

High-Grade Fluid Metasomatism on both a Local and a Regional Scale: the Seward Peninsula, Alaska, and the Val Strona di Omegna, Ivrea–Verbano Zone, Northern Italy. Part I: Petrography and Silicate Mineral Chemistry

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RECEIVED DECEMBER 21, 2000; REVISED TYPESCRIPT ACCEPTED NOVEMBER 9, 2001

K-feldspar–plagioclase–quartz mineral textures as well as biotite and hornblende compositions are compared for suites of metamorphosed mafic rocks from two widely separated traverses. A portion of either traverse has experienced a high-grade dehydration event transforming it from an H₂O-rich, hornblende-bearing zone to an H₂O-poor, hornblende-free, orthopyroxene-bearing, ‘granulite facies’ zone at 700–800°C and 7–8 kbar. In the Kigluaik Mountains, Seward Peninsula, Alaska, dehydration took place over an 85 cm thick layer of metatonalite in contact with a marble during regional metamorphism and involved a CO₂-rich fluid, whereas for the Val Strona di Omegna traverse, Ivrea–Verbano Zone, northern Italy, dehydration took place over a 3–4 km thick sequence of metabasites interlayered with metapelites in a contact metamorphic event involving basaltic magmas intruded at the base of the sequence. Orthopyroxene-bearing samples from both dehydration zones show micro-veins of K-feldspar along quartz and plagioclase grain boundaries as well as replacement antiperthite in plagioclase. K came primarily from the breakdown of hornblende + quartz to orthopyroxene ± clinopyroxene, feldspar and fluid. Biotite either was stabilized or formed in the dehydration zones and is enriched in Ti, Mg, F and Cl relative to biotite in the amphibolite facies zone.

KEY WORDS: KCl–NaCl brines; metasomatism; granulite facies metamorphism; charnockite–enderbite; orthopyroxene; K-feldspar; biotite; hornblende

INTRODUCTION

During granulite facies metamorphism, H₂O-bearing minerals such as hornblende and biotite break down, in the presence of quartz, into orthopyroxene, clinopyroxene, feldspar, and a fluid phase. Vapour absent melting has been proposed by a number of workers as the principal force behind these dehydration reactions (e.g. Clemens, 1990; Thompson, 1990). However, what ultimately induces these minerals to break down is apparently not only limited simply to pressure, temperature, and subsequent spontaneous partial melting. Solid-state dehydration induced by pervasive fluid infiltration, without any direct evidence of a melt being present, has been shown to be a distinct reality, at least over limited distances. Geological evidence exists that, over a scale of centimetres to a few metres, localized dehydration zones in meta-igneous rocks are fluid induced under granulite facies conditions (e.g. Janardhan *et al.*, 1982; Allen *et al.*, 1985; Hansen *et al.*, 1987; Stähle *et al.*, 1987; McLelland *et al.*, 1988; Harris & Bickle, 1989; Santosh *et al.*, 1990, 1991; Harris *et al.*, 1993; Raith & Srikantappa, 1993; Todd & Evans, 1994; Harley & Santosh, 1995; Knudsen & Lidwin, 1996; Satish-Kumar & Santosh, 1998; van den Kerkhof & Grantham, 1999; Dobmeier & Raith,

*Extended dataset can be found at <http://www.petrology.oupjournals.org>

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2000). The principal component in these low H_2O activity fluids is conjectured, from both stable isotope and fluid inclusion data, to be CO_2 .

Other workers have expanded on the possible role of low H_2O activity fluids, suggesting that, on a more regional scale, concentrated or supercritical Cl-rich brines could also play a role in inducing the transformation of hornblende-bearing gneiss to orthopyroxene-bearing granulite (e.g. Aranovich *et al.*, 1987; Hansen *et al.*, 1995; Franz & Harlov, 1998; Harlov *et al.*, 1998; Newton *et al.*, 1998). In a number of these rocks, K-feldspar reaction textures (micro-veins) along quartz–plagioclase and plagioclase–plagioclase grain boundaries (e.g. Hansen *et al.*, 1995; Franz & Harlov, 1998; Harlov *et al.*, 1998; Harlov & Wirth, 2000; Perchuk *et al.*, 2000) as well as replacement antiperthite (Griffin, 1969; Todd & Evans, 1994) have been proposed as evidence for the presence and passage of these low H_2O activity fluids, whether CO_2 or brines. The K required for these micro-veins and the replacement antiperthite has been suggested to have either already been an integral part of the infiltrating fluid or to have come from the localized, fluid-induced, solid-state breakdown of biotite and/or hornblende to orthopyroxene, clinopyroxene and feldspar in the presence of quartz. However, it has not been conclusively demonstrated whether concentrated and/or supercritical brines could be responsible for initiating the ‘dehydration’ event associated with regional granulite facies metamorphism. In retrospect, however, the composition of common OH-bearing minerals, such as biotite, hornblende and apatite, might be expected to record evidence of these brines both in the ‘fluid-induced’ dehydration zone as well as outside of it.

In this study, two traverses consisting of orthopyroxene-bearing granulite facies rocks and their precursor amphibolite facies rocks are compared. The first traverse is taken from a metatonalite in contact with a marble from the Seward Peninsula, Alaska (SP), whereas the second consists of a series of intervening metabasite and metapelite layers from the Val Strona di Omegna of the Ivrea–Verbano Zone, northern Italy (IVZ). Both the SP metatonalites and IVZ metabasites experienced a high-grade dehydration event transforming them from hornblende-bearing rocks to hornblende-free, orthopyroxene ($\pm$ clinopyroxene)-bearing granulite facies rocks at approximately the same temperature and pressure (700–800°C, 7–8 kbar). The basic difference is that for the SP this dehydration event took place over 85 cm and has been demonstrated, using stable isotope data ($\delta^{18}O$) and modal mineral analysis, to have involved a CO_2 -rich fluid given off by an underlying marble layer in contact with the metatonalite gneiss (Todd & Evans, 1993, 1994), whereas for the IVZ, a 3–4 km thick section of the metabasite layers was dehydrated in an event that previous workers such as Henk *et al.* (1997) have proposed

involved the heat given off by a series of sheet-like intrusions of basalt magma at the base of the original traverse. Other workers, however, such as Franz & Harlov (1998), have proposed that, in addition to heat, the infiltration of concentrated or supercritical brines, given off during the crystallization of these intrusions, was involved as well.

Comparison between the SP metatonalites and the IVZ metabasites has been undertaken in two parts. Part I focuses on feldspar–quartz relationships as well as on biotite and hornblende chemistry. The latter permits estimation of both HF and HCl fugacities relative to H_2O for the fluids last in equilibration with the biotite. These, in turn, provide insights into the chemistry of the fluids present in these rocks during and/or shortly after the actual dehydration event. Part II (Harlov & Förster, 2002) concentrates on the (Y + REE) and halogen chemistry of apatite as a function of distance from the perceived heat or fluid source, as well as on monazite and xenotime genesis in either dehydration zone.

