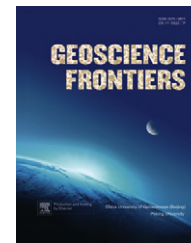


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RESEARCH PAPER

The potential role of fluids during regional granulite-facies dehydration in the lower crust

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 Solid-state dehydration;
 Petrology

Abstract High-grade dehydration of amphibolite-facies rocks to granulite-facies is a process that can involve partial melting, fluid-aided solid-state dehydration, or varying degrees of both. On the localized meter scale, solid-state dehydration, due to CO₂-rich fluids traveling along some fissure or crack and subsequently outwards along the mineral grain boundaries of the surrounding rock, normally is the means by which the breakdown of biotite and amphibole to orthopyroxene and clinopyroxene occur. Various mineral textures and changes in mineral chemistry seen in these rocks are also seen in more regional orthopyroxene-clinopyroxene-bearing rocks which, along with accompanying amphibolite-facies rocks, form traverses of lower crust. This suggests that solid-state dehydration during high-grade metamorphism could occur on a more regional scale. The more prominent of these fluid-induced textures in the granulite-facies portion of the traverse take the form of micro-veins of K-feldspar along quartz grain boundaries and the formation of monazite inclusions in fluorapatite. The fluids believed responsible take the form of concentrated NaCl- and KCl- brines from a basement ultramafic magma heat source traveling upwards along grain boundaries. Additional experimental work involving CaSO₄ dissolution in NaCl-brines, coupled with natural observation of oxide and sulfide mineral associations in granulite-facies rocks, have demonstrated the possibility that NaCl-brines, with a CaSO₄ component, could impose the oxygen fugacity on these rocks as opposed to the oxygen fugacity being inherent in their protoliths. These results, taken together, lend credence to the idea that regional chemical modification of the lower crust is an evolutionary process controlled by fluids migrating upwards from the lithospheric mantle along grain boundaries into and through the lower crust where they both modify the rock and are modified by it.

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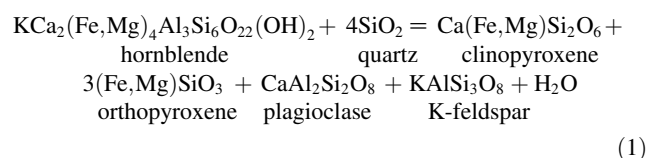
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Their presence allows for rapid mass and heat transport and subsequent mineral genesis and mineral re-equilibration in the rocks through which they pass.

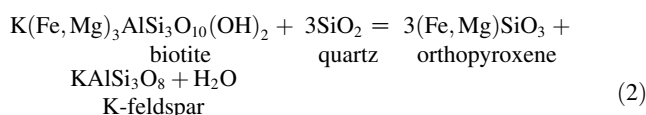
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1. Introduction

Formation of orthopyroxene-bearing granulite-facies rock (charnockite), nominally from lower-grade, H₂O-rich, amphibolite-facies rock, with a granitic to mafic igneous protolith, is a common, local to regional, dehydration process in the lower crust involving the conversion of OH-bearing biotite and amphibole to ortho- and clinopyroxene via the following generalized reactions:



and:



The process by which this occurs can either take the form of partial melting or be induced to occur due to the infiltration of low H₂O-activity fluids in a process known as solid-state dehydration. The latter process is commonly accepted to be responsible for localized (cm to m) dehydration zones with an obvious fluid source (see discussion in Harlov et al., 2006a), whilst the former is commonly accepted in the literature as one of the main mechanisms by which regional granulite-facies metamorphism occurs (Thompson, 1982; Rigby and Droop, 2011).

While there are certain evidences that metamorphism of metapelitic rocks to kyanite- and/or sillimanite-bearing granulite-facies rocks does occur as a result of partial melting, metamorphism of igneous or meta-igneous rock to charnockite is not so clearly delineated. Korzhinskii (1959, 1962) proposed that dehydration mineral reactions (1) and (2) were prompted by variations in various pervasive chemical potentials throughout the rock, such as a high $\mu_{\text{K}_2\text{O}}$ for the formation of K-feldspar and a low $\mu_{\text{H}_2\text{O}}$ (or low H₂O activity) for the stabilization of anhydrous mineral assemblages and concluded that such variations are due to fluid-rock interaction processes. Utilizing extensive field data, these ideas have been further promulgated by a series of other workers such as Perchuk and Gerya (1993, 1995), Touret (1985), and Newton et al. (1998), among others. These authors have concluded, in concordance with Korzhinskii (1959), that the two principle high-grade, low H₂O-activity fluids, characteristic of the lower crust and lithospheric mantle, which could be associated in promoting reactions (1) and (2), are CO₂-rich fluids, usually with a minor NaCl component, (cf. Aranovich et al., 1987; for background on the chemistry of such fluids see Johnson, 1991; Heinrich, 2007) and supercritical brines (cf. Aranovich and Newton, 1996, 1997, 1998; Shmulovich and Graham, 1996). The limited ability of CO₂-rich fluids to flow along grain boundaries (due to a high wetting angle; e.g. Gibert et al., 1998)

potentially make them the principle fluid involved in the formation of localized (cm to m) orthopyroxene-bearing dehydration zones. Workers, such as Newton et al. (1998), have proposed that the low wetting angle, characteristic of supercritical brines (Watson and Brenan, 1987; Gibert et al., 1998), could allow for their transport along grain boundaries over vast distances on the km scale. This would allow them to play a possible role in regional granulite-facies metamorphism by promoting the solid-state dehydration of amphibolite-facies rock via reactions (1) and (2).

In this overview, well documented textural and geochemical studies of fluid-induced, localized, orthopyroxene-bearing dehydration zones (cm to m scale) are compared with similar studies of regional orthopyroxene-bearing granulite-facies terranes (km scale), which form an integral part of a lower crustal traverse including amphibolite-facies and possible lower-grade rocks. Textural and geochemical similarities and dissimilarities between localized dehydration zones and regional granulite-facies terranes are then used to form the basis for arguments regarding the active role of fluids (supercritical brines) in the formation of the latter.

2. Localized dehydration zones

Solid-state, high-grade dehydration of hornblende- and biotite-bearing rock, by low H₂O-activity fluids, to orthopyroxene ± clinopyroxene-bearing rocks on a localized scale (cm to m) is a widespread phenomenon. Also referred to, more generally, as “incipient” or “arrested charnockitisation”, localized, solid-state dehydration zones occur worldwide in metabasites, tonalites, and granitoids (cf. Harlov et al., 2006a for background regarding specific examples). Localized dehydration zones were first described, and have subsequently been extensively documented, in the Archean amphibolite-facies terranes of southern India (e.g. Kumar, 2004).

Sources for low H₂O-activity fluids include magmatic dykes (e.g. Knudsen and Lidwin, 1996; van den Kerkhof and Grantham, 1999), volatile-rich rocks such as marbles (e.g. McLelland et al., 1988; Harlov and Förster, 2002a), or tectonic features such as faults, cracks, and/or shear zones, which act as conduits for fluid flow from a distant source (e.g. Hansen et al., 1987; Harris and Bickle, 1989; Radhika and Santosh, 1996; Harlov et al., 2006a). Fluid inclusion data indicate that CO₂, coupled with a minor NaCl-KCl-rich brine fraction, are the principal components in the dehydrating fluid (e.g. Andersen et al., 1997; Tsunogae et al., 2002; Fonarev et al., 2003; Santosh and Tsunogae, 2003; Sarkar et al., 2003). CO₂-rich fluids along the CO₂-H₂O join (500–1300 MPa; 950–1200 °C) are known to have large wetting angles such that they do not form an interconnected network along grain boundaries, but rather isolated pockets of fluid, primarily at three-grain junctions (Watson and Brenan, 1987; Brenan and Watson, 1988; Holness, 1997; Gibert et al., 1998). However, the possibility that CO₂ could also migrate over short distances as a consequence of micro-fracturing cannot be discounted (e.g. Touret and Huizenga, 2012). The inability of CO₂ to flow

easily along grain boundaries limits its ability to penetrate deep into the rock, resulting in dehydration zones extending from cm to m only. This observation is supported by $\delta^{18}\text{O}$ isotope studies of incipient charnockite formation in southern India, which suggest that, in general, high-grade, CO_2 -rich fluids have a limited infiltration range of approximately 2 m under granulite-grade conditions (Harris and Bickle, 1989).

Examples of two well-studied, localized CO_2 -induced dehydration zones include the Söndrum stone quarry, Halmstad, southwestern Sweden (Harlov et al., 2006a) and an amphibolite-granulite transition zone, Kigluaik Mountains, Seward Peninsula, Alaska (Todd and Evans, 1994; Harlov and Förster, 2002a,b). The Söndrum traverse consists of a central, 1 m wide granitic pegmatoid dyke, on either side of which extends a 2.5–3 m wide granitoid dehydration zone (650–700 °C; 800 MPa; orthopyroxene-clinopyroxene-(Ti-enriched biotite)-amphibole-garnet) overprinting a local, amphibolite-facies, migmatized granitic gneiss (amphibole-biotite-garnet). Whole-rock chemistry indicates that dehydration of the granitic gneiss was predominantly isochemical (Fig. 1; Harlov et al., 2006a).

The Seward traverse consists of a 50 m thick layer of very uniform appearing, tonalitic hornblende-biotite-plagioclase-quartz-bearing orthogneiss with a broadly tonalitic composition overlying an equally thick, coarse-grained marble layer (Todd and Evans, 1994). Proceeding away from the contact with the marble into the orthogneiss, the first 50 cm has been dehydrated at 800 °C and 800 MPa by a CO_2 -rich fluid, presumably originating from the marble. The dehydration zone consists of plagioclase, minor K-feldspar, quartz, Ti-enriched biotite, orthopyroxene, and clinopyroxene but no hornblende. This is followed by a 35 cm intermediate zone containing this assemblage plus hornblende. Fluorapatite grains in the dehydration zone are characterized by co-existing inclusions of monazite and xenotime (cf. Harlov and Förster, 2002b). Again, whole-rock chemistry indicates that the dehydration event was essentially isochemical (Todd and Evans, 1994).

