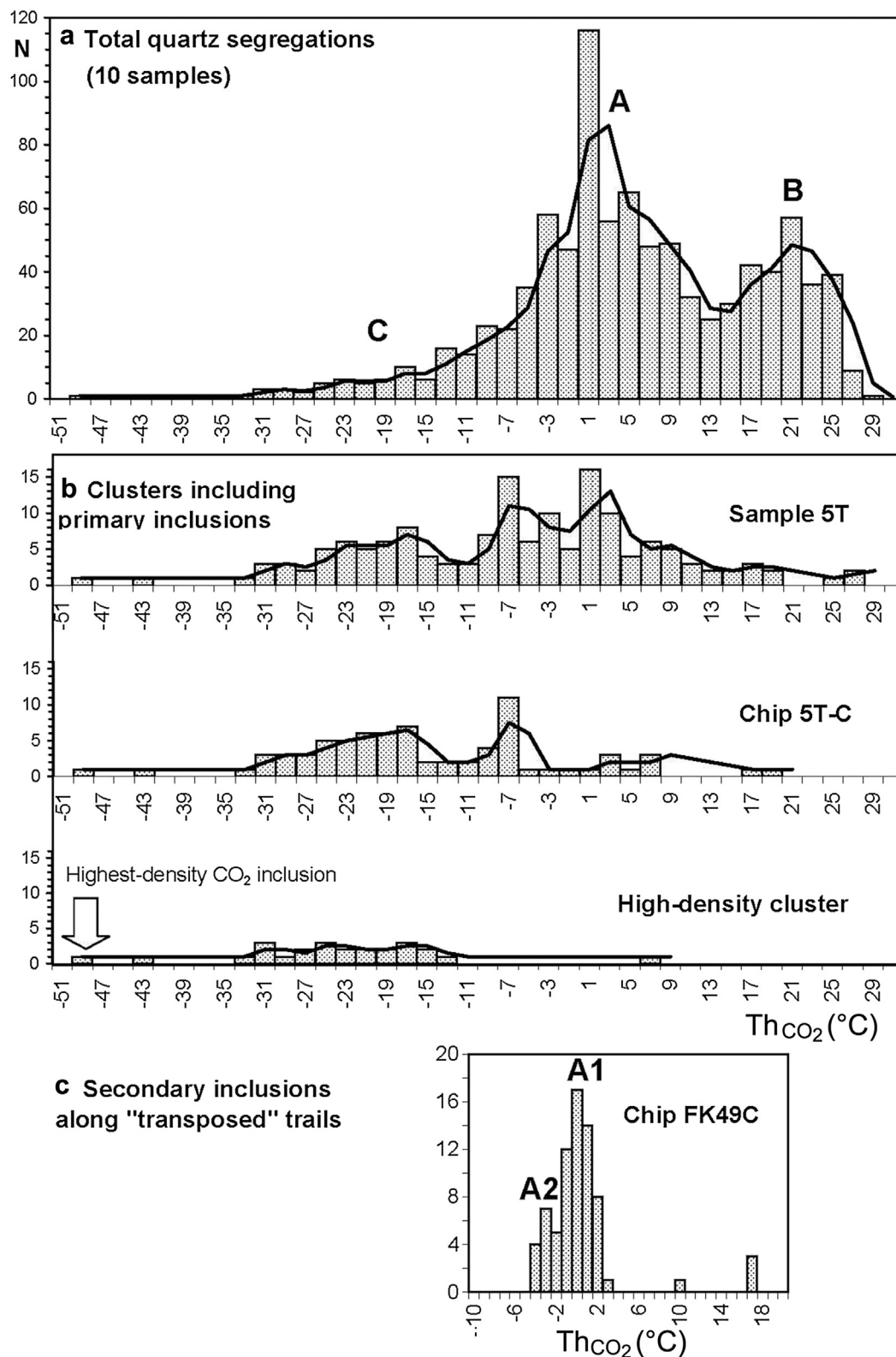
Figure 3. Histograms presenting CO_2 homogenization temperatures for a granulite-facies sample from the Bamble Sector, southern Norway. (a) Results for 10 samples from quartz segregations; (b) results for one sample, one chip, and one cluster with relatively high-density inclusions, including the highest-density primary inclusions; (c) result for the most frequent secondary inclusions in "transposed" trails.

have not been successful (Vityk and Bodnar, 1995). On the other hand, fluid inclusion clusters can be easily reproduced during re-equilibration experiments which create fluid under-pressure, i.e. "implosion" decrepitation (Sterner and Bodnar, 1989). In natural quartz, fluid inclusion clusters can be observed in high-grade rocks, which were subject to a thermal event during the emplacement of relatively shallow magmatic bodies, followed by an episode of approximate isobaric cooling (e.g. Rogaland high-grade

metamorphic complex, Norway; Swanenberg, 1980; Bakker and Jansen, 1993). In the latter case, the fluids are also strongly chemically re-equilibrated towards CH_4-rich compositions.

Trail-bound inclusions are very common for granulites and indicate fluid trapping along microfractures. These inclusions are always secondary and clearly postdate peak-metamorphic conditions. Quartz deformation grades from plastic towards brittle behaviour during uplift (Passchier and Trouw, 2005) so that fluid inclusions tend to form along healed fractures at lower temperatures. Continuing re-crystallisation, however, may result in the forming of new quartz mineralization. Intra-granular trails (see Simmons and Richter and Simmons, 1977 for trail nomenclature) are very common in granulite-facies quartz and must represent fluid trapping during an early stage of deformation, but before the formation of subgrains. These processes are expected to take place in the semi-brittle deformation P-T range (essentially greenschist facies) as the result of retrograde fluid-controlled processes between ca. 220 to 500 °C.

3.2. Fluid inclusion mapping

The preparation of detailed sketches of fluid inclusions and related microtextures has been a tradition since the earliest fluid inclusion descriptions (e.g. Sorby, 1858). This means of documentation is particularly helpful for unravelling the chronology of fluid inclusion trails as can be deduced from intersecting relationships (e.g. Touret, 1981). Photographs have the disadvantage that only one focus level can be recorded, so that more photos must be combined. In hand-mapped fluid inclusion plates the distribution of homogenisation temperatures on a sub-millimetre scale can give insight into the process of fluid inclusion modification and re-trapping.