GEOLOGICAL BACKGROUND

Seward Peninsula, Alaska (SP)

The samples described in this study come from an antiformal gneiss terrane in the Kigluaik Mountains that experienced high-grade metamorphism (800°C; 8 kbar) at ~ 105 –100 Ma (Todd & Evans, 1993, 1994). Near the axis of this terrane, a transition zone from amphibolite to granulite facies is exposed. Within this zone, a 50 m thick layer of very uniform appearing, hornblende–biotite–plagioclase–quartz-bearing orthogneiss with a broadly tonalitic composition occurs overlying an equally thick, coarse-grained marble that contains minor diopside, phlogopite and small quantities of plagioclase, scapolite and orthoclase. Accessory minerals in the orthogneiss include apatite, allanite, zircon, pyrrhotite and graphite. Proceeding away from the contact into the orthogneiss, the first 50 cm has been dehydrated and consists of plagioclase, minor K-feldspar, quartz, Ti-enriched biotite, orthopyroxene and clinopyroxene but no hornblende (Todd & Evans, 1994). Modal amounts of biotite remain nearly unchanged in the dehydration zone compared with the amphibolite facies zone. Accessory minerals include pyrrhotite partially altered to a secondary Fe-bearing phase (goethite?) along cracks, apatite, allanite, zircon and garnet. Contrary to what has been reported by Todd & Evans (1994), no ilmenite was observed, despite an extensive search. A minority (10–20%) of the apatite grains contain tiny inclusions of monazite and xenotime (Harlov & Förster, 2002). Between the dehydration zone and the original hornblende-bearing orthogneiss, a 30 cm wide transition zone is developed. Here the same mineral assemblage

occurs as found in the dehydration zone with the addition of hornblende.

Val Strona di Omegna, Ivrea–Verbano Zone, northern Italy (IVZ)

Geology and mineralogy

The Ivrea–Verbano Zone represents a steeply dipping, continuous succession of high-grade metamorphic rocks, which make up part of the pre-Alpidic basement of the southern Alps (e.g. Schmid, 1993). It takes the form of a SW–NE-striking crustal cross-section ~ 120 km in length with a maximum width of ~ 15 km (Fig. 1a). It is bounded to the NW by the Insubric fault zone, which separates it from the Mesozoic rocks of the inner arc of the Alpine chain. To the SE, a pre-metamorphic tectonic contact, the Cossato–Mergozzo–Brissago Line (CMB Line) separates the IVZ from the Strona–Ceneri Zone. The base of the IVZ (northwestern part) consists of the so-called Mafic Formation (Sinigoi *et al.*, 1994). The Mafic Formation is made up principally of a massive gabbro–norite grading into diorite at the contact with the country rock. The base of the Mafic Formation, in the vicinity of the Insubric Line, consists of layers of mafic and ultramafic cumulus rocks.

In the area of the Val Strona di Omegna, near the centre of the IVZ, the Mafic Formation is overlain by a 14 km long sequence of interlayered metapelites and metabasites with minor marbles and metapsammities which range in metamorphism from middle amphibolite to granulite grade (Schmid, 1993) (Fig. 1b). In the amphibolite facies zone these layers consist of distinct hornblende-, clinopyroxene- and titanite-bearing metabasites and sillimanite–biotite-bearing metapelites (Table 1a and 1b; Fig. 1b). Going towards the NW along the Val Strona di Omegna, the amphibolite facies metabasites and metapelites grade smoothly into granulite facies via a transition zone. The transition zone is marked by the granulite facies metamorphism of the metapelite layers into leucocratic garnet-bearing gneisses locally known as ‘stronalites’, which represent a restite left over from the partial melting of the metapelites during granulite facies metamorphism (Voshage *et al.*, 1990; Schnetger, 1994). They contain abundant quartz, Mg-rich garnet, coarse crystalline sillimanite, and plagioclase with minor rutile, Ti-enriched biotite, K-feldspar (principally as mesoperthite), monazite and zircon (Schnetger, 1994). Apatite is rare to absent (Table 1b). Amphibolite grade continues in the metabasite layers with a general increase in the modal amount of clinopyroxene (Table 1a). Some clinopyroxene grains contain cores of hornblende suggesting arrested dehydration (Fig. 2a). In both the transition and amphibolite facies zones, titanite is usually observed rimming ilmenite. However, it also occurs as discrete grains (Fig. 2b).

Granulite facies conditions in both the metapelites and metabasites occur beyond the transition zone and for the next 3–4 km up to the contact with the Mafic Formation with the continuation of the stronalites and the appearance of orthopyroxene in the metabasite layers coupled with the total disappearance of hornblende (Table 1c; Fig. 1b). The metabasite layers now consist of plagioclase, quartz, orthopyroxene, $\pm$ clinopyroxene, garnet, K-feldspar, Ti-rich biotite, ilmenite, rutile (both as large grains and as needles in the quartz), apatite, monazite, zircon, pyrrhotite, chalcopyrite and graphite (Table 1c). The presence of coexisting Fe^{3+} -absent end-member ilmenite, rutile and pyrrhotite as well as the absence of magnetite indicate equilibration under conditions of relatively low $f\text{O}_2$. Bulk-rock analysis suggests a minor but variable (10–30 wt %) contamination (Si, Na, K, P, ...) of the granulite facies metabasite samples used in this study with metapelitic material (unpublished bulk-rock data, this study). This is not surprising considering the fine interlayering (with band thickness of the order of 25–100 cm in places) between both the metapelite and metabasic layers (Bertolani, 1968; Sills & Tarney, 1984).

Tectonic and thermal history

During the late Carboniferous (~ 300 Ma; Vavra *et al.*, 1996, 1999; Henk *et al.*, 1997), a major thermal and tectonic event occurred in an extensional environment at the base of the IVZ, somewhere in the vicinity of the Moho. This event resulted in the emplacement of a series of sheet-like intrusions of ultramafic and mafic magmas (the progenitor for the Mafic Formation) over a short period of time in a progressively thinning crust (Schmid, 1993; Quick *et al.*, 1994; Sinigoi *et al.*, 1994, 1995). It is commonly postulated that thermal input, in the form of contact metamorphism during the magmatic underplating event, induced granulite facies metamorphism, which resulted in the partial melting of the metapelite layers and the dehydration of the metabasite layers, both of which are surmised to have been regionally metamorphosed to amphibolite grade before this event (Quick *et al.*, 1994; Sinigoi *et al.*, 1994; Henk *et al.*, 1997; Barboza & Bergantz, 2000). Evidence for this thermal input can be seen in the systematic decrease in PT conditions from $810 \pm 50^\circ\text{C}$ and 8.3 ± 2 kbar at the contact with the Mafic Formation to $720 \pm 30^\circ\text{C}$ and 6.2 ± 1 kbar for the last orthopyroxene-bearing metabasite right before the transition zone (Fig. 1b). This decrease continues in the amphibolite grade rocks reaching temperatures and pressures of $615 \pm 30^\circ\text{C}$ and 4.3 ± 1 kbar at the CMB Line (Henk *et al.*, 1997). Following emplacement of the Mafic Formation and accompanying granulite facies overprint, the Ivrea–Verbano Zone underwent a long period of crustal attenuation and