Feldspar-quartz textures and chemistry in the Söndrum dehydration zone are identical to those in the surrounding granitoid gneiss (Fig. 2a, b; cf. Harlov et al., 2006a). Plagioclase is enriched in albite ($X_{\text{Ab}} \approx 0.83$ –0.84). This albitic component is reflected in the K-feldspar ($X_{\text{Ab}} \approx 0.2$ –0.3), which shows numerous exsolution

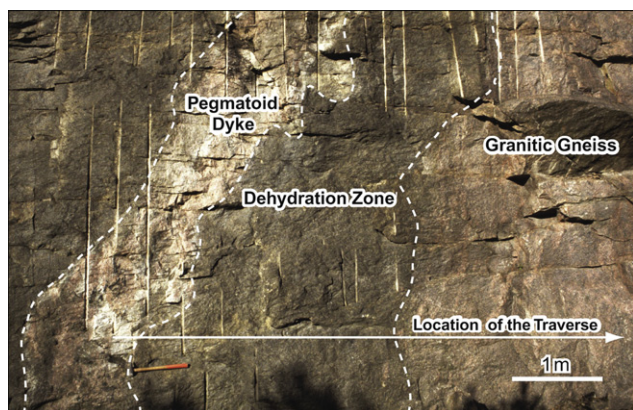


Figure 1 Söndrum dehydration zone — photograph showing the pegmatoid dyke and surrounding dehydration zone along with the approximate location of the sample traverse designated by the elongate, horizontal arrow. Bar in figure is 1 m (refer to Harlov et al., 2006a).

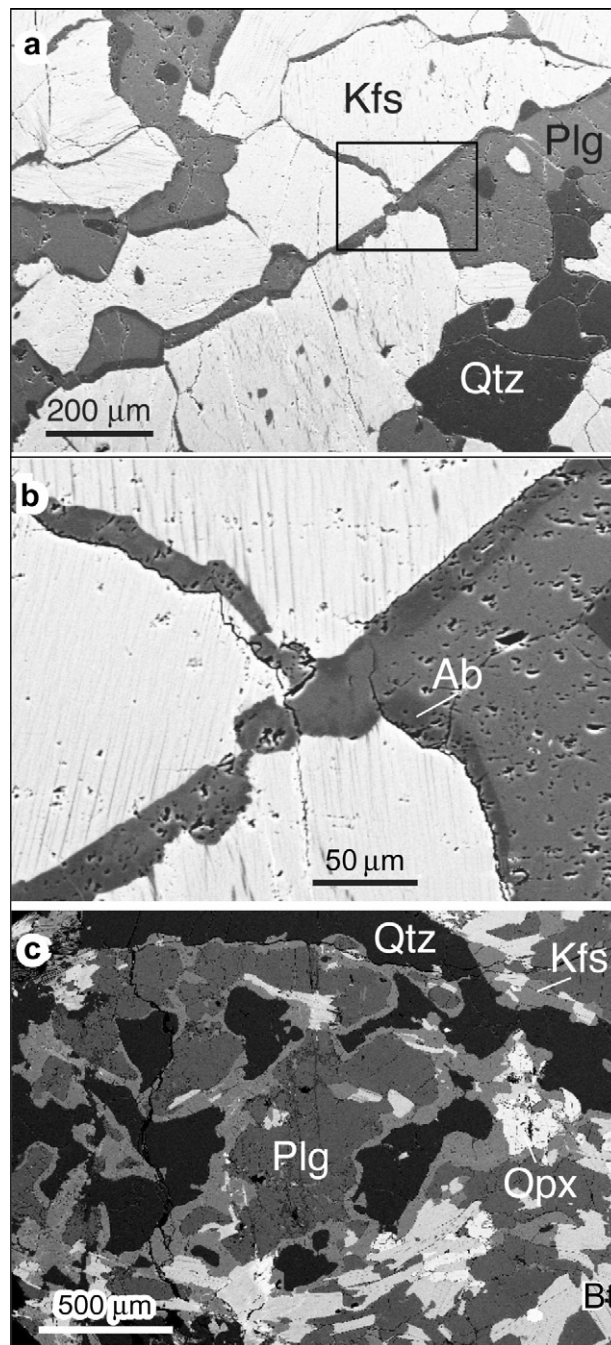
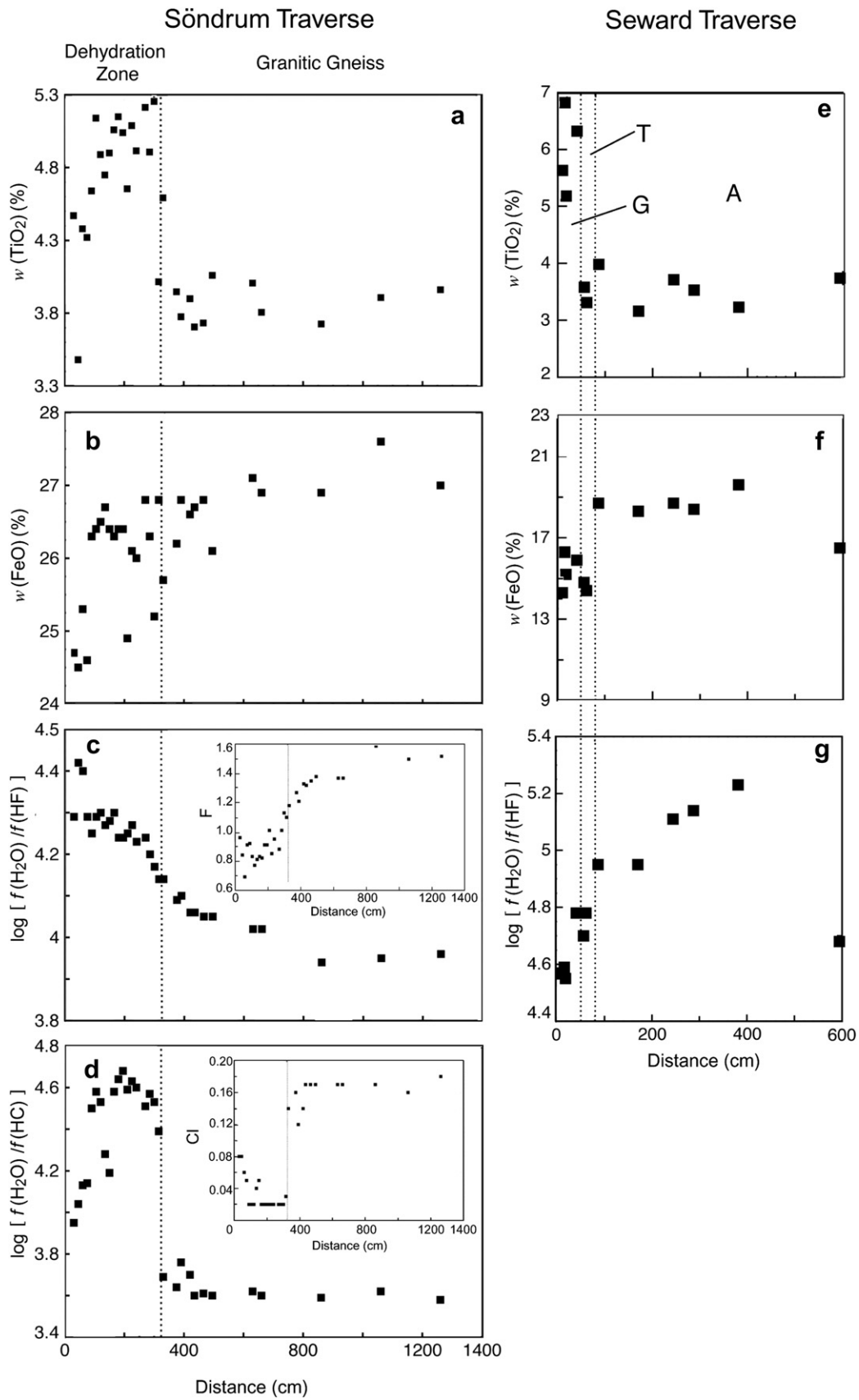


Figure 2 BSE photograph showing a typical K-feldspar-albite-plagioclase-quartz texture in the Söndrum dehydration zone [(a); cf. Harlov et al., 2006a]. The K-feldspar is enriched in an albitic component, which takes the form of albite exsolution lamellae (dark streaks in the K-feldspar). (b) Is an enlargement of the area outlined by a black box in (a). Note the presence of rims of plagioclase enriched in an albitic component, which outline the rims of the K-feldspar grains. These rims represent the partial diffusion of Na from K-feldspar into the plagioclase. (c) Shows a high-contrast BSE image of K-feldspar micro-veins along quartz-plagioclase and plagioclase-plagioclase grain boundaries in a sample from the Seward Peninsula dehydration zone (cf. Harlov and Förster, 2002a).



lamellae of albite as well as diffusion of Na into the plagioclase along the grain boundary between the K-feldspar and plagioclase (Fig. 2b). In contrast the tonalitic Seward dehydration zone is characterized by extensive micro-veins of K-feldspar along quartz/plagioclase and plagioclase/plagioclase grain boundaries (Fig. 2c). These K-feldspar micro-veins are not seen in the original, non-dehydrated orthogneiss. Here Reaction (2) is the most likely source of the K-feldspar. Presumably, the reason that K-feldspar micro-veins are not seen in the granitoid Söndrum dehydration zone is due to the abundance of K-feldspar, which would have absorbed any excess K produced during conversion of biotite and amphibole to pyroxene.