The highest-density carbonic inclusions can be found by the examination of a set of successive, separate doubled polished thick section samples. As an example we show results obtained from quartz segregations from granulite-facies rocks in the Bamble Sector (Southern Norway) (Fig. 3a). The microthermometry of 10 samples results in homogenization temperatures (Th, i.e. the phase transition liquid + vapour → liquid), which cluster in 3 frequency ranges: the strongest mode (A) between ca. −5 and 9 °C (mean ca. 0 °C), the second-largest mode (B) between ca. +15 and +26 °C (mean about +21 °C) and a weak mode (C) between ca. −25 and −15 °C (mean ca. −20 °C). These modes can be found also for each of the individual samples, although their relative frequencies strongly differ. It is assumed that these frequency modes correspond to regional events during uplift, which resulted in the partial re-trapping of inclusion fluids. In searching for the highest-density inclusion, we selected one sample showing only Th_{CO_2} in the low-temperature A and C modes and only a very few high Th, for a more detailed study (Fig. 3b). We selected a ca. 5 mm-sized doubly polished chip containing fluid inclusions with the lowest Th after measuring three for each sample (Fig. 3b). On this chip we mapped the fluid inclusion in order to identify those inclusions with the highest density and to locate their position among re-equilibrated inclusions of lower density (Fig. 4a). The highest-density inclusion, which consists of nearly pure CO_2 (<1% N_2) shows a Th of −48.7 °C, which corresponds to a density of 1.15 g/cm³. So far, the lowest Th that has been recorded for this area is −40 °C (Touret, 1985). An interesting observation from fluid inclusion mapping is the large spread in Th within one cluster (Fig. 3b). The cluster containing the highest-density inclusion contains not only inclusions with "mode C" homogenisation temperatures, but also a "mode A" inclusion within a 20 μm distance. A similar observation was made in granulite-facies quartz from Söndrum, Sweden (Harlov et al., 2014). Here, the highest-density inclusions

(Th −39.3 °C) occur in the same cluster together with low-density carbonic inclusions. This type of high-density inclusion cannot be easily recognized as they do not show primary characteristics, but occur as unremarkable relic inclusions among decrepitated ones.

The majority "mode A" inclusions, however, occur on healed microfractures and are clearly secondary (Fig. 4b). Often we observe textures, which indicate multi-stage deformation resulting in the "transposition" of fluid inclusion trails, forming subparallel or *en echelon* short trails. Contrary to the decrepitation clusters, the density of fluid inclusions within one trail is almost the same. In the Bamble Sector example, a typical "transposed trail" shows Th_{CO_2} between −5 and +4 °C with two fine modes, one around 0 °C (A1) and another around −3 °C (A2) (Fig. 3c). The inclusions with higher Th are found in the central part of the trail, which indicates that a part of the inclusions must have been retrapped after the reopening and subsequent healing of the same structure. The short trails arranged *en echelon* have a higher density than the inclusions in the central part. This type of inclusion is common in high-grade rocks and shows that the same fractures can be repeatedly opened and sealed during deformation.

3.3. Isochore calculations for carbonic inclusions

Isochores for the highest-density CO_2 fluid inclusions found in granulite-facies rocks are the key for estimating the fluid trapping depth. Calculations can be made e.g. with equations of state collected in the "FLUIDS" software (Bakker, 2003). For high-density CO_2 we used the equation of state of Span and Wagner (1996) whose highest accuracy is in the range of 489–1373 °C and 0.5–800 MPa. The lowest homogenization temperatures collected for a number of granulite-facies terrains show a remarkably small range between −53 and −39 °C (Fig. 5) corresponding to densities between 1.11 and 1.17 g/cm³. When considering peak-metamorphic temperatures of 750 to 850 °C these densities correspond to trapping pressures of 800 to 1000 MPa, i.e. at 30 to 35 km. These conditions are in agreement with a geothermal gradient of ca. 25 °C/km, which is typical for the stable continental crust. Exceptions are areas with a high thermal flow at lower crustal levels, e.g. the West-Uusimaa Complex, southern Finland, which is interpreted as a thermal dome (Schreurs, 1985) with a corresponding geothermal gradient of ca. 50 °C/km (number 3 in Fig. 5). Peak conditions for charnockites in relation to the "wet" granite melting curve plot at lower temperatures (650–720 °C), but are also in agreement with the continental geothermal gradient (e.g. the Swedish charnockites, number 5 and 6 in Fig. 5) and trapped at ca. 30 km depth. Thus most "dry" granulites have preserved high-density carbonic inclusions with homogenization temperatures of −40 °C and lower, even when these inclusions are rare.