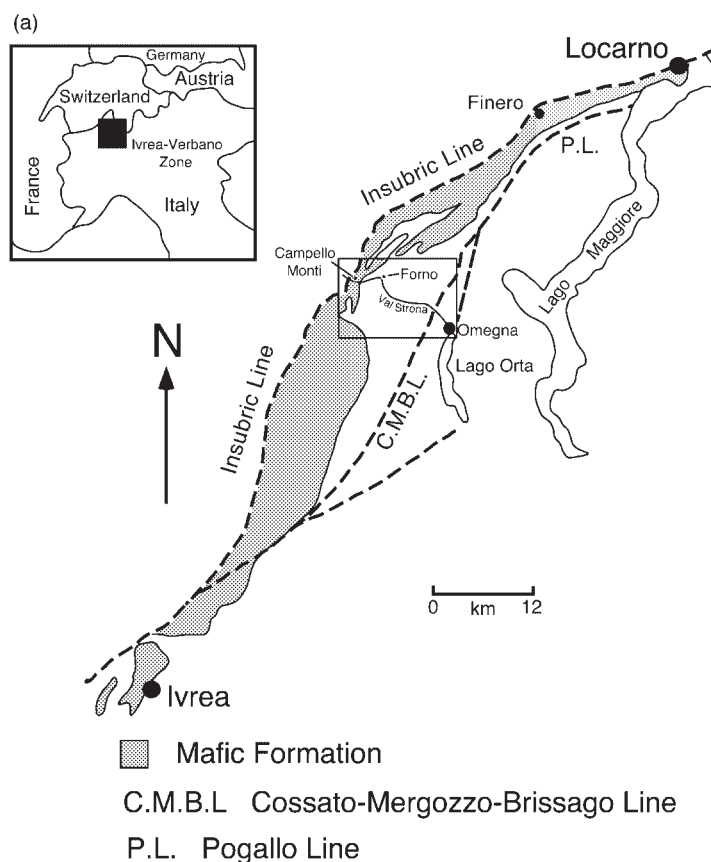


Fig. 1.

isobaric cooling to temperatures of $<300^{\circ}\text{C}$ by the late Triassic to Middle Jurassic in what was apparently a passive continental margin setting (Schmid, 1993). There is no petrographic or geochemical evidence to suggest that the Val Strona di Omegna area was affected by later hydrothermal pulses, which effectively metasomatized certain areas of the Ivrea-Verbano Zone (e.g. von Quadt *et al.*, 1992; Vavra & Schaltegger, 1999).

ANALYTICAL PROCEDURES

Sample selection

Our goal was to undertake a systematic study of petrographic relationships and mineral chemistries across metamorphic grade. For the SP this meant selecting samples of the orthogneiss at various distances from the contact with the marble. A total of 12 samples collected by Todd & Evans (1994) were studied: four from the granulite facies zone (within 55 cm from the contact), two from the transition zone (55–85 cm from the contact) and six from the amphibolite facies zone (>85 cm from the contact). Our traverse ends with sample AB90+13-594 collected 594 cm away from the contact. For the

IVZ we selected 30 samples at various distances along the Val Strona di Omegna from the contact with the Mafic Formation collected by Henk *et al.* (1997) and others (Table 1; Fig. 1). These include 10 metabasites from the amphibolite facies zone and two metabasites from the transition zone (Table 1a) (ranging from 4 to 14 km from the contact); six metapelites from the granulite facies zone, one metapelite from the transition zone and one metapelite from the amphibolite facies zone (Table 1b) (within 4–6 km of the contact); nine metabasites from the granulite facies zone and one sample from the Mafic Formation (Table 1c) (within 4 km of the contact). Our traverse ends with sample IV93-105 collected ~ 13.2 km from the contact with the Mafic Formation.

BSE and microprobe analysis

Microscopic investigation was carried out using both reflected and transmitted light as well as back-scattered electron (BSE) imaging. BSE pictures were made using a Zeiss DSM 962 digital scanning electron microscope with either 15 or 20 kV acceleration voltage. Analyses of feldspar (Table 2), biotite and hornblende were carried

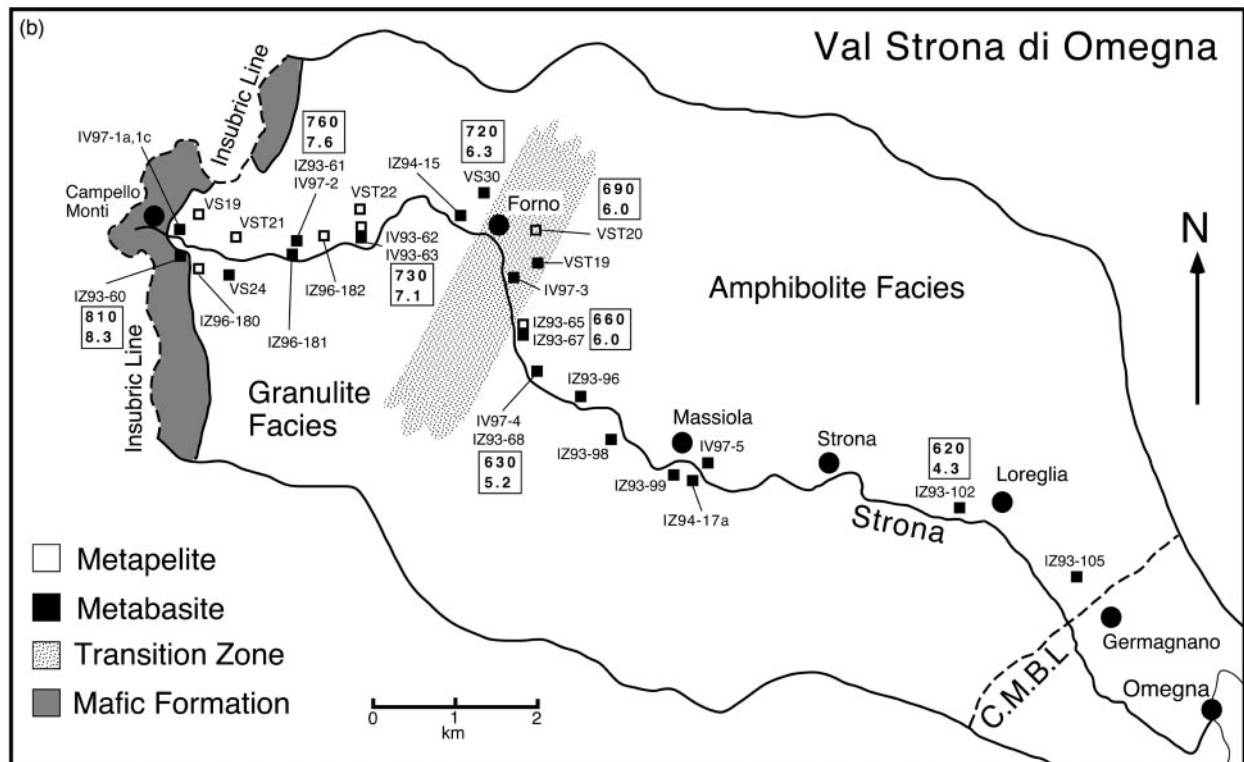


Fig. 1. (a) Simplified geological map of the Ivrea–Verbano Zone after Schmid (1993). (b) Highly simplified schematic representation of the Val Strona di Omegna. ■, metabasites; □, metapelites. Each of these symbols is identified by a sample number. Numbers in the boxes indicate the peak metamorphic temperatures (upper number) and pressures (lower number) as estimated by Henk *et al.* (1997). For simplicity, the complex interlayering between the metapelite and metabasite layers, which occur along the entire length of the Val Strona, is not shown (see Bertolani, 1968).

out using CAMECA SX50 and SX100 electron microprobes at the GeoForschungsZentrum Potsdam under the following analytical conditions: 15 kV acceleration voltage; 20 nA beam current; 15 μm beam spot; and counting times of 10–30 s depending on the element. Standards were taken from both the CAMECA and Smithsonian standard sets (Jarosewich *et al.*, 1980). The CAMECA PAP program was used for matrix correction (Pouchou & Pichoir, 1985). Reintegration of K-feldspar grains with exsolution lamellae of albite or replacement antiperthite involved a systematic succession of 15 μm diameter electron beam spot analyses in a crosswise sweep such that the entire surface of the mineral grain was sampled. Individual analyses (up to 350 per grain) were then averaged to produce a composite analysis. Anywhere from two to 12 biotite and hornblende grains scattered evenly over the length and breadth of the thin section were analysed per sample. To ensure that the relative differences observed are correct within microprobe error, all biotite and hornblende analyses per sample were obtained during a single measuring session including multiple checks of the calibration. Mean biotite analyses are contained in Tables 3a and 4a. Mean

hornblende analyses are contained in Tables 5 and 6. The full dataset representing all individual biotite and hornblende analyses taken from the SP and IVZ traverses may be downloaded from the *Journal of Petrology* Web site at <http://www.petrology.oupjournals.org>.