Systematic trends in the Fe-Mg silicate and fluorapatite mineral chemistry are seen in both dehydration zones going outwards from the contact with the fluid source. For example, these trends for biotite in the Söndrum dehydration zone include depletion in Fe, (Y + HREE), Na, K, F, and Cl, and enrichment in Mg, Mn, Ca, and Ti (Fig. 3a–d). Fluid inclusion chemistry is similar in all three zones and indicates the presence of a fluid containing CO₂, NaCl, and H₂O components (Harlov et al., 2006a). Water activities in the dehydration zone average 0.36, or $X_{\text{H}_2\text{O}} = 0.25$ (Harlov et al., 2006a). H₂O activities for the Seward Peninsula dehydration zone average around 0.4 (Todd and Evans, 1994). Similar to the Söndrum traverse, biotite in the Seward traverse is enriched in Ti and depleted in Fe and F (Fig. 3e–f).

3. Regional amphibolite- to granulite-facies traverses of lower crust

To date several detailed petrologic studies have been made of regional amphibolite- to granulite-facies traverses of the lower crust. These include a traverse of Carboniferous lower crust, Ivrea-Verbanò Zone, Italy (Harlov and Förster, 2002a,b) and a north-south traverse of lower Archean crust in the Dharwar craton, Tamil Nadu, southern India (Hansen and Harlov, 2007).

The Val Strona di Omegna traverse of the Ivrea-Verbanò Zone, northern Italy represents a Carboniferous age, steeply dipping, 14 km long, continuous sequence of interlayered metapelites and metabasites ranging from middle amphibolite- to granulite-facies grade. The granulite-facies, metabasite layers (tonalitic composition) are orthopyroxene-bearing whereas the metapelite layers represent sillimanite-bearing restites. The granulite-facies rock is underlain by the so-called Mafic Formation, which is presumed to have formed the heat and fluid source for the granulite-facies metamorphism (Harlov and Förster, 2002a,b).

The Tamil Nadu traverse is 95 km long from north to south and consists predominantly of tonalitic orthogneisses (Hansen and Harlov, 2007). Metamorphic grade ranges from amphibolite-facies in the north (northern amphibolite-facies zone – NAF) to moderate granulite-facies metamorphism in the center (central granulite-facies zone – CGF) and high-grade, garnet-bearing granulite-facies metamorphism in the south of the traverse (southern granulite-facies zone – SGF).

The changes in mineral assemblages and abundances are roughly paralleled by changes in the whole-rock abundances of

some LIL trace elements (Hansen and Harlov, 2007). Most intermediate and felsic gneisses in the NAF and northern CGF have moderate to high Rb (30–150 ppm), Cs (0.05–0.25 ppm), Th (4–27 ppm), and U (0.2–2.1 ppm) concentrations and K/Rb ratios below 500 (Fig. 4; Hansen et al., 1995, 2002). Low concentrations of Rb (<30 ppm), Cs (<0.005 ppm), U (<0.2 ppm), and Th (<2 ppm), and high K/Rb ratios (>500 ppm) become common in the southern, orthopyroxene-rich portion of the area, i.e. SGF and southern CGF (Fig. 4). Total REE concentrations (Fig. 4e) show greater variability with somewhat higher average values in the NAF and CGF. However, these regional trends are fairly weak.

Trends in silicate mineral chemistry are also seen in the Tamil Nadu traverse. Utilizing biotite as the most ubiquitous mineral common to most of the samples, these trends include high Ti and F in the granulite-facies zone followed by a drop off in the amphibolite-facies zone as well as steadily increasing Fe and Mn as a function of metamorphic grade (Fig. 5). In contrast, Cl appears to peak in the CGF (Fig. 5e). Similar trends are seen in the amphiboles (Hansen and Harlov, 2007) and the pyroxenes (Harlov and Hansen, 2005). These same trends in biotite mineral chemistry are also mirrored in the Ivrea-Verbanò Zone traverse going from granulite- to amphibolite-facies (Harlov and Förster, 2002a).

A striking feature common to the Seward, Ivrea-Verbanò (Harlov and Förster, 2002a) and Tamil Nadu (Hansen et al., 1995; Harlov et al., 1998; Hansen and Harlov, 2007) orthopyroxene-bearing, tonalite sample suites is the remarkable similarity in their K-feldspar-quartz and K-feldspar-plagioclase textures (Figs. 2c and 6). Under BSE imaging, samples from each of these traverses show extensive micro-veins of K-feldspar along quartz/plagioclase and plagioclase/plagioclase grain boundaries, with variable widths ranging from <0.01 to 0.4 mm sometimes grading into broad, K-feldspar-rich patches. K-feldspar micro-veins along plagioclase/plagioclase grain boundaries only occur in the immediate vicinity of quartz. K-feldspar micro-veins, along quartz grain boundaries, have the appearance of replacing the quartz giving a rounded look to the quartz grains (Fig. 6). Contact between these veins and Fe-Mg silicate minerals, such as orthopyroxene or garnet, is clean with no evidence of sheet silicates or amphiboles. Contact between the veins and Ti-enriched biotite show no sign of corrosion, incongruent melt textures, or resorption. Under crossed polars, large regions of these micro-veins are single crystals from 0.1 to >0.5 mm in length as evidenced by their uniform, undulatory extinction (cf. Harlov and Wirth, 2000; Harlov and Förster, 2002a).

Antiperthite occurs in a random scattering of plagioclase grains in samples from both the localized Seward and Söndrum dehydration zones and the Ivrea-Verbanò and Tamil Nadu regional granulite-facies suites (Fig. 7). Re-integration of the antiperthite grains gives feldspar compositions, which plot on or above the 1000 °C isotherm. This defines them as replacement antiperthite, i.e. perthites, that when re-integrated, give compositions that fall well within the two-phase field under the prevailing metamorphic conditions (800 °C and 8 kbar) (Griffin, 1969; Todd and Evans,

Figure 3 Plot of biotite mineral chemistry as a function of distance (cm) along the Söndrum traverse (cf. Fig. 1; Harlov et al., 2006a) outwards from the center of the pegmatoid dyke (0 cm) for TiO₂ (a); FeO (b); for $\log[f(\text{H}_2\text{O})/f(\text{HF})]$ (inset shows the F content as a function of distance) (c); and for $\log[f(\text{H}_2\text{O})/f(\text{HCl})]$ (inset shows the Cl content as a function of distance) (d). Dotted line designates the approximate boundary between the dehydration zone and the granitic gneiss. The first symbol in each plot designates the boundary with the pegmatoid dyke. (e–g) Shows plots of Ti, Fe, and F from the Seward Peninsula traverse from the contact at the marble layer (0 cm) outwards into the amphibolite-facies gneiss (Harlov and Förster, 2002a). G is the dehydration zone. T is a hornblende- and orthopyroxene-bearing transition zone. A is the massive amphibolite-facies layer.

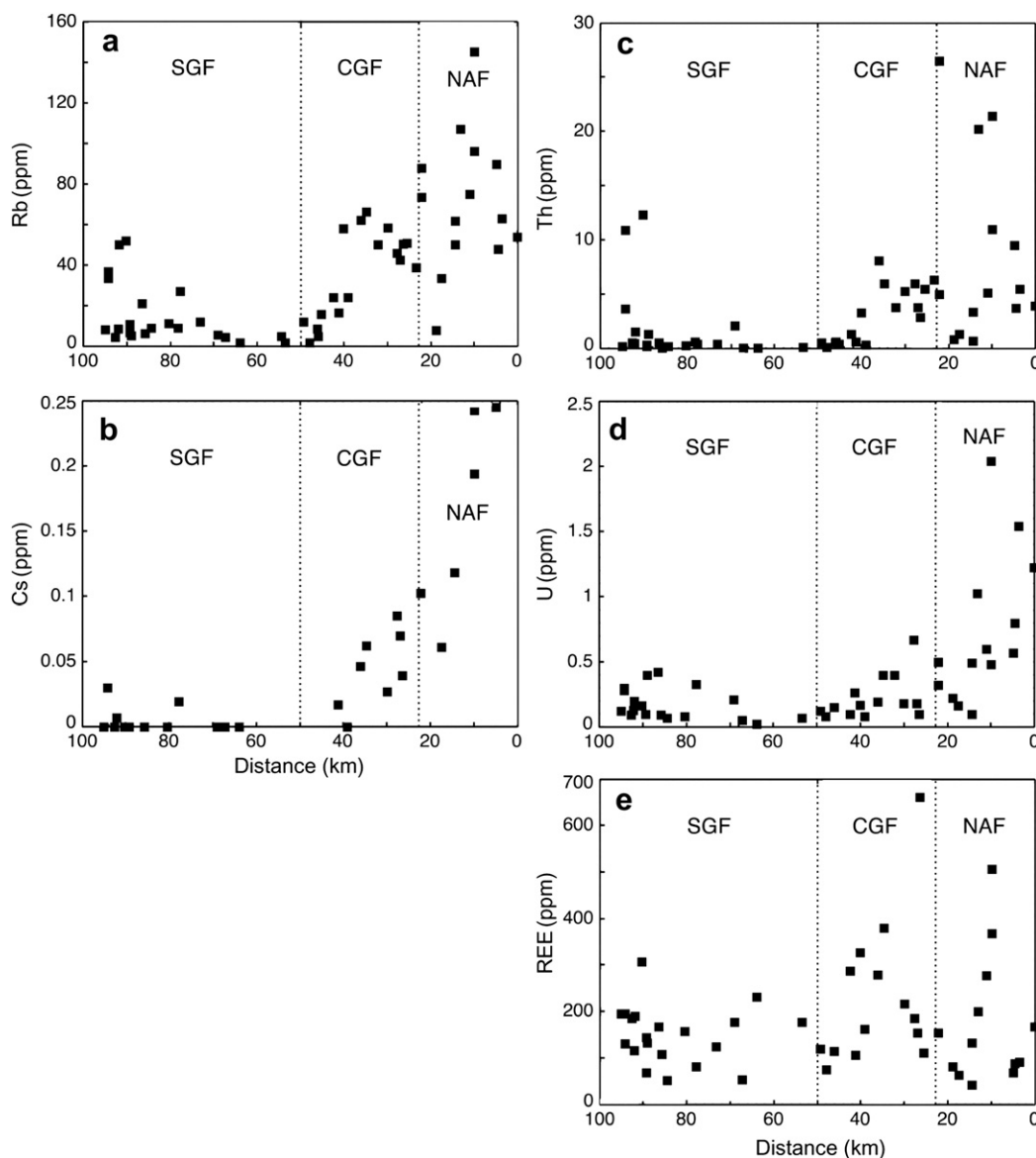


Figure 4 Plot of whole-rock Rb (a), Cs (b), Th (c), U (d), and total REE (e) (ppm) as a function of distance along the Tamil Nadu traverse going southwards from the northernmost sample in the amphibolite-facies zone (cf. Hansen and Harlov, 2007). Dotted lines designate the approximate boundaries between the higher-grade southern granulite-facies zone (SGF), the lower-grade central granulite-facies zone (CGF), and the northern amphibolite-facies zone (NAF).