3.4. Aqueous fluid inclusions in high-grade metamorphic rocks

In addition to carbonic inclusions, remnants of NaCl-rich brines are found in a great number of granulite-facies rocks (Touret, 1995). There are strong arguments to believe that brine-rich fluids are present at peak metamorphic conditions. However, due to their steep isochore slopes, aqueous inclusions almost never survive uplift unchanged, though some aqueous inclusions with a primary character can sometimes be found, e.g. in quartz blebs in garnet (Fu et al., 2003). Other arguments for the existence of high-grade metamorphic brines are the relationship between the fluid and certain types of host rocks (e.g. detrital and meta-evaporite rocks in Bamble granulite), or the traces left by intergranular fluids (K-feldspar micro-veins and/or myrmekite, see Touret and Nijland, 2012). The densities of associated brine inclusions are often high (small or no bubble) and indicate (re)
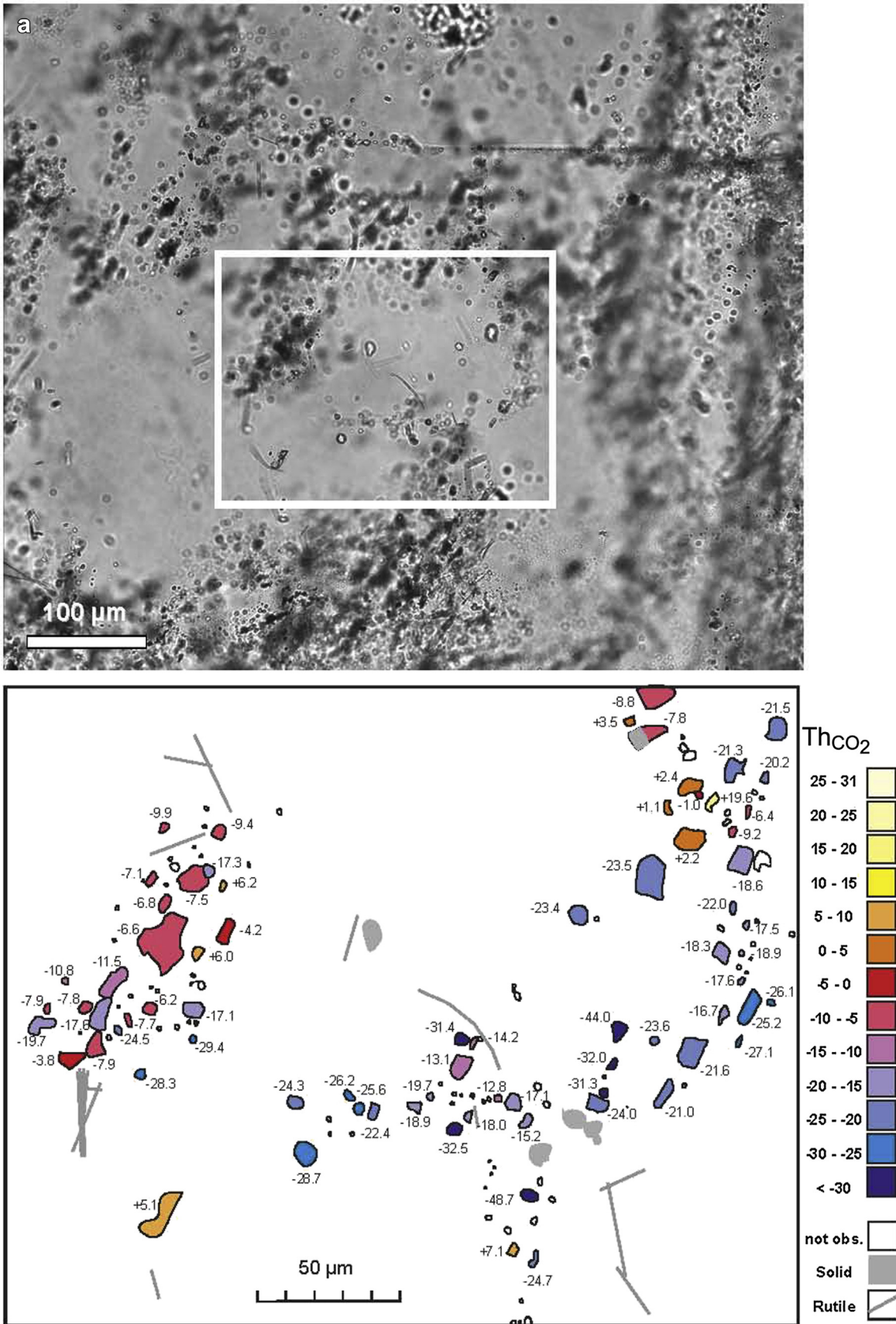
Figure 4. Result from fluid inclusion "mapping" with an indication of the homogenisation temperature distribution. Example from the quartz segregations in granulite-facies rocks from the Bamble Sector, southern Norway. The insets marked in the photographs are shown in the drawings below. (a) Decrepitation clusters including the highest-density carbonic inclusions (−48.7 °C), possibly dating from peak-metamorphic conditions (dark purple signature); (b) transposed trail of carbonic inclusions with homogenization temperatures between −5 and +4 °C corresponding to the most frequent CO_2 densities found in this sample material (c.f. Fig. 3c). Note the somewhat higher homogenization temperatures in the central part of the structure indicating later retrapping.
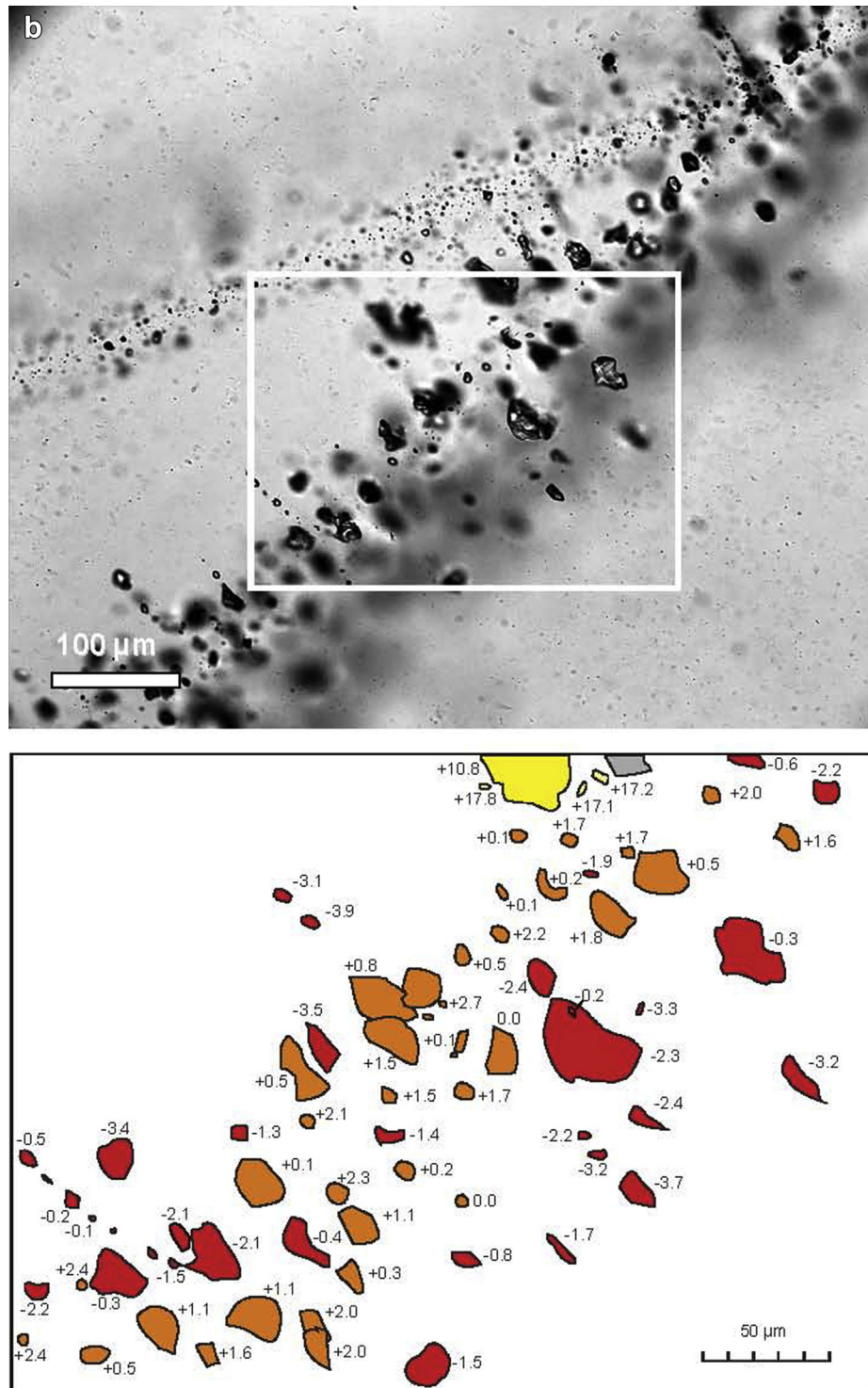
Figure 4. (*continued*).