TEM analysis

Transmission electron microscopy (TEM) was carried out using a Philips CM200 electron microscope with a twin-lens configuration at 200 kV. Suitable specimens of the K-feldspar micro-veins were selected from specially prepared thin sections using BSE photographs of selected areas. During extraction of the specimen, these areas were protected from damage or deformation by a Technovit resin. The sample was then mounted on a copper grid and the resin dissolved away using acetone. Ion beam thinning by Ar ions was performed using a Gatan Duo Mill ion beam thinning machine at 5 kV with a tilt angle of 11°. The sample was coated very lightly with carbon to prevent charging in the transmission electron microscope.

Table 1a: Mineralogy of metabasites from the Val Strona di Omega di the Itria-Verbano Zone

Zone	Sample	Distance (m)*	Qtz	Plg	Kfs	Cpx	Gt	Hbl	Bt	Ttn	Ap	Ilm	Ru	Po	Py	Cp	Gr
transition	VST19	4540	X	X	AP	X	X		X	R	X	X	X	X			
transition	IV97-3	4570	X	X		X		X			X	X			X	X	
amphibolite	IZ93-67	5220	X	X		X		X	X	X	X						
amphibolite	IV97-4	5980	X	X		X	X	X		R	X	X					
amphibolite	IZ93-68	5980	X	X		X	X	X	X	X	X	X	X				
amphibolite	IZ93-96	6370	X	X		X	X	X		X	X	X	X				
amphibolite	IZ93-98	7100	X	X		X	X	X		X	X	X	X				
amphibolite	IZ93-99	7720	X	X		X	X			X	X	X		X	X	X	
amphibolite	IZ94-17a	8110	X	X		X		X	L	X	X					X	X
amphibolite	IV97-5	8300	X	X		X		X	L	X	X						
amphibolite	IZ93-102	11220	X	X				X		X	X	X	X				
amphibolite	IZ93-105	13240	X	X				Ac		R	X	X	X				

Abbreviations: Qtz, quartz; Plg, plagioclase; Kfs, K-feldspar; Cpx, clinopyroxene; Gt, garnet; Hbl, hornblende; Bt, biotite; Ttn, titanite; Ap, apatite; Ilm, ilmenite; Ru, rutile; Po, pyrrhotite; Py, pyrite; Cp, chalcopyrite; Gr, graphite; Ac, actinolite; AP, anti-perthite; R, titanite rims around the ilmenite grains; L, low-grade secondary biotite.

*Distance from the contact with the Mafic Formation.

Table 1b: Mineralogy of metapelites from the Val Strona di Omegna di the Ivrea–Verbano Zone

Zone	Sample	Distance (m)*	Qtz	Plg	Kfs	Sill	Gt	Bt	Ap	Mz	Ru	Po	Cp	Gr	Other
granulite	IZ96-180	5	X	X	AP		X			X	X	X	X	X	
granulite	VS19	180	X	X	X AP	X		X		X	X				
granulite	VST21	740	X	X	AP	X	X	X		X	X	X		X	
granulite	IZ96-182	1800	X	X		X	X		X	X	X	X	X	X	
granulite	VST22	2030	X	X	AP		X			X	X			X	Aln
granulite	IV93-62	2240	X	X	AP		X	X	X	X	X				
transition	VST20	3980	X	X	AP	X	X	X	X	X	X	X	X		
amphibolite	IV93-65	5220	X	X	X	X	X	X	X	X					Ilm, Py

Abbreviations: Sill, sillimanite; Mz, monazite; Aln, allanite (see Table 1a for additional abbreviations and explanations)

*Distance from the contact with the Mafic Formation.

RESULTS

K-feldspar–plagioclase–quartz textures

A striking feature common to both sample suites is the remarkable similarity in their K-feldspar–quartz and K-feldspar–plagioclase associations (Figs 3 and 4; Table 2). Under BSE imaging, orthopyroxene-bearing gneisses from both 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 (Fig. 3). K-feldspar micro-veins along plagioclase–plagioclase grain boundaries only occur in the immediate vicinity of quartz (Fig. 3). K-feldspar micro-veins along quartz grain boundaries have the appearance of replacing the quartz giving a rounded look to the quartz grains [Fig. 4; see also Harlov & Wirth (2000, fig. 4)]. 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 shows no sign of corrosion, incongruent melt textures or resorption (see Cesare, 2000). 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 (Fig. 4). When randomly selected areas of the K-feldspar micro-veins are examined using TEM, a wavy or modulated contrast which grades into a fine tweed pattern is visible (Fig. 5). This results from the superimposition of mutually orthogonal transverse distortion waves (McConnell, 1971; Kroll *et al.*, 1991). It represents the partial ordering of Al and Si in what was originally a disordered monoclinic *C2/m* host phase to the more ordered triclinic *C1* structure of microcline and implies formation at temperatures >500°C (Kroll *et al.*, 1991). With increasing distance from the contact with the marble or Mafic Formation, the abundance of K-feldspar micro-veins in the metabasite samples tends to diminish such that near the boundary with the transition zone they are relatively scarce. They are not present in rocks in which orthopyroxene is absent, i.e. purely hornblende- and/or clinopyroxene-bearing rocks.

The K-feldspar micro-veins from the IVZ differ from those in the SP with the occurrence of rim myrmekite and rim intergrowths of nearly pure albite growing into the K-feldspar at random intervals along the K-feldspar–plagioclase grain boundary interface (Fig. 3; Table 2; see also Harlov & Wirth, 2000). However, both the rim myrmekite and the albitic rim intergrowths occur only sporadically in the granulite facies metabasites from the IVZ with the albitic rim intergrowths found principally in samples IZ97-181 and IZ93-63 and the rim myrmekite found chiefly in samples IZ93-61 and IZ93-63. More detailed petrographic descriptions of either feature have been given by Harlov & Wirth (2000).