1994). Replacement antiperthite is interpreted as plagioclase grains, which have been metasomatised by a K-rich fluid (see discussion in Griffin, 1969).

4. Oxidation states as a function of regional metamorphic grade

Oxidation states across the Ivrea-Verbano traverse are relatively reduced consisting of co-existing pyrrhotite, ilmenite, and rutile with an absence of magnetite (Harlov and Förster, 2002a). However, in the Tamil Nadu traverse, oxide-sulphide textures and relative oxidation states show definite trends as a function of metamorphic grade (Harlov et al., 1997; Harlov and Hansen, 2005).

Ilmenite is widespread throughout the traverse increasing in abundance with increasing metamorphic grade and occurring primarily as hemo-ilmenite (up to 60 mole percent hematite; Fig. 8a) in the highest-grade granulite-facies rocks. Magnetite is widespread throughout the traverse and is commonly associated with ilmenite and hemo-ilmenite in the form of 2- and 3-oxide grains (Fig. 8b, c, d). Magnetite and ilmenite decrease in abundance with increasing metamorphic grade. In the granulite-facies zone, reaction rims of magnetite + quartz occur along Fe-Mg silicate grain boundaries (Fig. 9). These reaction rims represent an oxidation effect resulting from the partial subsolidus reduction of the hematite component in ilmenite to magnetite, which is confirmed by the presence of composite three-oxide grains consisting of hematite, magnetite and ilmenite (Fig. 8b).

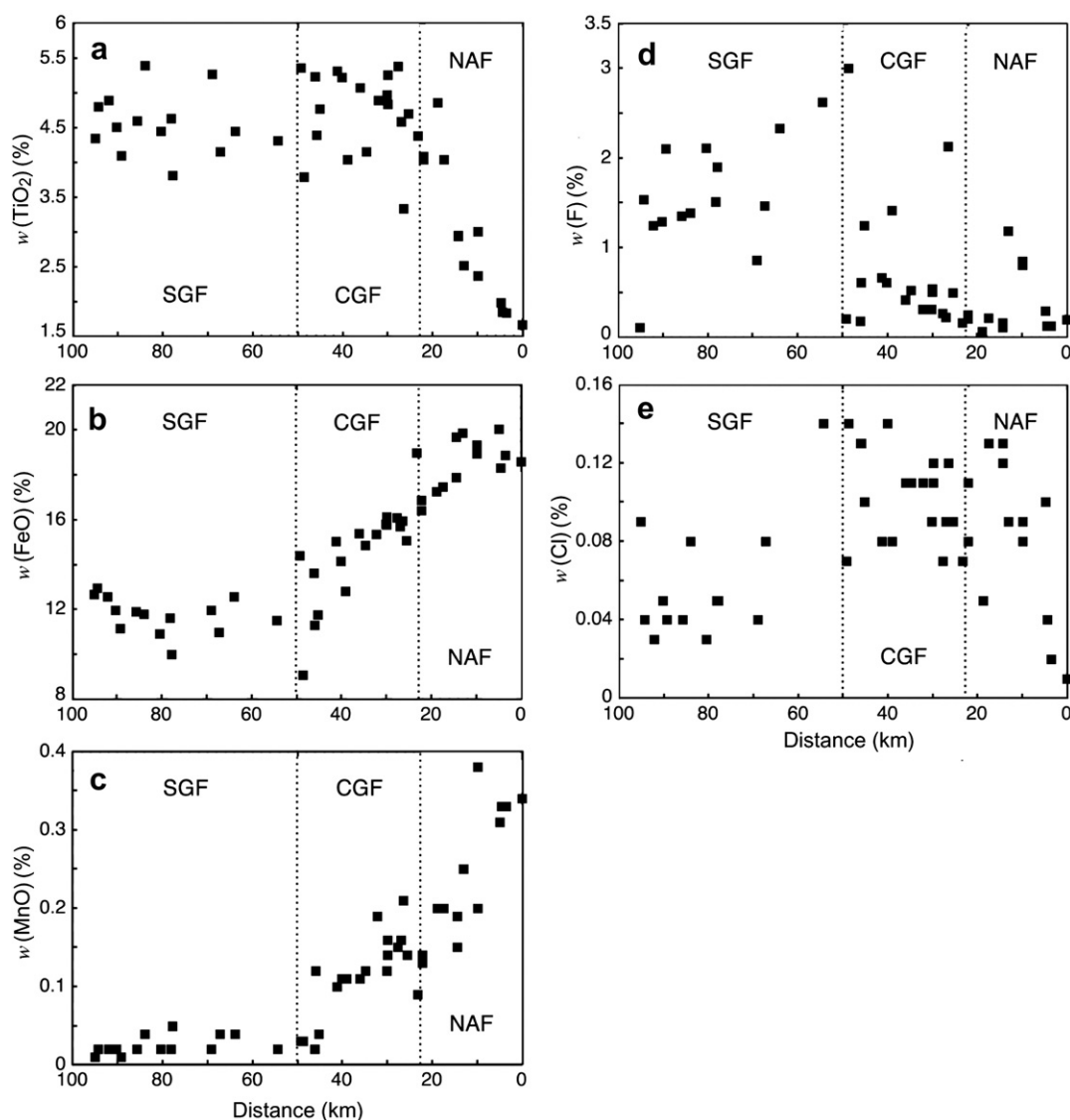


Figure 5 Plot of biotite composition for TiO_2 (a), FeO (b), MnO (c), F (d), and Cl (e), as a function of distance along the Tamil Nadu traverse going southwards from the northernmost sample in the amphibolite-facies zone (cf. Hansen and Harlov, 2007). Dotted lines designate the approximate boundaries between the higher-grade southern granulite-facies zone (SGF), the lower-grade central granulite-facies zone (CGF), and the northern amphibolite-facies zone (NAF).

Pyrite is widespread throughout the Tamil Nadu traverse increasing in abundance with increasing metamorphic grade. In contrast, pyrrhotite is found only in the highest-grade granulites. In the most oxidized granulite samples pyrite is the dominant sulfide and pyrrhotite is absent. Pyrite grains in these samples tend to have marginal alteration to magnetite along the rims, signifying a high-temperature oxidation event (Fig. 10a, b). Moderately oxidized samples have abundant co-existing pyrrhotite, pyrite, and magnetite. The most reduced granulite samples have pyrrhotite as the dominant sulfide with little or no pyrite and no co-existing magnetite. Chalcopyrite is commonly associated with pyrrhotite in all the samples. Magnetite-pyrite micro-veins along silicate grain boundaries formed over a wide range of post-peak metamorphic temperatures and pressures ranging from high-grade SO_2 to lower-grade H_2S dominated conditions (Fig. 10c; see discussion in Harlov and Hansen, 2005).

Pyroxenes from the highest-grade region of the Tamil Nadu traverse have high $\text{Mg}/(\text{Mg} + \text{Fe})$ (0.5–0.7) (Harlov et al., 1997). Utilizing three independent oxygen barometers (ferrosilite-magnetite-quartz, ferrosilite-hematite-quartz, magnetite-hematite) in conjunction with garnet-orthopyroxene exchange temperatures, the samples yield an average oxygen fugacity about 2.5 log units above the fayalite-magnetite-quartz buffer (FMQ). Less oxidized samples show some scatter with indications of having equilibrated under more reducing conditions 1 or more log units below FMQ. Internally consistent temperature- $\log f(\text{O}_2)$ arrays range from 660°C and $\log f(\text{O}_2) = -16$ bars to 825°C and $\log f(\text{O}_2) = -11.5$ bars (Harlov et al., 1997; Harlov and Hansen, 2005).