trapping of aqueous fluids at low temperature and pressure. Fluid re-trapping does not necessarily imply changes in the salt composition and concentration, so that the study of aqueous inclusions may indeed provide information on the solutes acting during high-grade metamorphic conditions. The brines play an important role in controlling the chemical potential of alkalis and LILE elements. The inventory of aqueous inclusions largely depends on the protolith, while low-salinity aqueous-carbonic fluids are common in igneous rocks. Metapelites contain almost only aqueous fluids. Aqueous fluids play an essential role in the metasomatic changes observed for granulite-facies rocks. In the localized orthopyroxene-bearing dehydration zone at Söndrum, SW Sweden, the dehydration event was accompanied by the depletion of the charnockite in Fe, Y+HREE, Na, K, F, and Cl, and the enrichment in Mg, Mn, Ca, and Ti compared to the surrounding granitic gneiss (Harlov et al., 2006).
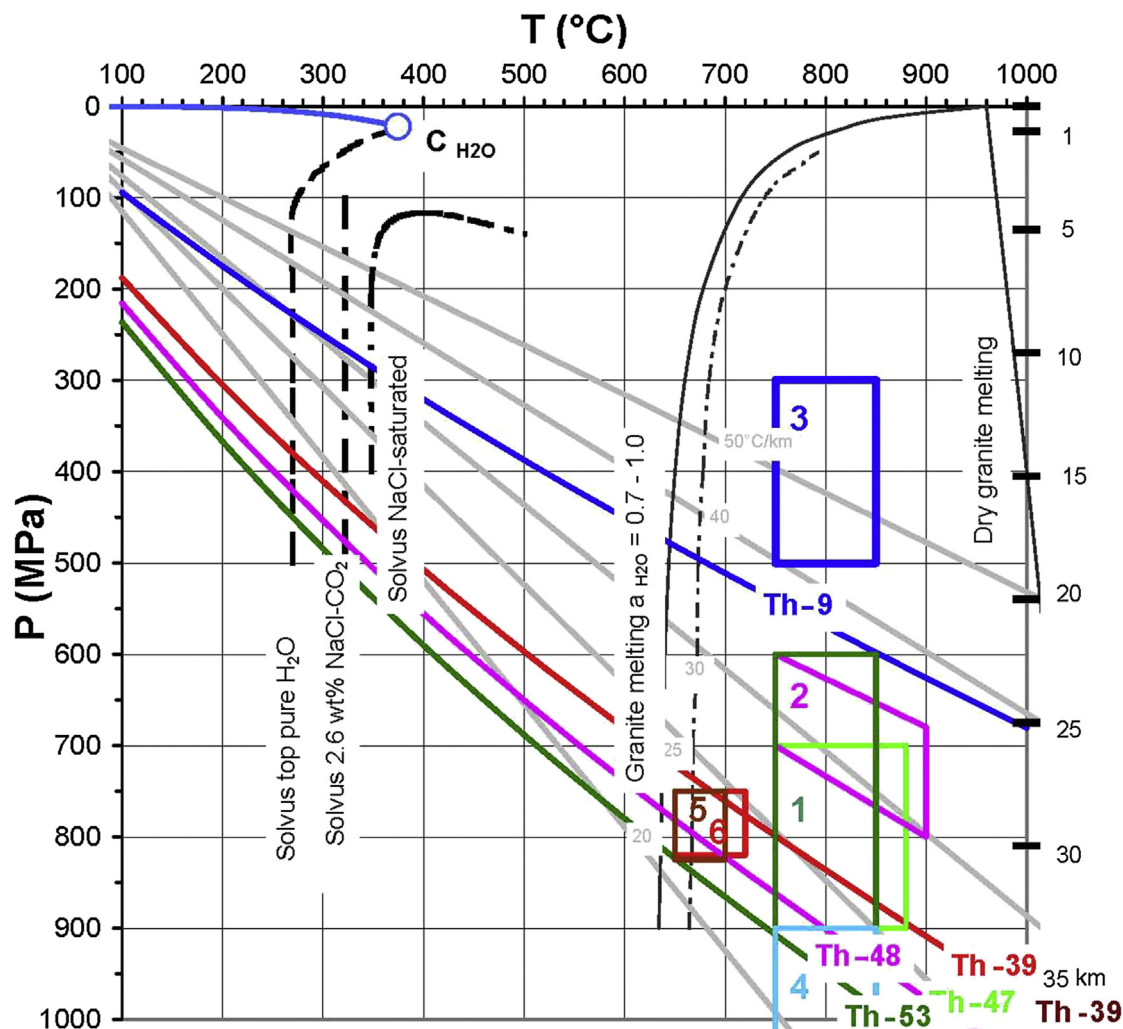
Figure 5. Isochores with indicated Th corresponding to the highest-density CO_2 found in selected granulite-facies rocks from 1. Furua Granulite Complex, southern Tanzania (Coolen, 1980); 2. Bamble Sector, southern Norway (Touret, 1985); 3. West-Uusimaa Complex, southern Finland (Schreurs, 1985); 4. Doddabetta, southern India (Touret and Hansteen, 1988); 5. Söndrum, Halmstad, SW Sweden (Harlov et al., 2006); 6. Varberg, SW Sweden (Harlov et al., 2013). CO_2 isochores calculated utilizing the equation of state from Span and Wagner (1996). The upper limit of immiscibility is given for H_2O-CO_2, and 2.6 wt.% NaCl brine + CO_2 fluid inclusions (Crawford, 1981). Granite melting curves (Newton, 1986) are given for dry granite melting, and for H_2O activities of 0.7 and 1.