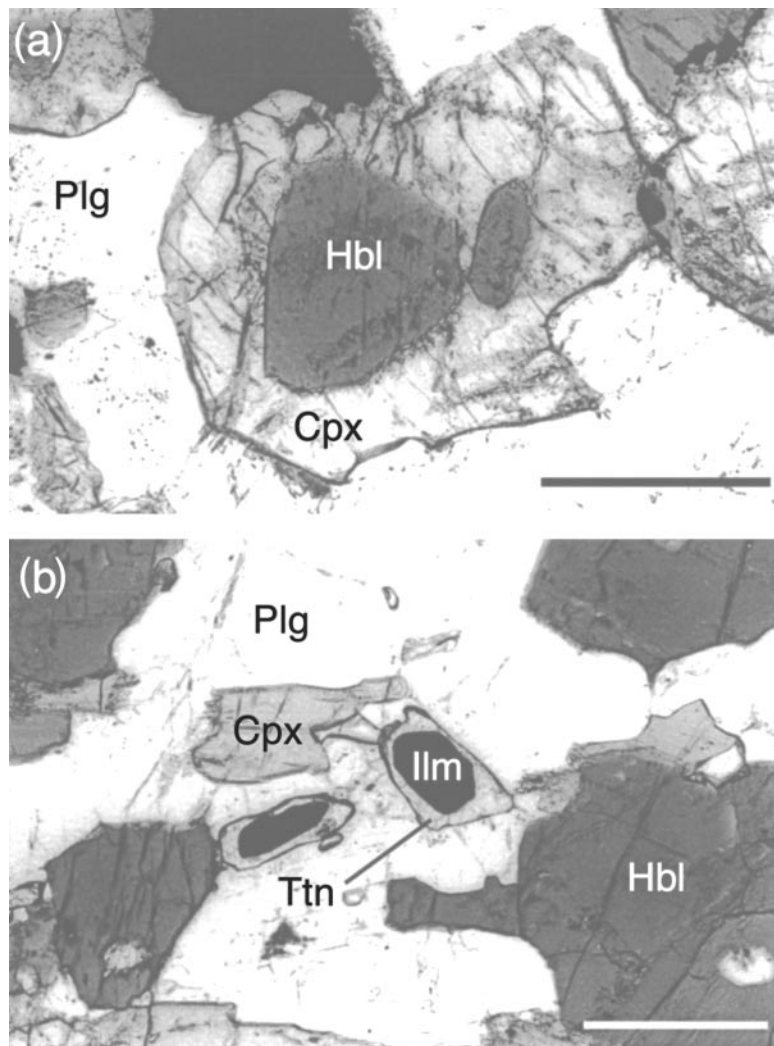


Fig. 2. (a) A relict hornblende grain in the core of a clinopyroxene grain in a sample (IV97-3) from the IVZ transition zone. (b) Titanite rimming grains of ilmenite in a sample (IV97-4) from the IVZ amphibolite facies zone. Scale bars represent 50 μm .

Antiperthite occurs in a random scattering of plagioclase from both sample suites (Fig. 6). Reintegration of the antiperthite grains gives feldspar compositions, which plot on or above the 1000°C isotherm (Fig 7). This defines them as replacement antiperthite: i.e. perthites, that when reintegrated, give compositions that fall well within the two-phase field under the prevailing metamorphic conditions (800°C and 8 kbar) (Griffin, 1969; Todd & Evans, 1994). Replacement antiperthite is interpreted as plagioclase grains which have been metasomatized by a K-rich fluid (Griffin, 1969).

Biotite and hornblende compositions

When comparing the composition of biotite and hornblende from the SP and the IVZ, several important

observations need to be kept in mind. The first is that in the case of the SP, any compositional variation occurs over a traverse of 600 cm whereas for the IVZ, any compositional variation is spread out over a distance of ~ 14 km and occurs in metabasite layers separated from each other by intervening metapelite layers. Second, there is no variation in temperature or pressure over the SP traverse, whereas samples from the IVZ traverse experienced a systematic rise in temperature and increase in pressure from $\sim 600^\circ\text{C}$ and 4 kbar at the CMB Line to $\sim 800^\circ\text{C}$ and 8 kbar at the contact with the Mafic Formation.

Biotite

When various cation and the halogen components in biotite are plotted as a function of distance from the

Table 1c: Mineralogy of metabasites from the Val Strona di Omega di the Ivrea–Verbano Zone

Zone	Sample	Distance (m)*	Qtz	Plg	Kfs	Opx	Cpx	Gt	Bt	Ap	Mz	Ilm	Ru	Po	Cp	Gr	Other
MFT	I293-60	0	X	X		X		X	X	X		X		X			Hbl
granulite	IV97-1a	5	X	X	V AP	X		X	X	X	X		X			X	
granulite	IV97-1c	10	X	X	V AP	X		X	X	X	X		X			X	
granulite	VS24	720	X	X	V AP	X		X	X	X	X		X		X		
granulite	I293-61	1560	X	X	V AP	X		X	X	X	X		X		X		
granulite	IV97-2	1560	X	X	V AP	X		X	X	X	X		X			X	
granulite	I296-181	1560	X	X	V AP	X		X	X	X	X		X			X	
granulite	I293-63	2240	X	X	V AP	X	X	X	X	X	X		X		X	X	
granulite	I294-15	3020	X	X	V AP	X		X	X	X	X		X		X	X	
granulite	VS30	3120	X	X	V AP	X		X	X	X	X		X		X	X	

Abbreviations: Opx, orthopyroxene; V, K-feldspar micro-veins (see Tables 1a and 1b for additional abbreviations and explanations).

*Distance from the Mafic Formation.

†Mafic Formation—sample consists principally of brown hornblende and some clinopyroxene with very rare quartz and biotite.

contact with the marble or the Mafic Formation, a series of patterns become readily discernible (Fig. 8; Tables 3a, 3b and 4a, 4b). For example, biotite in both dehydration zones is enriched in Ti and depleted in Fe compared with biotite from the amphibolite facies zone (Fig. 8a and b). Whereas Mg shows a more varied pattern (Fig. 8c), it tends to be higher in biotite from the dehydration and transition zones compared with biotite from the amphibolite facies zone.

The F content in biotite from both traverses decreases with increasing distance from the marble or Mafic Formation (Fig. 8d). With respect to the SP, this decrease occurs over a short distance from the contact (<100 cm) and consists of the dehydrated and transition zones with relatively constant F values in the amphibolite gneiss. The one exception is biotite in the sample furthest away from the contact (AB90 + 13-594), which is distinguished by enrichment in F despite having the same approximate Ti content compared with biotite in other samples from the amphibolite gneiss (Fig. 8a). With respect to the IVZ, this decrease in F in both the granulite facies and transition zone biotite is more gradual with increasing distance from the Mafic Formation and over a much larger distance (4000 m).

The log of HF and HCl fugacities relative to H₂O for a fluid in equilibrium with biotite were estimated using the commonly referenced calibrations of Munoz & Swenson (1981) and Munoz (1984), as well as the much less frequently used updated calibrations of Munoz (1992) (Tables 3b and 4b). With respect to the calculated relative HCl fugacity, the difference between the two Munoz calibrations is particularly large, in this case by a factor of three. In contrast, relative HF fugacities show much closer values when the two calibrations are compared. The calibration in Munoz (1992) is preferred, as it incorporates the updated experimental data of Zhu & Sverjensky (1991, 1992) as well as taking into account a series of other factors not considered by Munoz (1984) (J. Munoz, personal communication, 2000). As a consequence, all HF and HCl fugacities relative to H₂O discussed and plotted in this study will be those estimated using Munoz (1992).