Overall oxygen fugacity decreases with decreasing metamorphic grade. This is seen in the Fe-Mg minerals, which show decreasing Mg and increasing Fe fractions with decreasing oxidation states as Fe is partitioned out of the oxides into the Fe-

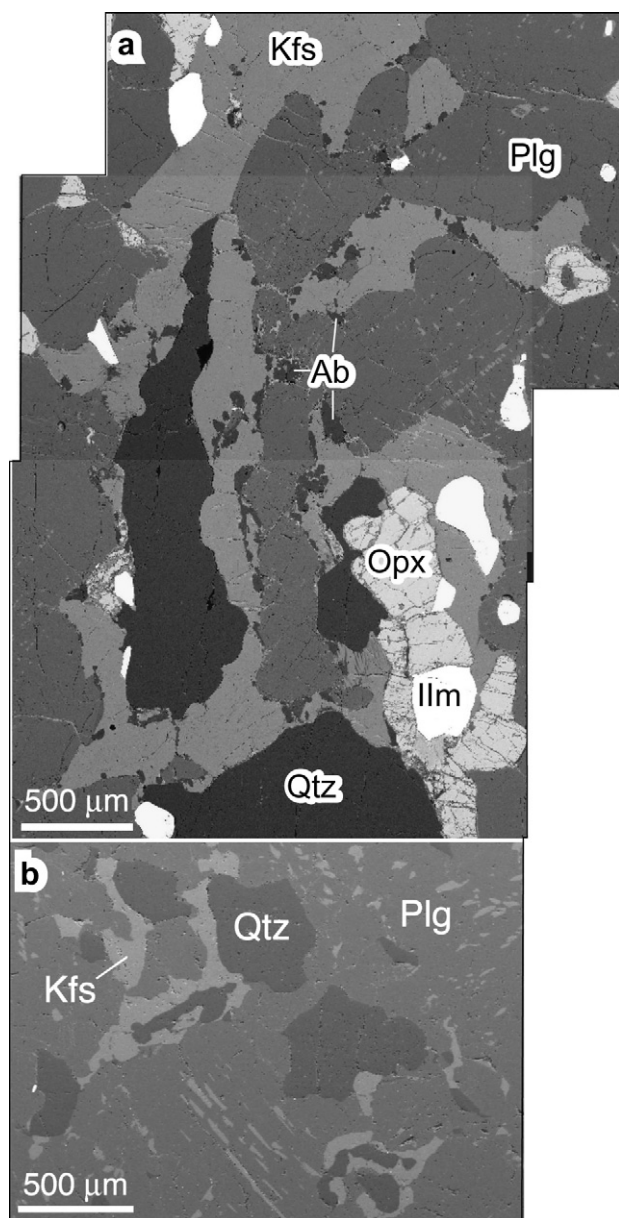


Figure 6 BSE images of K-feldspar micro-veins along quartz-plagioclase and plagioclase-plagioclase grain boundaries in a granulite-facies metabasite sample from the Ivrea-Verbano Zone traverse (Harlov and Förster, 2002a) (a) and a metatonalite from the Tamil Nadu traverse (Hansen and Harlov, 2007) (b). Note the presence of the albite rim intergrowths in the K-feldspar micro-veins in (a) and their total absence in (b).

Mg silicate minerals. The abundance of oxide minerals also decreases as a function of decreasing metamorphic grade (Harlov et al., 1997). Harlov and Hansen (2005) proposed that trends in silicate-oxide-sulfide mineral assemblages, textures, and composition along the Tamil Nadu traverse are the result of an external, infiltrating concentrated NaCl-KCl brine during high-grade metamorphism, which contains an oxidizing component such as CaSO_4 (experimentally shown to be highly soluble in NaCl-brines under high-grade conditions; cf. Newton and Manning, 2005). These same mineral assemblages were then later acted upon by post-peak, metamorphic, retrograde mineral reactions that did not involve an externally-derived fluid phase.

5. Behavior of accessory minerals as a function of metamorphic grade

5.1. Fluorapatite

Fluorapatite REE and halogen chemistry show a number of regional trends (for a more detailed discussion see Harlov, 2011). In the amphibolite-facies zone the fluorapatite grains contain no monazite inclusions in either the Ivrea-Verbano or Tamil Nadu traverses (Harlov and Förster, 2002b; Hansen and Harlov, 2007). Similar to what is seen for the localized Seward traverse, monazite inclusions and rim grains, associated with fluorapatite, first appear in the immediate region of the orthopyroxene-in isograd and are commonly found in the orthopyroxene-bearing portion of the traverse. In the orthopyroxene-bearing granulite-facies portion of the Tamil Nadu and Ivrea-Verbano traverses, monazite inclusions and rim grains occur in 80%–90% of the fluorapatite grains (Harlov and Förster, 2002b). The monazite inclusions vary from multiple very large ($>10 \mu\text{m}$) inclusions (Fig. 11a), to moderately large ($>1 \mu\text{m}$) inclusions (Fig. 11b) to numerous, very fine ($<1 \mu\text{m}$) inclusions (Fig. 11c, d). The very fine monazite inclusions tend to be elongated in cross-sections of fluorapatite cut parallel or obliquely to the *c*-axis (Fig. 11c) and as numerous small dots (Fig. 11d) in fluorapatite grains cut perpendicular to the *c*-axis. In the case of the Tamil Nadu traverse, monazite inclusions in the highest-grade granulites tend to be coarser, larger, and more sparsely distributed than observed in the lower-grade granulites (Fig. 11). Experimental evidence (e.g. Harlov and Förster, 2003; Harlov et al., 2005) indicates that these monazite inclusions and rim grains were metasomatically induced to form from the fluorapatite. Re-integration of the monazite inclusions and rim grains back into the fluorapatite host implies that the original fluorapatite was substantially more enriched in (Y + REE) (2–4 oxide wt%) than from the monazite inclusion-absent fluorapatite (0.5 oxide wt%) in the amphibolite-facies rocks of either traverse. The (Y + REE) are incorporated in the fluorapatite most commonly via the coupled substitutions $(\text{Y} + \text{REE})^{3+} + \text{Si}^{4+} = \text{Ca}^{2+} + \text{P}^{5+}$ and $(\text{Y} + \text{REE})^{3+} + \text{Na}^+ = 2 \text{Ca}^{2+}$ (cf. Harlov and Förster, 2003). Lack of inclusions in fluorapatite from the Söndrum traverse, due to the Na-rich nature of the granitoid gneiss (see Harlov et al., 2006a) and the subsequent NaCl-rich component in the CO_2 -dominated dehydrating fluid, have been shown to retard formation of monazite and xenotime inclusions in fluorapatite (Harlov and Förster, 2003). In contrast, KCl brines can promote the formation of monazite inclusions in fluorapatite (see Harlov and Förster, 2003).

5.2. Monazite

Monazite grains, independent of fluorapatite, are found in the region straddling the orthopyroxene-in isograd in both the Ivrea-Verbano and Tamil Nadu traverse (cf. Harlov and Förster, 2002b; Hansen and Harlov, 2007) (Fig. 12). Independent monazite grains all have detectable Th typically ranging from 1% to 10% $w(\text{ThO}_2)$, though values of up to 18% $w(\text{ThO}_2)$ are found. In the Tamil Nadu traverse, whole-rock Th concentrations drop sharply in approximately the same area where independent monazite grains almost completely disappear (cf. Fig. 4c), suggesting that independent monazite grains are the most important host for Th in this area. Uranium abundances also decrease in about the same region (Fig. 4d). However, since the monazite grains contain only small amounts of U, another mineral, probably zircon, must be the major host for U. The monazite grains range from featureless to highly

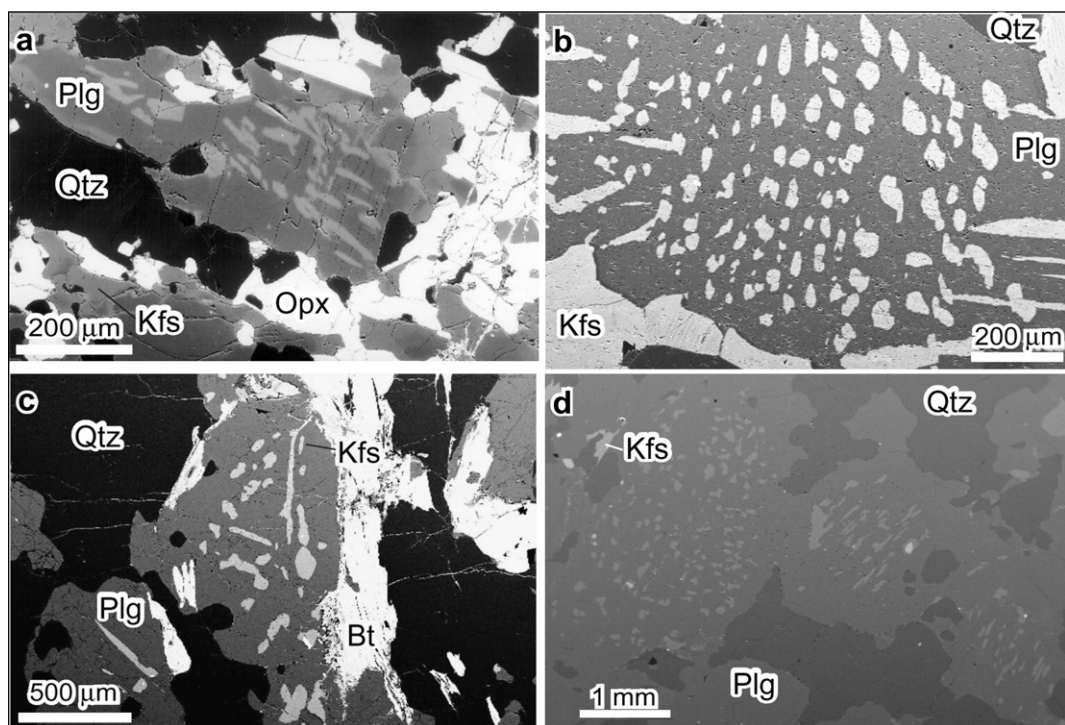


Figure 7 Back-scattered electron images of replacement antiperthite in plagioclase grains from the Seward Peninsula traverse (Harlov and Förster, 2002a) (a), the Söndrum traverse (Harlov et al., 2006a) (b), the Ivrea-Verbano Zone traverse (Harlov and Förster, 2002a) (c), and the Tamil Nadu traverse (Hansen and Harlov, 2007) (d).