3.5. Retrograde fluids in high-grade rocks

Fluid interaction with the rock during uplift may result in changes in the fluid chemistry. The most obvious are the methane-rich compositions found in many fluid inclusions, e.g. Rogaland (Swanenberg, 1980). These granulites are metapelitic in origin and contain traces of organic carbon. The fluid composition represents fluid-rock equilibrium, which is essentially a function of temperature and the oxygen fugacity as determined by the mineralogy in the C-O-H system (Huizenga, 2001; Bakker, 2003). The pressure is a less sensitive parameter. In this way the fluid composition, e.g. defined as the CO_2/CH_4 ratio, can be used as a thermometer for a given oxygen fugacity (e.g. van den Kerkhof et al., 1991). At high-grade conditions, however, the gas composition in these fluid inclusions is essentially pure CO_2.

There are also instances of late fluid inclusions having highly saline $CaCl_2$ compositions. The presence of $CaCl_2$ brines can be considered as a result of extreme retrograde alteration during low temperature albitisation. These brines are thought to be the result of feldspar alteration from the reaction:

$$CaAl_2Si_2O_8 + 2Na^+ + 4SiO_2 = 2NaAlSi_3O_8 + Ca^{2+} \qquad (1)$$
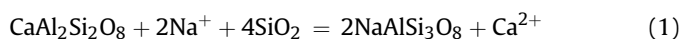
which results in higher Ca-concentrations with increasing fluid salinity (Yardley and Shmulovich, 1995). These fluid inclusions form typically during the last stages of rock evolution and always show homogenization temperatures below ca. 200 °C. Although these high-salinity inclusions are found in many granulites they do not represent high-grade metamorphic conditions.

4. Cathodoluminescence (CL) and trace element analysis

4.1. Technical details

CL studies with the optical CL-microscope is highly suitable for distinguishing quartz textures related with different quartz generations, which differ by their trace element and structural defect inventory. We used the high-power HC3-LM-Simon-Neuser CL microscope (Neuser et al., 1995). Additional studies with an electron microprobe (JEOL JXA 8900RL) equipped with a CL-detector (200–900 nm) have the advantage of combining CL-imaging and resolving trace element compositions (EPMA). Quantitative analysis of Al, Ti, Fe, K and Na can be carried out on metamorphic quartz (Müller, 2000; Müller et al., 2003; van den Kerkhof et al., 2004).

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) analysis can be used for measuring Al, Ti, Fe, Li, Th, U, and Ge in quartz for spot sizes of about 100 μm. We used a VG PQ2+ mass spectrometer equipped with an S-option to raise sensitivity. The laser ablation system is a 266 nm Nd: YAG VG UV microprobe. The detection limits in order of the detectability (ppm) are Al (9), Fe (4), Ti (3), Li (2), Ge (2), U (0.1) and Th (0.05). These values are in agreement with the findings of Flem et al. (2002) and substantially better compared to the EPMA results. The laser ablation craters are 30–50 μm in diameter and 100–150 μm deep. Subsequently, this method has a lower spatial resolution compared to EPMA. On the other hand, LA-ICPMS has the advantage of eliminating some of the distortion effects implicit for EPMA and the higher sensitivity of measuring some other trace elements. In this respect both methods are complementary.

4.2. Microtextures in cathodoluminescence

Granulites show a wide variety of CL-contrasting textures, which in part may correlate with textures visible under the microscope, such as micro-fractures and fluid inclusions (Frentzel-Beyme, 1989; van den Kerkhof and Hein, 2001; van den Kerkhof et al., 2004). These microtextures are thought to form during different stages of uplift and show a number of distinguishing features (see also Fig. 6):

(1) Diffusive textures around grain boundaries or around micro-fractures characterized by reduced CL-intensity. Concentrations of Ti and Al were found to be lower in these zones (van den Kerkhof et al., 2004). Migrating fluids may have taken up these elements from the quartz in a zone of up to ca. 100 μm from the fluid-quartz phase boundary.

(2) Healed fractures and patches of secondary quartz (non-CL) are part of a typical dark contrasting pattern consisting of secondary quartz interconnected by fine healed fractures (e.g. Behr and Frentzel-Beyme, 1987). These textures have been referred to as "crackling" textures (Frentzel-Beyme, 1989) or "decrepitation" textures (Behr, 1989), and are assumed to form by the dissolution-precipitation of quartz during brittle deformation. The pattern is characterized by dark, practically non-luminescent quartz patches connected by dark thin lines (healed fractures). Sometimes several generations of crackling patterns can be distinguished with later structures showing a cross-cutting relationship with the older structures and the younger textures normally being darker than the older ones. EPMA analysis indicates that the dark patches have reduced trace element concentrations, particularly in Ti and Al. The host quartz around the dark patches often shows slightly elevated concentrations of Fe and K.

(3) Recrystallized quartz shows idiomorphic growth nuclei of secondary quartz (dark CL). These textures are assumed to have formed by recrystallization on the cooling of quartz with overall high trace element contents (van den Kerkhof et al., 2004). Almost pure quartz nuclei, with notably low Ti and Al, are assumed to grow by the replacement of impure quartz. The higher stability of pure quartz is supposed to be the driving force for this quartz growth at low temperatures.

(4) Open, non-healed fractures are late structures, which formed at low temperatures and have no CL contrasts.