For either traverse, the relative HF fugacities show the same evolution (Fig. 8e). Namely, $\log(f_{\text{HF}}/f_{\text{H}_2\text{O}})$ decreases with increasing distance from the marble or the Mafic Formation. Again, the one exception to this trend in the SP is sample AB90 + 13-594. The relative HCl fugacities show a distinct contrast between the two traverses (Fig. 8f). For the SP, they are somewhat variable and show no trend. In contrast, $\log(f_{\text{HCl}}/f_{\text{H}_2\text{O}})$ recorded in biotite from the IVZ shows a distinct decrease with respect to increasing distance from the Mafic Formation. Plotting the Cl vs Mg content in biotite (Fig. 9a) shows a positive correlation between Mg and Cl for the IVZ in distinct contrast to what is usually observed

Table 2. Representative feldspar analyses

	Seward Peninsula			Ivrea–Verbano Zone		
	plagioclase	rep-antiperthite*	K-feldspar micro-vein	plagioclase	rep-antiperthite*	K-feldspar micro-vein
SiO ₂	54.9	57.1	65.0	57.0	58.8	63.4
Al ₂ O ₃	29.2	27.0	18.7	27.2	25.6	18.2
Fe ₂ O ₃	0.16	0.08	0.04	0.20	0.14	0.02
CaO	11.3	9.24	0.09	9.41	7.77	0.13
BaO	0.00	0.07	0.29	0.02	0.14	0.78
K ₂ O	0.19	3.46	14.0	0.16	2.63	15.1
Na ₂ O	4.95	3.66	1.07	5.86	5.89	0.73
Total	100.7	100.6	99.2	99.9	101.0	98.4
Si	2.465	2.587	3.032	2.560	2.621	2.990
Al	1.543	1.439	1.028	1.440	1.343	1.014
Fe ³⁺	0.006	0.003	0.001	0.008	0.005	0.001
Ca	0.544	0.447	0.004	0.453	0.369	0.007
Ba	0.000	0.001	0.005	0.000	0.003	0.014
K	0.011	0.203	0.833	0.009	0.154	0.907
Na	0.431	0.320	0.097	0.510	0.507	0.067
Total	5.000	5.000	5.000	4.980	5.002	5.000
An	55.2	46.1	0.47	46.6	35.7	0.66
Ce	0.00	0.12	0.56	0.04	0.24	1.45
Or	1.07	20.9	88.7	0.94	14.9	91.2
Ab	43.7	32.9	10.3	52.5	49.1	6.70
						96.4

Representative feldspar analyses for the SP are taken from sample AB90 + 13-15. Representative feldspar analyses for the IVZ are taken from IZ94-15 for the mesoperthite and from IZ93-63 for the K-feldspar micro-vein, plagioclase and the albite rim intergrowth.

*Replacement antiperthite.

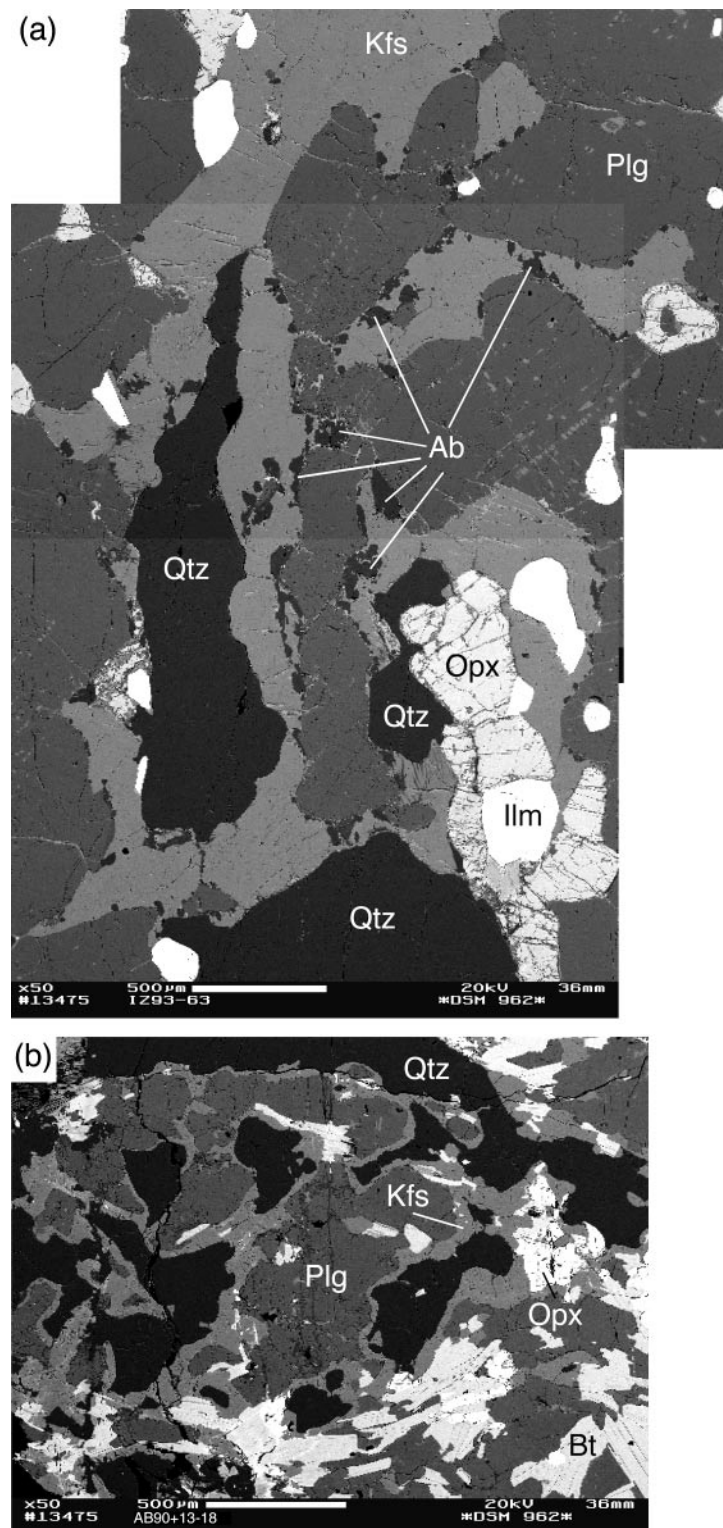


Fig. 3. BSE (back-scattered electron) images of K-feldspar micro-veins along quartz–plagioclase and plagioclase–plagioclase grain boundaries in (a) a metabasite (sample IZ93-63) from the IVZ and (b) a metatonalite (sample AB90 + 13-18) from the SP. (Note the presence of the albitic rim intergrowths as described in the text in the IVZ sample and their total absence in the SP sample.)