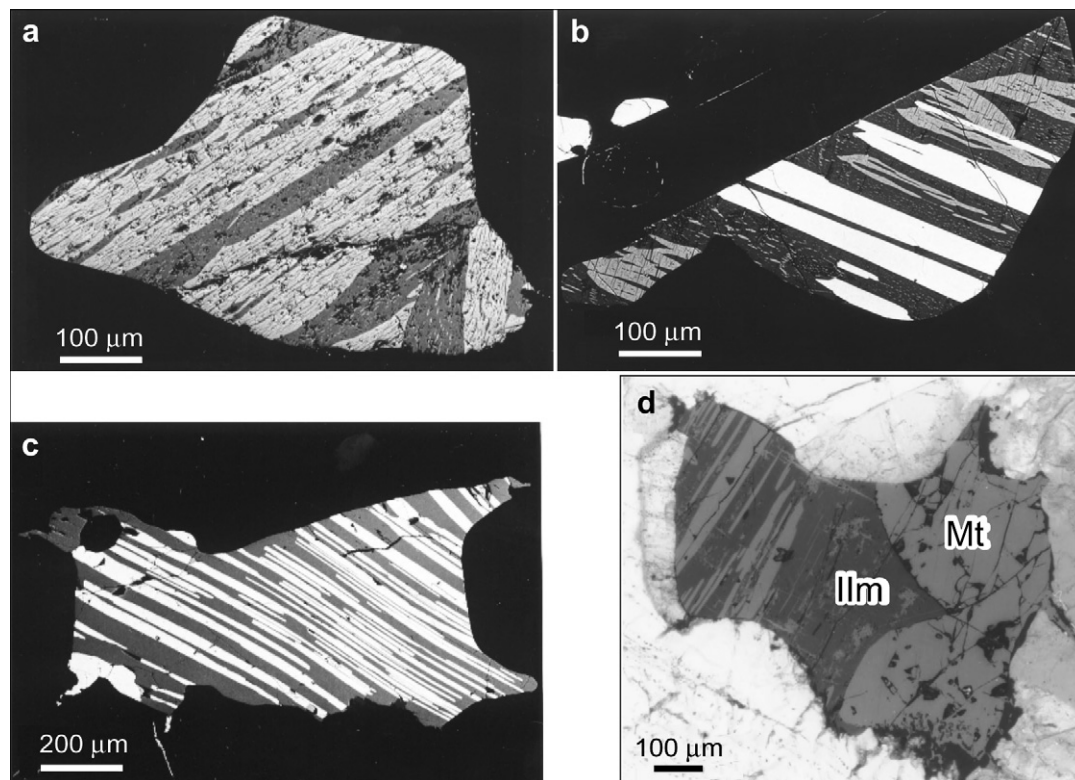


Figure 8 Back-scattered electron images of hemo-ilmenite and magnetite-ilmenite grains from the Tamil Nadu traverse. All figures are taken from Harlov and Hansen (2005). These include examples of a typical hematite-rich hemo-ilmenite grain with extensive primary and second generation hematite exsolution lamellae (light gray) in ilmenite (dark gray) (a); a three-oxide grain containing magnetite laths (white) and hematite lamellae and lenses (intermediate gray) within an ilmenite grain (dark gray) (b); a magnetite-ilmenite grain, which contains laths of magnetite (light gray) in ilmenite (dark gray) (c); and a reflected light photograph of a second magnetite-ilmenite grain, which, in addition to showing magnetite laths (light gray) in ilmenite also shows a large discrete magnetite grain adjacent to the ilmenite grain (d).

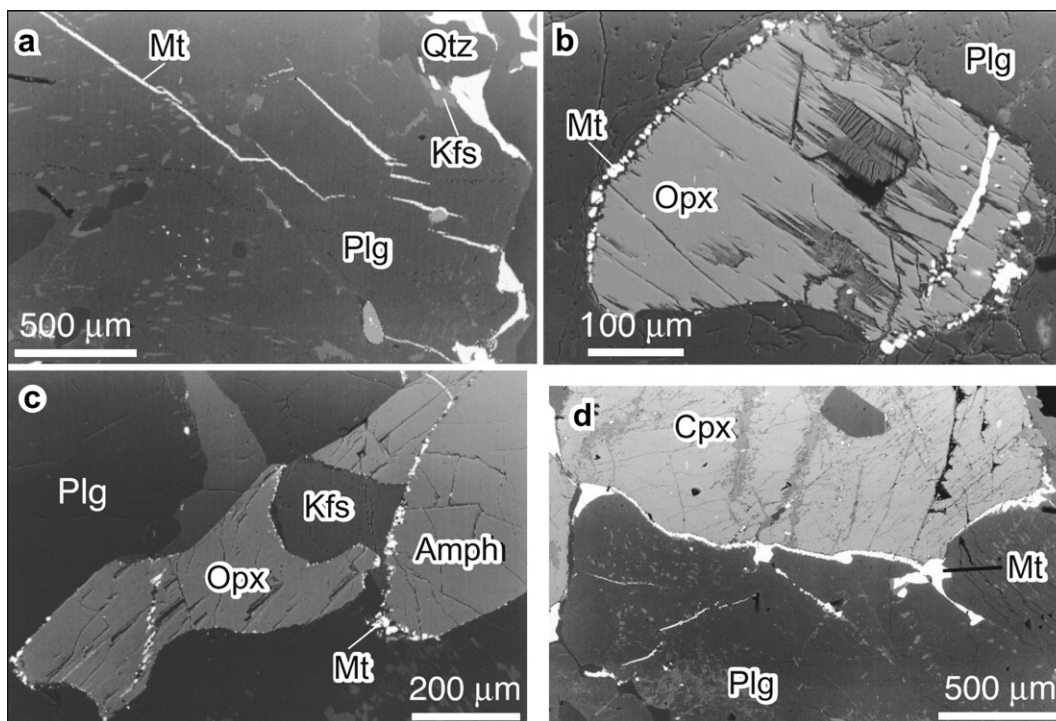


Figure 9 Back-scattered electron photos of magnetite-silicate textures from the Tamil Nadu traverse. All figures are taken from Harlov and Hansen (2005). (a) Shows late stage magnetite (Mt) micro-veins within plagioclase (Plg) along cracks, which appear to be apparent cleavage planes. Other minerals include K-feldspar (Kfs) and quartz (Qtz). (b–d) Show reaction rims of magnetite, associated with quartz, rimming orthopyroxene (Opx), amphibole (Amph), and clinopyroxene (Cpx).

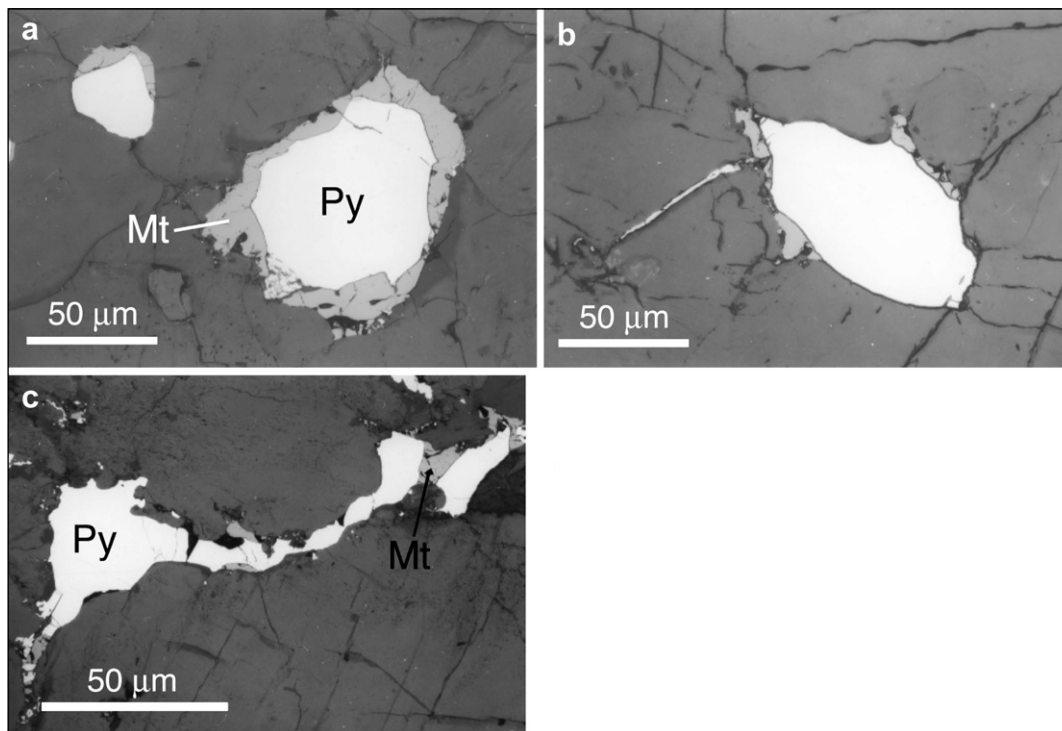


Figure 10 Reflected light images of a variety of pyrite-magnetite associations from the Tamil Nadu traverse varying from magnetite (Mt) totally surrounding the pyrite (Py) grain as a thick rim in (a) to a thin partial rim of magnetite associated with the pyrite grain (b). (c) Shows a third type of texture consisting of a massive pyrite micro-vein associated with isolated blebs of magnetite. All figures are taken from Harlov and Hansen (2005).