Structural H_2O in quartz is manifested by the strong reddish CL emission, which typically increases the intensity by modification of the structural defects in the electron beam (e.g. Stenina et al., 1984;
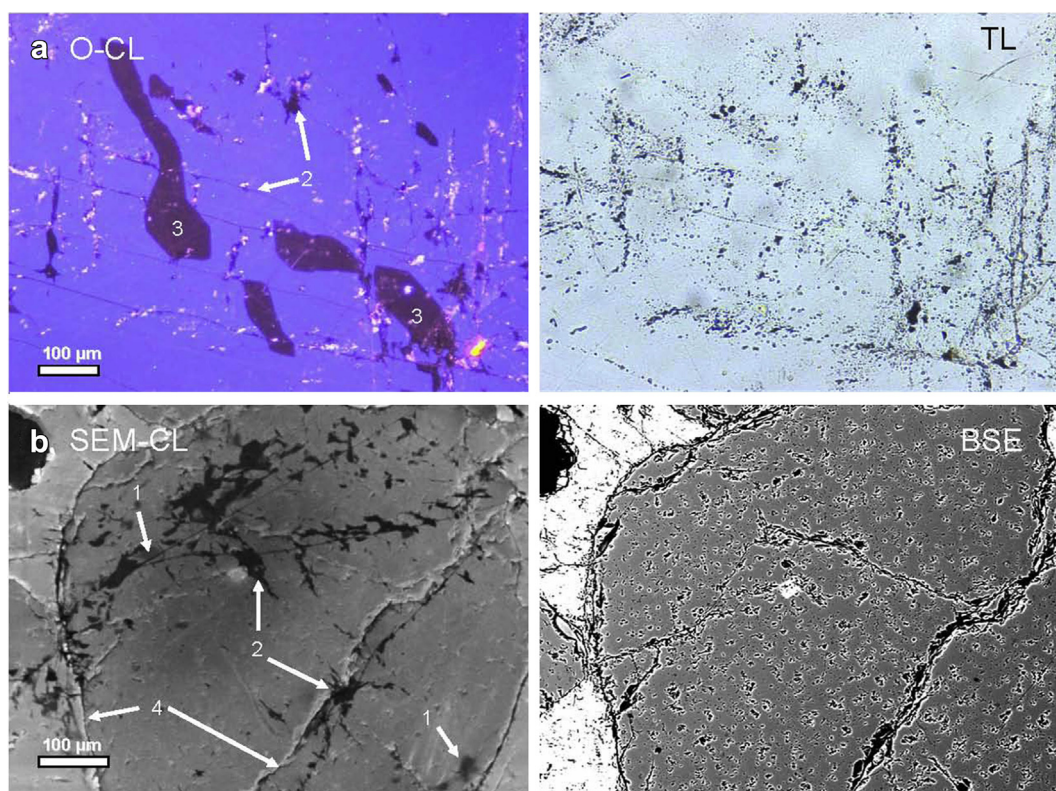

Figure 6. Examples of (a) optical CL recorded for granulite-facies rocks from the Bamble Sector, southern Norway and (b) SEM-CL from granulite-facies rocks from the Wilson terrane (northern Victoria Land, Antarctica) (Sample: F. Talarico; van den Kerkhof et al., 1993). 1 = diffuse alteration textures; 2 = secondary quartz in patches and healed fractures; 3 = euhedral quartz nuclei; 4 = open, non-healed fractures (see text for explanation).

Kalceff and Phillips, 1995; Müller, 2000). This type of luminescence has commonly been observed in hydrothermal and granitic quartz, but is exceptional in high-grade metamorphic quartz. Here, textures around aqueous fluid inclusions are typically dark in CL and indicate reduced trace elements in the host quartz (e.g. van den Kerkhof and Hein, 2001; van den Kerkhof et al., 2004). It is thought that these trace elements are enriched along the grain boundaries and in the fluid inclusions. Carbonic inclusions typically do not show halo structures under CL (Behr, 1989), which suggests that small amounts of H_2O originally present in the carbonic fluid must be still present in the inclusions. These small amounts of H_2O normally cannot be observed under the microscope. Experiments of Doppler et al. (2013) show possible fast diffusion of H_2O at temperatures above 450 °C, if the fugacity gradient is sufficiently high. In natural rocks this would imply that pore spaces are H_2O saturated with an "infinite" fluid source. However, as the porosity in high-grade metamorphic rocks is very low, the re-equilibration of fluid inclusions with external fluids can be neglected. On the other hand, our observations from CL show that trace elements from the host quartz are able to diffuse into the fluid inclusions during cooling.

4.3. Trace element-in-quartz geothermometry

Trace elements in quartz can be used as an independent thermometer and compared with isochore calculations obtained from fluid inclusion studies. Several tests involving Al in quartz have been made (e.g. Scotford, 1975) but its application as a geothermometer does not give reliable results. The Ti-in-quartz geothermometer (Wark and Watson, 2006) is more reliable provided that rutile is also present in the rock (Ti saturation). The detection limits for measuring Ti are in the range 18—43 ppm for EPMA and ca. 3 ppm for LA-ICPMS (van den Kerkhof et al., 2004), which corresponds to 575—650 °C and 450 °C, respectively. This implies that the Ti-in-quartz geothermometer can be best applied under high-grade conditions.

If the Ti-in-quartz thermometer is applied to that sample from the Bamble granulite whose fluid inclusions contain the highest CO_2 densities (sample FK5T, see above), an overall quartz formation temperature of 810—850 °C (164—218 ppm Ti) is estimated for the primary quartz (Fig. 7). Secondary quartz shows much lower Ti concentrations, which point to temperatures below ca. 650 °C, i.e. in the amphibolite-facies range down to greenschist facies. On the other hand, Fe is somewhat higher in the secondary quartz and around fractures.
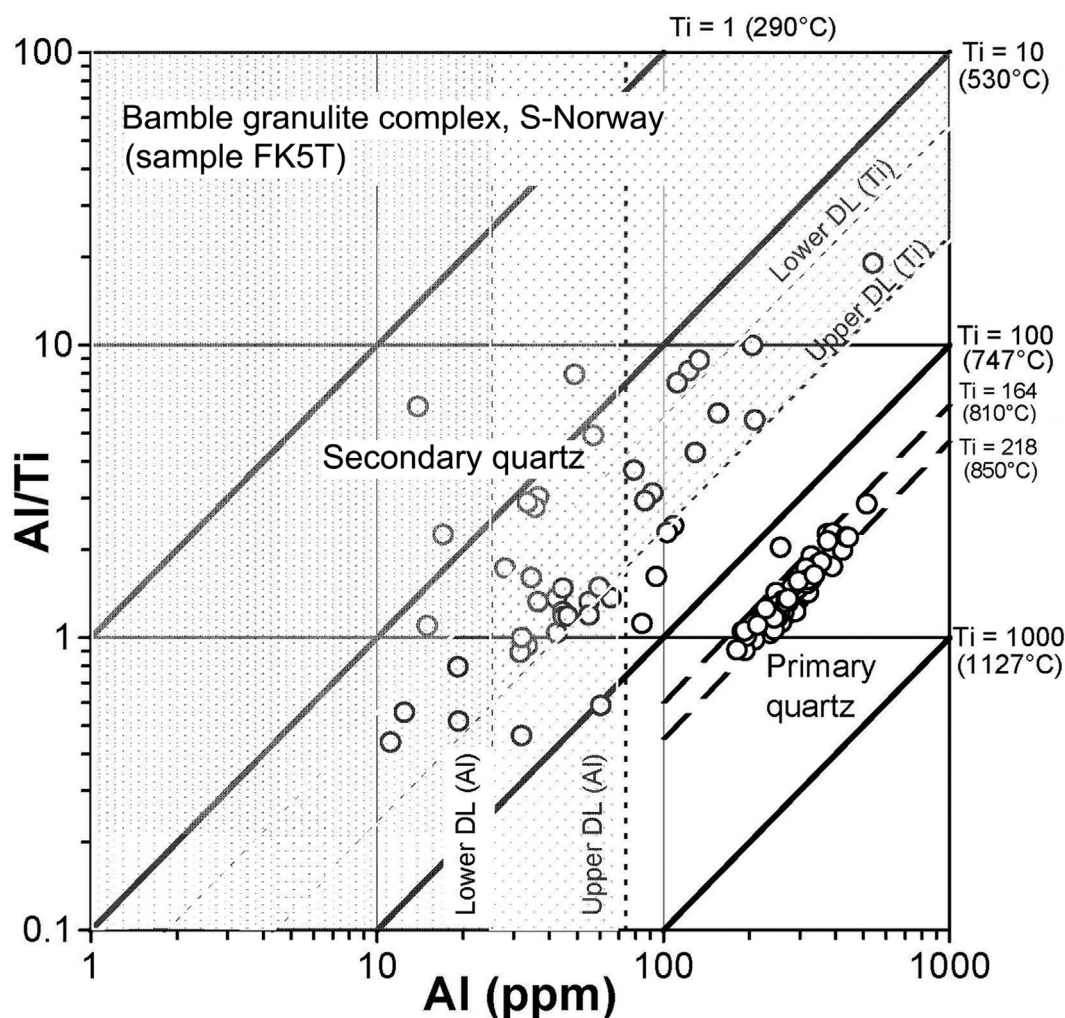