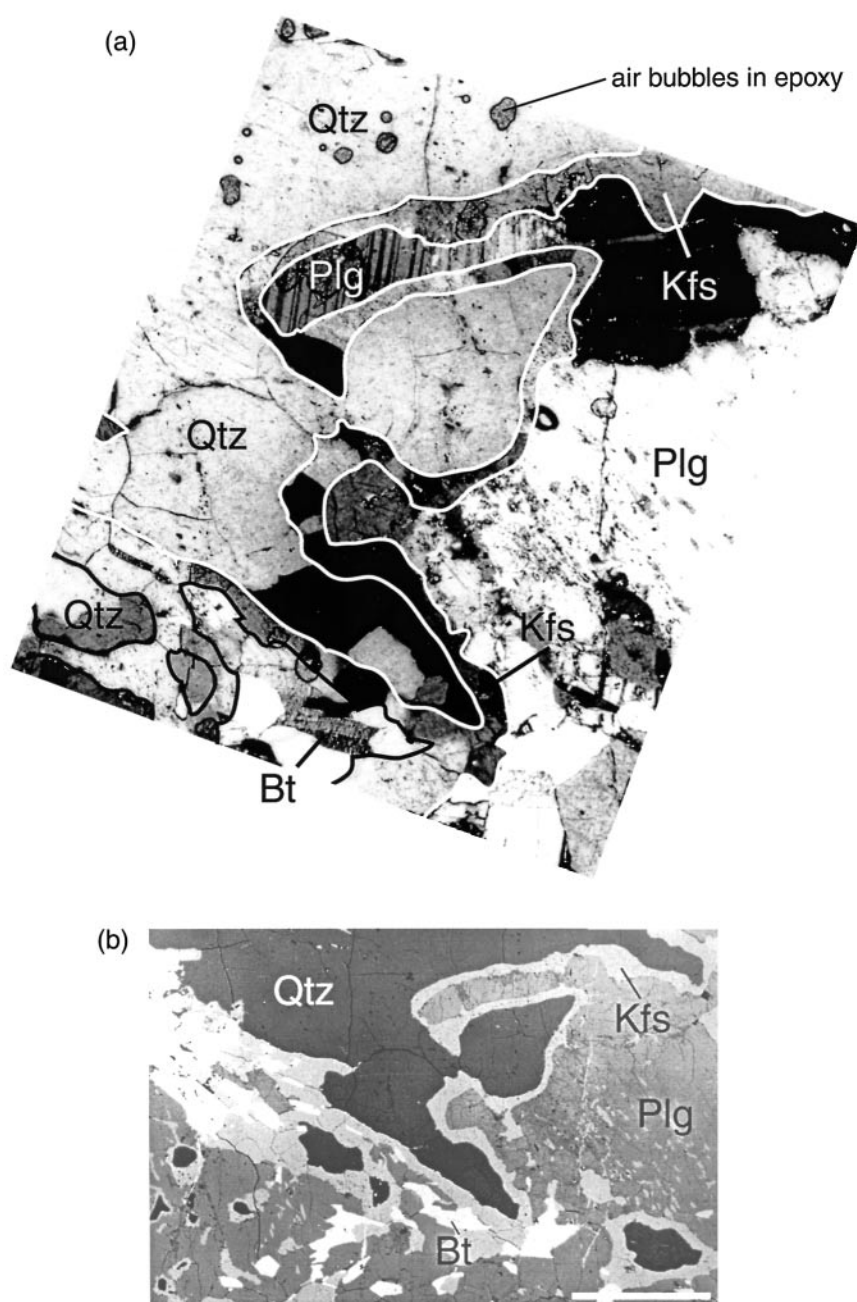


Fig. 4. (a) Transmitted light photograph of a K-feldspar micro-vein along quartz and plagioclase grain boundaries from sample AB90+13-18 (SP). The K-feldspar micro-vein is outlined in white and black. (b) BSE photograph of the same vein. Uniform extinction shows the extent of single crystals of K-feldspar along the plagioclase-quartz grain boundary. Scale bar represents 100 μm .

(Munoz & Swenson, 1981; Munoz, 1984). This positive correlation has also been observed by others in both natural biotite (e.g. Nijland *et al.*, 1993) as well as in phlogopite synthesized in a supercritical (K, Rb)Cl brine (Harlov & Melzer, 2002). These observations imply that Mg-Cl 'avoidance' is not a universal rule for biotite. However, for either sample suite, the F-Fe 'avoidance rule', as described by Munoz (1984), is clearly evident,

i.e. biotite highest in Fe tends to incorporate the least amount of F (Fig. 9b).

Hornblende

Patterns in hornblende compositions are less distinct. The Ti, Al, Ca, Mn, K and Na contents in the SP hornblendes are almost constant within the uncertainties

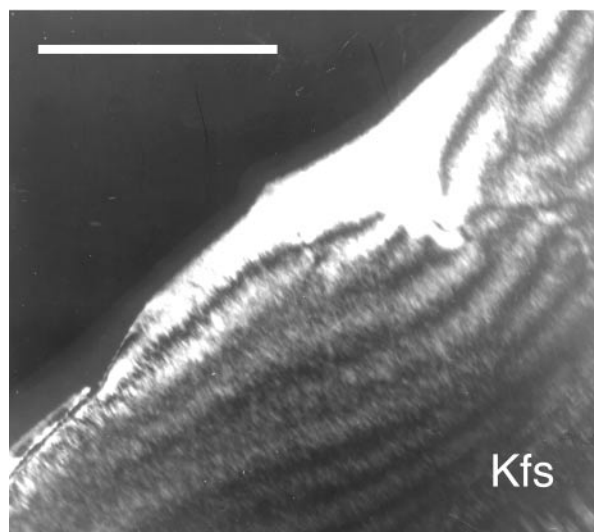


Fig. 5. TEM (transmission electron microscopy) dark-field image of K-feldspar with wavy or modulated contrast tweed structure in a K-feldspar micro-vein from sample AB90+13-18 (SP). (See text for detailed description.) Dark area in upper left-hand corner is empty space along the sample edge. Scale bar represents 200 nm.

inherent in the microprobe analyses (Table 5; Fig. 10a–c). However, hornblende from the transition zone is significantly higher in Mg and lower in Fe relative to hornblende in the amphibolite facies zone. In addition, hornblende in or near the transition zone is also enriched in F compared with hornblende deep within the amphibolite facies zone. This F enrichment falls off to negligible values 100 cm into the amphibolite facies gneiss. In contrast, the Cl content is generally more variable and shows no distinct pattern.

Although there is a greater variability in both the Ti and Na content of hornblende from the IVZ (Table 6; Fig. 10a and b), there is also some indication of decreasing content with increasing distance from the transition zone. K is heterogeneous in abundance as well but does not show a systematic pattern across the traverse (Fig. 10c). The same holds for Al, Mg and Fe. In addition, both F and Cl are systematically very low, indicating that hornblende in this traverse makes up a negligible reservoir for either halogen (Table 6).

DISCUSSION

In both the SP and IVZ dehydration zones, there are a set of common features that support the proposal that orthopyroxene and the K-feldspar micro-veins are a high-grade, solid-state reaction product of the breakdown of hornblende via the general reaction

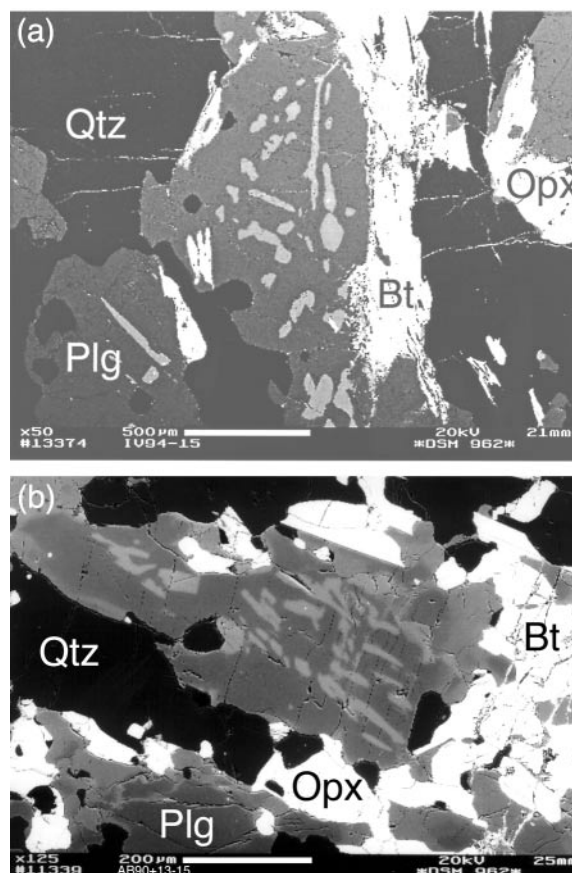


Fig. 6. BSE images of replacement antiperthite in plagioclase grains from (a) sample IZ94-15 (IVZ) and (b) sample AB90+13-15 (SP). Reintegrated replacement antiperthite values are contained in Table 2 and plotted in Fig. 7.