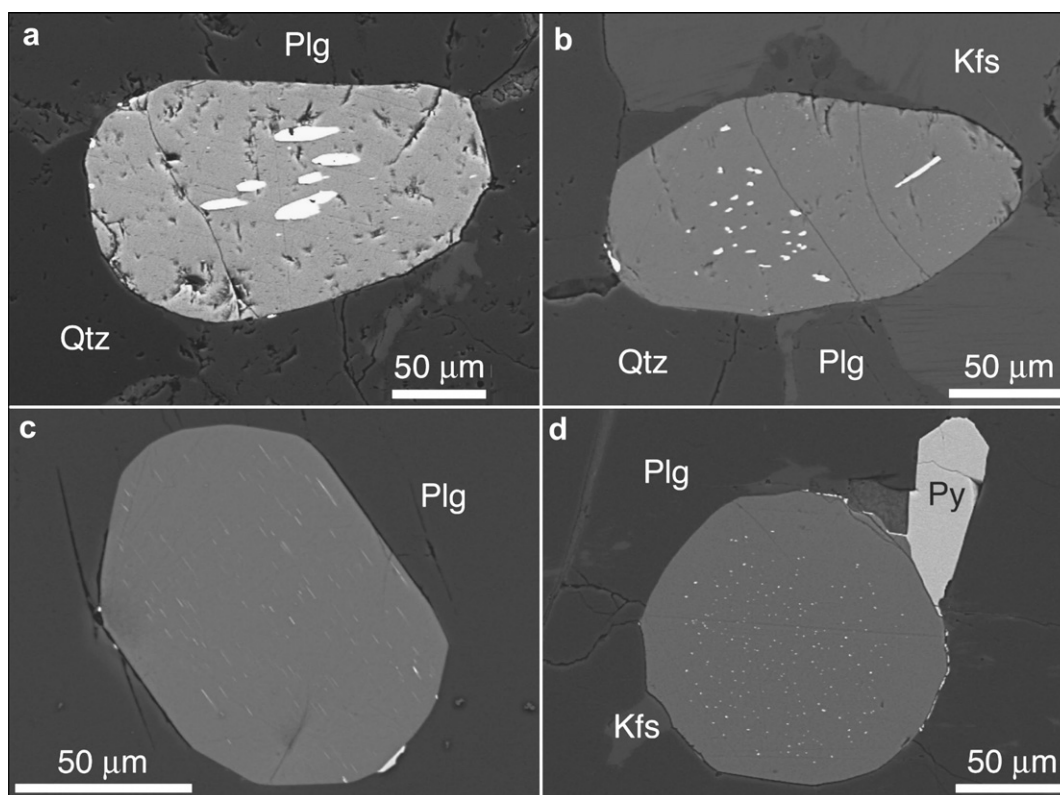


Figure 11 High-contrast back-scattered electron images of a variety of fluorapatite (dark gray) texture with monazite inclusion and rim grains (bright) in a series of samples across the Tamil Nadu traverse. All figures are taken from Hansen and Harlov (2007). (a) Fluorapatite grain with moderate to large sized monazite inclusions partially elongated parallel to the *c*-axis. (b) Fluorapatite grain with moderately sized monazite inclusions; a fine powdering of very small (<0.5 μm) monazite inclusions is seen in some areas. (c) Fluorapatite grain with numerous, very thin monazite inclusions preferentially elongated parallel to the *c*-axis. Monazite rim grain on lower right side. (d) Small monazite inclusions (<1 μm) in a fluorapatite grain cut perpendicular to the *c*-axis. Note, because the monazite grains are elongated parallel to the fluorapatite *c*-axis in (d), they appear as bright dots due to the cut of the fluorapatite crystal. Note the partial (bright) rim of secondary allanite.

and variably textured. These textures typically takes the form of a series of curvilinear, ThSiO₄- and ThCa(PO₄)₂-enriched, lobate-like intergrowths with sharp compositional boundaries occurring both along grain rims and in grain interiors, which overprint earlier, probable igneous zoning (Fig. 12). These intergrowths are very similar to intergrowths produced experimentally by the reaction of Th-bearing monazite with high pH fluids such as NaOH, KOH, and Na₂Si₂O₅ + H₂O (Harlov et al., 2011). Dating these intergrowths can also potentially date the metasomatic event responsible for them (Williams et al., 2011; also see Harlov et al., 2011).

5.3. Titanite and allanite

Titanite, commonly rimming ilmenite as a reaction texture, is widespread in the amphibolite-facies region of the Tamil Nadu (Fig. 13a) and Ivrea-Verbano Zone traverses (Fig. 13b). It is totally absent in the granulite-facies zone of either traverse. The titanite is relatively rich in *w*(Y + REE) (up to 2.5%), contains variable amounts of Nb₂O₅, negligible amounts of ThO₂, UO₂, and ZrO₂, and substantial amounts of F. Titanite-ilmenite-silicate relationships are discussed in detail in Harlov and Hansen (2005) and Harlov et al. (2006b).

Allanite is also found as patchy, large (10–100 μm), independent grains in some samples from the amphibolite-facies zone in either traverse (Harlov and Förster, 2002b; Hansen and Harlov,

2007), as well as occasional thick rims on monazite (compare Figs. 12d and 13c). Independent allanite grains contain moderate amounts of *w*(ThO₂), generally less than 1%.

5.4. Comparisons with Rogaland-Vest-Agder, southwestern Norway

Similar to what is seen in the Ivrea-Verbano and Tamil Nadu traverses, Bingen et al. (1996) also describe an amphibolite- to granulite-facies transition within orthogneisses from Rogaland-Vest-Agder, southwestern Norway in which monazite only occurs in a relatively narrow zone between the clinopyroxene- and orthopyroxene-in isograds. The monazite also commonly shows curvilinear, ThSiO₄- and ThCa(PO₄)₂-enriched, lobate-like intergrowth textures. Bingen et al. (1996) attribute the appearance of monazite at the clinopyroxene-in isograd to a prograde reaction involving the breakdown of allanite, titanite, and amphibole and the decline in monazite abundance after the orthopyroxene-in isograd to a prograde fluorapatite-forming reaction in which the fluorapatite was now the principal REE host. These observations are quite similar with what is seen in the Ivrea-Verbano and Tamil Nadu traverses. That is, discrete monazite grains tend to occur in a relatively narrow, clinopyroxene-rich region (straddling the orthopyroxene-in isograd) separating a titanite-allanite-bearing amphibolite-facies zone from a granulite-facies zone which

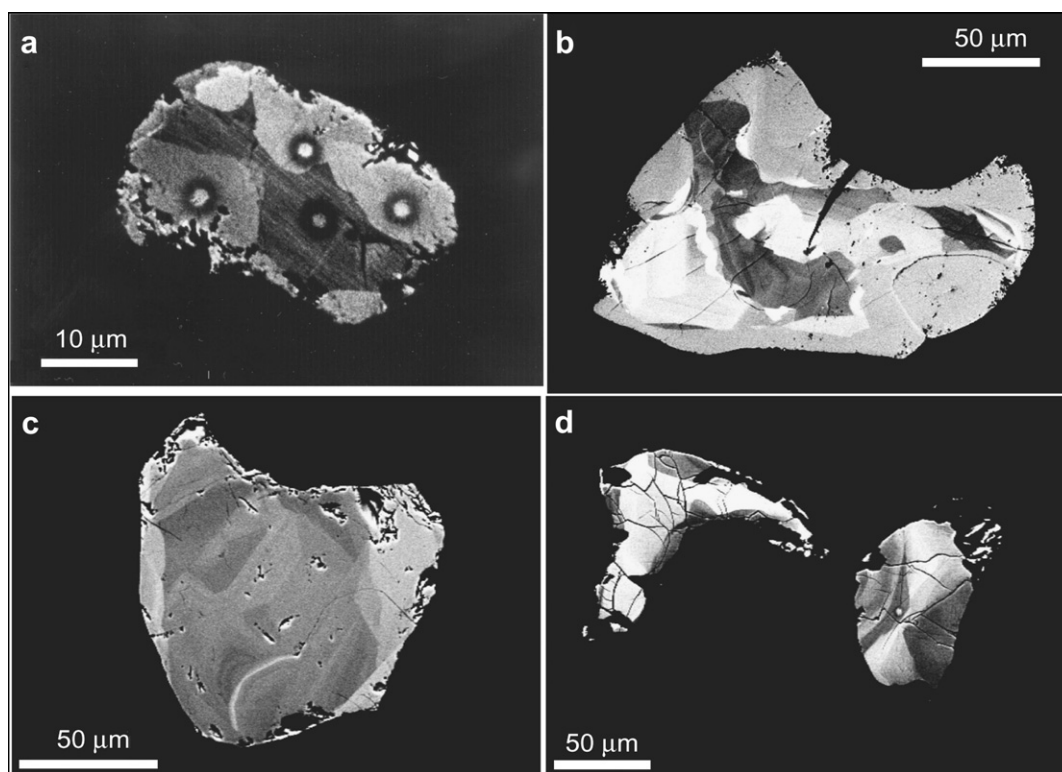


Figure 12 High-contrast BSE images of a series of independent monazite grains, i.e. not associated with fluorapatite. Zoned monazite grains showing various curvilinear ingrowths: the brighter the area, the higher the $\text{ThSiO}_4\text{-CaTh}(\text{PO}_4)_2$ component. (a, b) Are taken from the Ivrea-Verbano Zone traverse (Harlov and Förster, 2002b). (c, d) Are taken from the Tamil Nadu traverse (Hansen and Harlov, 2007). Dots on (a) are electron microprobe analysis points.

contains REE-enriched fluorapatite. Such trends may be a common feature in amphibolite- to granulite-facies traverses of granitoid rocks in general.

6. The role of low H_2O -activity fluids during large-scale dehydration of the lower crust

That fluid-induced solid-state dehydration occurs in the lower crust, at least on the local cm to m scale, is self-evident based on numerous studies of localized dehydration zones (for a more detailed list see Harlov et al., 2006a). In each of these cases, including the Seward Peninsula and Söndrum traverses described in this overview, there is absolutely no evidence of any sort of partial melting occurring. What, perhaps, is more interesting is that reactions (1) and (2) are occurring in nominally amphibolite-facies terranes, which, under the prevailing p - T conditions (>600 °C, >500 MPa), do not themselves experience any sort of granulite-facies metamorphism and/or partial melting. This strengthens the argument that the solid-state dehydration observed in these localized zones is fluid-induced. Consequently, comparison of various petrological and geochemical features between localized dehydration zones and more regional granulite-facies terranes, that are part of recognizable lower crustal traverses, can be useful in either strengthening or weakening arguments that the granulite-facies metamorphism observed in these lower crustal traverses could also have been a product of primarily fluid-induced, solid-state dehydration.