Figure 7. Trace element plot (Ti, Al) with application of the Ti-in-quartz geothermometer (Wark and Watson, 2006). Data from one granulite-facies sample from the Bamble Sector, southern Norway (see also van den Kerkhof et al., 2004) are shown. The granulite-facies temperature range as revealed from trace elements is 810—850 °C. Fluid inclusion data for this sample are shown in Figs. 3b and 4a.

5. Discussion

5.1. The preservation of peak-metamorphic fluids

Carbonic fluids trapped in the continental crust at 30–35 km depth are, even when rare, almost always preserved in granulite-facies rocks on the Earth's surface. The density of these inclusions, being typically 1.11–1.17 cm^3/mol, have pressures of 80–130 MPa at room temperature (Fig. 8, inset). The size of the inclusions ranges between 5 and 10 μm and the pressures recorded for these inclusions is in accordance with the maximum pressure that is required to initiate non-elastic deformation in the quartz around fluid inclusions of this size (Bodnar et al., 1989) and therewith may trigger decrepitation. As the maximum pressure of
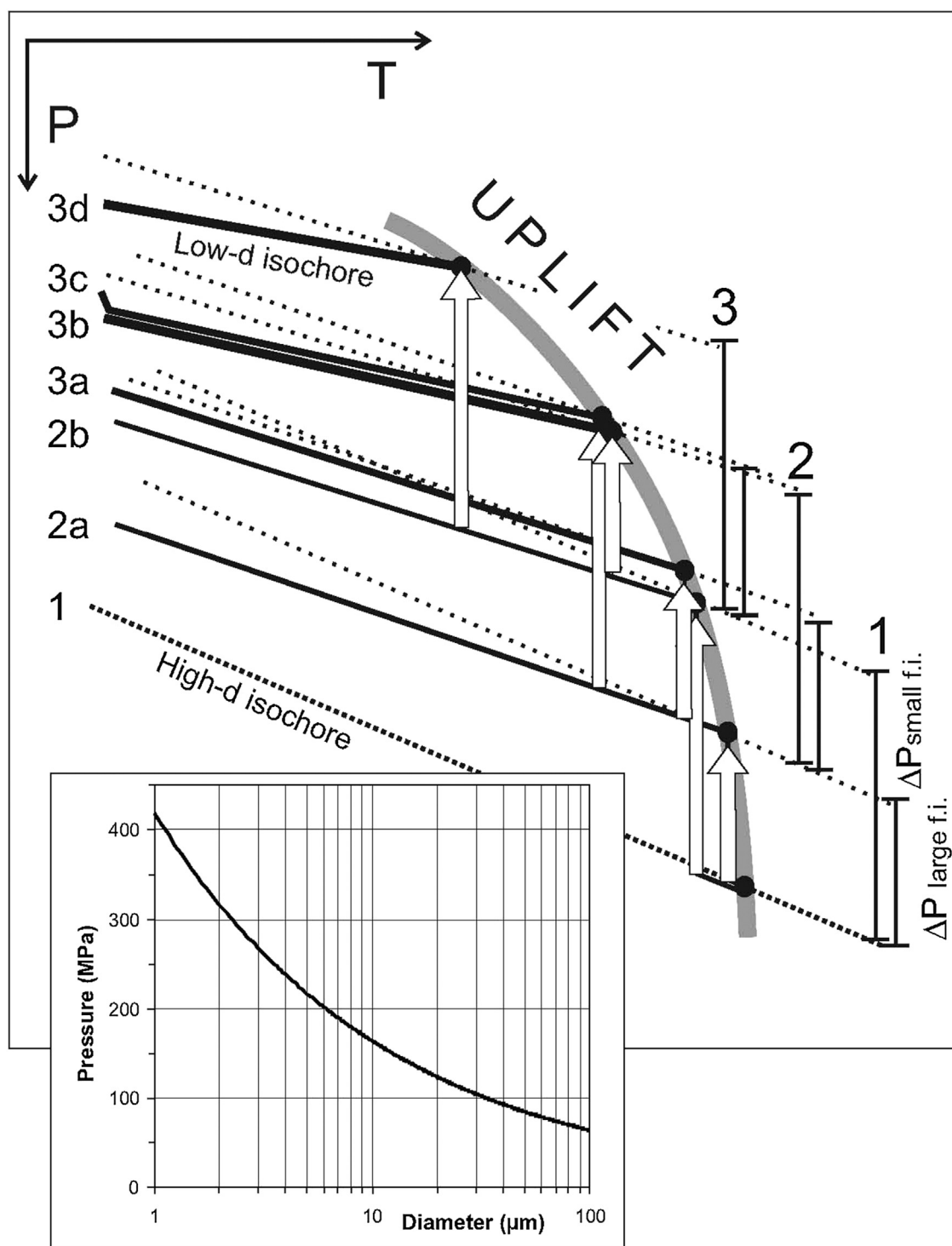

Figure 8. Re-equilibration of high-density (peak-metamorphic) fluid inclusions during uplift projected on to a P–T field (not to scale). Decompression results in stepwise re-trapping of fluids in clusters (1, 2 and 3), depending on the inclusion size, i.e. larger inclusions may leak earlier than smaller ones. Each newly trapped fluid defines a new iso-chore which defines the pressure in the inclusion on further cooling. Inset: Estimated maximum pressures in fluid inclusions in quartz (after Bodnar et al., 1989).

5–10 μm inclusions in quartz is ca. 170–220 MPa, none of these inclusions can survive heating up to 150 °C. During uplift, however, the pressure difference between the inclusion and lithostatic pressures (possibly 400–500 MPa) normally must far exceed these values. In spite of the fluid overpressure, a few inclusions always survive even these extreme conditions.

The uplift path can be complicated and characterized by metamorphic overprints. Retrograde P–T paths, characterised by decompression-cooling (e.g. Touret and Huizenga, 2012), are mostly marked in high-pressure granulites rather than isothermal decompression. However, in high-temperature and especially ultra-high-temperature granulites, rapid decompression is very late (below ca. 500 °C) and preceded by a long period of isobaric cooling. In the latter case, modified inclusions show a density increase (Touret, 1981). In the case of (isothermal) decompression, conditions corresponding to the normal continental geothermal gradient of ca. 25 °C/km may change to steeper gradients of around 50 °C/km. During this uplift most of the carbonic inclusions will be retrapped in inclusions of lower density, arranged in clusters as observed in many granulites. The maximum pressure under which the fluid inclusion remains largely intact depends on the inclusion diameter. Larger inclusions will leak earlier than smaller ones. The pressure difference between fluid inclusions and the ambient pressure can be estimated from the isochore calculations. The maximum inclusion pressure is on the order of 150 to 250 MPa above this pressure and depends on the inclusion size and shape (Bodnar et al., 1989). Fluid inclusions with an initial equal density but different size may therefore leak at different stages and form secondary fluid inclusions with a high variability in density, which define different isochores. Fig. 8 shows an example of fluid inclusion leakage in 3 steps, which results in a high variability in density for the newly formed inclusions. This is in accordance with the observation of high variability in density in fluid inclusion clusters, which have also preserved high-density inclusions. The majority of the carbonic fluid inclusions are assumed to re-equilibrate during the first episode of uplift.

5.2. The retrograde development of aqueous inclusions and cathodoluminescence structures

Aqueous fluid inclusions in granulites will be equilibrated under low PT conditions, corresponding roughly to 5–10 km depth. Only primary inclusions that have been "protected" in the mineral host are sometimes preserved, such as fluid inclusions in quartz inclusions in garnet. Re-equilibration normally occurs "in situ", with no change in the salinity. Sometimes even the difference between seawater or fresh H_2O can be identified, e.g. the Dabie Shan eclogites, which has been confirmed by stable isotope oxygen geochemistry (Fu, 2002). This indicates that during final equilibration under low PT conditions does not indicate that fluids have been necessarily introduced into the rock system at this moment. The only argument is the timing of inclusion formation in the mineral host. Microtextures observed by CL techniques show, in part, direct correlation with aqueous fluid inclusions, notably the healed fractures and patches. Aqueous inclusions are typically trapped in secondary quartz characterised by very low trace element concentrations. Correlation of carbonic inclusions with CL-textures has not been observed (see also Behr, 1989). Many aqueous inclusions in high-grade rocks typically show very high densities, i.e. showing small or no bubbles and cannot be trapped under high-grade metamorphic conditions. Homogenisation temperatures for these inclusions are mostly far below 200 °C. On the other hand, isochores corresponding with homogenisation temperatures of around 200 °C run across granulite-facies metamorphic conditions. However, microtextures demonstrate that they cannot be primary. Therefore it can be

concluded that aqueous inclusions (with Th < 400 °C) are always re-equilibrated at relatively low pressures during uplift when adapting to the mean continental geothermal gradient. These conditions correspond to the greenschist facies (300–450 °C) and lower. Secondary quartz with trapped aqueous inclusions may show different generations with clear timing relations. Even when the trace element contents are too low for doing temperature estimates, it has been observed that under CL the darker textures (lower temperatures) are always younger than the less dark ones (higher temperature). This observation demonstrates that aqueous inclusions normally form as a result of re-equilibration during cooling. The massive recrystallization of granulite quartz is evident from the occurrence of idiomorphic growth nuclei, visible as darkly contrasting quartz crystals in the bright luminescent host quartz. These textures are assumed to form by the growth of almost pure quartz crystals replacing impure high-temperature quartz. This recrystallization is assumed to be triggered by the formation of growth nuclei around aqueous fluid inclusions. Elevated Na-concentrations found in recrystallized quartz (van den Kerkhof et al., 2004) support this interpretation, which implies that the fluid inclusion contents are up taken in the newly formed quartz after complete disintegration (healing) of the fluid inclusion.

5.3. Concluding remarks

Extending fluid inclusion petrography and microthermometry with CL techniques and trace element analysis has shown to be helpful for deciphering the complex fluid inclusion inventory found in high-grade metamorphic rocks. It has been demonstrated that a number of microtextures directly relate to aqueous fluid inclusions, but that the interpretation of carbonic fluid inclusions almost totally relies on "traditional" fluid inclusion petrography. A part of the peak-metamorphic carbonic or aqueous-carbonic fluid inclusions almost always survives uplift. However, recognizing "primary" fluids is much more difficult than for other rock types like hydrothermal or diagenetic rocks. Textures typical for "primary" fluid inclusions, like negative crystal shape and the isolated or cluster arrangements are found in a number of igneous charnockites, but in most metamorphic granulites the earliest fluid inclusions are "hidden" in fluid inclusion clusters amongst decrepitated inclusions with highly varying densities. In the latter case detailed "fluid inclusion mapping" of selected samples appears to be quite helpful for finding relics of the peak-metamorphic fluids.

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