Features common to the orthopyroxene-bearing portion of the Seward, Ivrea-Verbano, and Tamil Nadu traverses include (1) K-feldspar micro-veins along the quartz-plagioclase grain boundaries (at least partly the result of the breakdown of biotite + amphibole to orthopyroxene) and (2) monazite inclusions in fluorapatite, which have been experimentally demonstrated to be fluid-induced. Features common to all four traverses include (1) similar trends in silicate mineral cation chemistry and (2) no obvious evidence of partial melting, such as restites, during the dehydration event. In the Seward, Söndrum, and Tamil Nadu traverses, this has been confirmed by the major element whole-rock chemistry of the dehydrated and non-dehydrated portions of the traverse, which are virtually the same (cf. Harlov et al., 2006a; Hansen and Harlov, 2007). In the two lower crustal traverses described here (Ivrea-Verbano Zone, Tamil Nadu, and Rogaland-Vest-Agder), gross similarities are also seen in accessory mineral behavior and chemistry with regard to REE and Th hosting (cf. Harlov, 2011), i.e. REE are hosted in fluorapatite in the granulite-facies rocks, in monazite in the region of the orthopyroxene-in isograd, and in titanite and/or allanite in the amphibolite-facies rocks. This similarity also extends to certain broad trends in silicate and halogen chemistry, though the behavior of certain cations (e.g. Fe and Mg) and anions can be affected by evolving external oxidation states (e.g. the highly oxidized Tamil Nadu traverse vs. the relatively reduced Ivrea-Verbano Zone traverse) as well as by the specific chemistry and evolution of the dehydrating fluid (e.g. compare the behavior of F in the Söndrum and Seward traverses in Fig. 3). The presence of

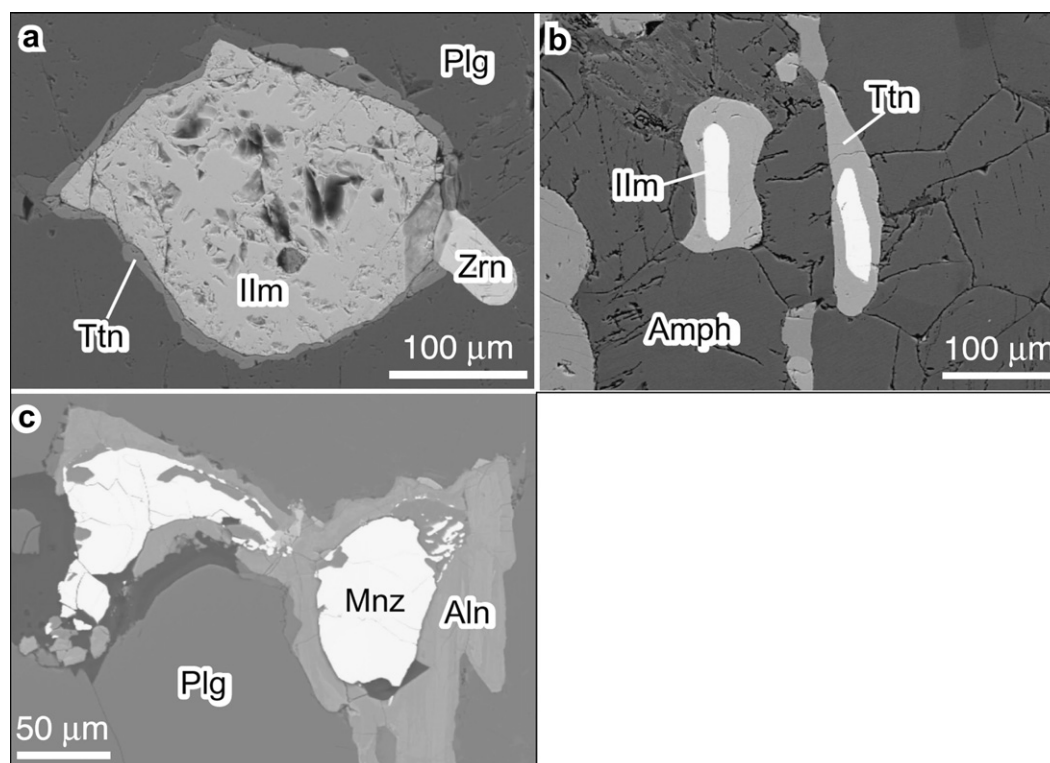


Figure 13 BSE photos of ilmenite-titanite and monazite-allanite relationships. (a) Shows a thin rim of titanite (Ttn) around ilmenite (Ilm) from the southern part of the northern amphibolite-facies zone of the Tamil Nadu traverse. Other minerals are zircon (Zrn) and plagioclase (Plg). (b) Shows thick titanite rims around ilmenite from the amphibolite-facies region of the Ivrea-Verbano Zone traverse (cf. Harlov and Förster, 2002a). (c) Shows allanite rimming monazite in a sample from the region of the orthopyroxene-in isograd, Tamil Nadu traverse (see Fig. 11d). (b, c) Are taken from Hansen and Harlov (2007).

a heat and fluid source, while cut off by shear zones for the Tamil Nadu traverse, is still present at the base of the Ivrea-Verbano Zone traverse in the form of the Mafic Formation, which approximates the mafic to ultramafic magmas at the base of the crust hypothesized to be responsible for granulite-facies metamorphism overall (Newton et al., 1998; Harlov and Förster, 2002a). Such magmas, when cooling, would give off low water activity fluids with both CO₂ and brine components (see discussion in Newton et al., 1998). Depending on the permeability of the rocks, the fluid naturally will rise upwards with varying degrees of success (see discussion in Connolly and Podladchikov, 2012). For example, the CO₂ will mostly travel along zones of weakness such as faults and shear zones, with a minority being mostly trapped along grain boundaries in the surrounding rock (due to their high wetting angles) as the ever abundant CO₂-rich fluid inclusions generally found in these granulite-facies terranes (e.g. Touret, 1985). The brines will separate out from the CO₂-rich fluid and have a far greater chance of traveling along grain boundaries due to their low wetting angles. This potentially allows them to flow along grain boundaries over relatively large distances, e.g. on the km scale (Newton et al., 1998). As a result, while the CO₂ is confined predominantly to shear zones and faults (locally dehydrating the surrounding rock), the brines have a real chance of moving upwards through the rock along grain boundaries as a dehydrating reaction front which, as it dehydrates the rock, is itself enriched in H₂O such that at some *p-T* regime, along the traverse, it loses its ability to convert amphiboles to pyroxenes. In either case these fluids would also be highly efficient in transferring heat from the crust-mantle boundary into the lower to mid

crust. Naturally the chemistry of such fluids, and their local interaction with minerals, is a matter of some speculation though experimentally it has been demonstrated that monazite and/or xenotime inclusions will form in fluorapatite in the presence of both KCl brines and CO₂-H₂O fluids (cf. Harlov and Förster, 2003). In addition, the complex zoning seen in the monazite characteristic of these terranes (specifically see Fig. 12a, b) has also been shown to be fluid-induced in the form of hydroxide-bearing fluids such as KOH, NaOH, and Na₂Si₂O₅ + H₂O (Harlov et al., 2011), all three of which would be presumed to exist in the K-feldspar- and plagioclase-rich gneisses of each of these traverses. The high solubility of CaSO₄ in these brines adds another component with respect to their being able to externally impose an oxidation state on the rocks through which they pass. The presence of REE-bearing titanite rims around ilmenite point to the presence of an active Ca component in the fluid in the amphibolite-facies *p-T* regime, perhaps, in the case of the Tamil Nadu traverse, due in part to a CaSO₄ component in the fluid. Though for both the Tamil Nadu and Ivrea-Verbano Zone traverses, the presence of Ca-bearing minerals, such as amphibole and plagioclase, would also provide a rich source of Ca.

Based on the observations contained above, a strong case can certainly be made that dehydration of the tonalitic-metabasic, lower crust during granulite-facies metamorphism, can occur at least partially as a result of fluid-induced solid-state dehydration. While knowledge is still somewhat limited regarding the states of such fluids at granulite-facies *p-T*, experimental studies of concentrated brines at high *p-T* indicate that the H₂O activity goes as $X_{\text{H}_2\text{O}}^2$, allowing for much more H₂O-rich fluids to dehydrate the rock than

what might be normally expected (Aranovich and Newton, 1996, 1997, 1998; Shmulovich and Graham, 1996). Interestingly, at p - T below 400 MPa and 600 °C, the H₂O activity in brines goes as $X_{\text{H}_2\text{O}}$, i.e. approximately at mid amphibolite-facies grade, thus dramatically decreasing their power to dehydrate.

Experimental studies, along the albite-H₂O join, indicate a lack of a miscibility gap at high p - T (650–760 °C; 1450 MPa) (cf. Shen and Keppler, 1997). Similar experimental studies, primarily at subduction zone p - T conditions, of hydrous melts and aqueous fluids above a second critical point, again indicate that complete miscibility exists between hydrous fluids and a variety of different melts at granulite-facies p - T conditions (Shen and Keppler, 1997; Bureau and Keppler, 1999; Stalder et al., 2001; Manning, 2004; Kessel et al., 2005; Hermann et al., 2006; Hack et al., 2007; Klimm et al., 2008). Consequently where fluids end and melts begin, especially in the supercritical case, is somewhat of a moot point especially when the feldspars are involved.

One thing that is certain is that more experimental work is needed in this area, especially regarding the behavior and logistics of such transitional fluids that are neither fluids nor melts (e.g. Na, K, Ca brines and feldspar melts) and their subsequent behavior with regard to mass transport of REE, Th, U, Rb, Sr, etc., i.e. their depletion or enrichment in the granulite- and amphibolite-facies rock characterizing these traverses of lower crust. A second line of experiments should then explore the behavior of minerals (especially monazite, xenotime, zircon, allanite, titanite, and fluorapatite) in such transitional fluids. Such experimental data, coupled with natural observation, both contained within this review as well as in additional future studies of similar traverses of lower crust, would go a long way in furthering our understanding regarding the role of fluids in the formation, evolution, and stability of the lower crust.

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