Hornblende + Quartz



These features include the presence of high-grade Ti-enriched biotite and the total absence of hornblende in the dehydration zone of either traverse. They also include the fact that the K-feldspar micro-veins and replacement antiperthite, present in the dehydration zone, are totally absent in amphibolite facies zone. Using singular value composition analysis, this same conclusion, i.e. reaction (1), was independently reached by Todd & Evans [1994; their reaction (3)] for the SP dehydration zone. With regard to the IVZ dehydration zone, bulk-rock analysis suggests that the interlayered metapelites could have contributed additional K to the metabasites in addition to that contributed by the breakdown of the hornblende.

Feldspar–quartz textures

On both the micron and sub-micron scale there are series of observations that are in accordance with a

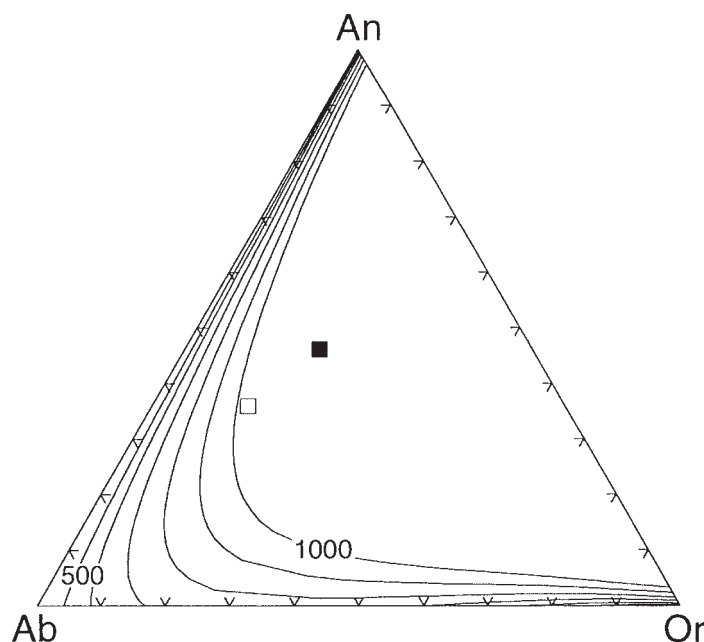
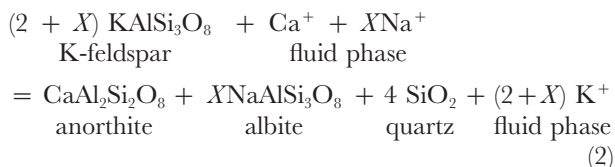


Fig. 7. Ternary plot of reintegrated replacement antiperthite grains from a granulite facies metabasite in the IVZ (sample IZ94-15) (□) and granulite facies metatonalite from the SP (sample AB90 + 13-15) (■). Images and the compositions of these grains are contained in Fig. 6 and Table 2, respectively. Isotherms are calculated at 8 kbar using the formulation of Fuhrman & Lindsley (1988).

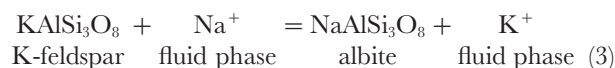
high-grade origin for the K-feldspar micro-veins. For example, results from TEM analysis indicate partial ordering of Si and Al in the K-feldspar which consequently implies formation at temperatures $>500^{\circ}\text{C}$ (Fig. 5; see also Harlov & Wirth, 2000). On the micron scale, electron microprobe reintegration of a typical K-feldspar micro-vein from the IVZ (Table 2) gives values of X_{An} , X_{Or} and X_{Ab} that plot approximately on the 750°C isotherm calculated using the ternary feldspar thermometer of Fuhrman & Lindsley (1988). This temperature is in good agreement with a garnet–orthopyroxene temperature of $728 \pm 30^{\circ}\text{C}$ estimated for the same sample (Henk *et al.*, 1997). Similar reintegration of a typical K-feldspar micro-vein from the SP gives a slightly lower temperature of $\sim 700^{\circ}\text{C}$ (Table 2) although these are still within 100°C of peak metamorphic temperatures for the region, i.e. 800°C (Todd & Evans, 1994).

In the IVZ, the presence of both myrmekite and albitic rim intergrowths in the K-feldspar (e.g. Harlov & Wirth, 2000) along the K-feldspar–plagioclase phase boundary also favour a high-grade origin for the micro-veins. In general, myrmekite is considered to represent a solid-phase mass transport reaction in the form of an incoherent grain boundary moving into the K-feldspar:



in conjunction with an alkaline fluid phase during isobaric cooling at temperatures $>500\text{--}600^{\circ}\text{C}$ (Wirth & Voll, 1987; Smith & Brown, 1988).

In contrast, the albitic rim intergrowths (Fig. 3) appear to represent a migrating grain boundary in the form of a simple cation exchange reaction:



where K-feldspar is replaced by albite along the K-feldspar–plagioclase grain boundary. As there is no microprobe evidence of Na depletion in plagioclase or K-feldspar in the immediate vicinity of these intergrowths but rather some Na enrichment in the plagioclase (see Harlov & Wirth, 2000), this suggests that the source for Na must have been from an external fluid phase. It is highly unlikely that hornblende could have served as a source of Na for the albitic rim intergrowths (Tables 5 and 6), as any Na released during hornblende breakdown would have been directly incorporated into both the growing K-feldspar micro-veins as well as product plagioclase [reaction (1); Table 2]. Texturally, the evidence points to the albitic rim intergrowths having grown after the K-feldspar micro-veins had formed. This would suggest that the most likely source was some sort of fluid-induced exchange with the metapelites, which indeed do show some depletion in Na relative to the amphibolite facies metapelites (Schnetger, 1994; unpublished bulk rock data, this study). This agrees with Korzhinskii (1959),

Table 3a: Average composition of biotite in metatonalites from the Seward Peninsula

Zone	Sample-(cm)*	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO†	MnO	MgO	Li ₂ O‡	CaO	BaO	K ₂ O	Na ₂ O	H ₂ O§	F	Cl	Sum	O = (F + Cl)	Total
1	AB90+13-10	36.6 <i>0.27</i>	5.63 <i>0.33</i>	14.1 <i>0.14</i>	0.40 <i>0.16</i>	14.3 <i>0.27</i>	0.05 <i>0.03</i>	14.2 <i>0.18</i>	0.06 <i>0.03</i>	0.05 <i>0.03</i>	0.18 <i>0.07</i>	9.32 <i>0.14</i>	0.08 <i>0.01</i>	3.81 <i>0.01</i>	0.36 <i>0.03</i>	0.05 <i>0.01</i>	99.2	0.16	99.0
1	AB90+13-15	36.9 <i>0.17</i>	6.82 <i>0.25</i>	13.9 <i>0.14</i>	0.21 <i>0.04</i>	16.3 <i>0.26</i>	0.05 <i>0.03</i>	12.4 <i>0.27</i>	0.08 <i>0.06</i>	0.02 <i>0.02</i>	0.15 <i>0.06</i>	9.46 <i>0.10</i>	0.08 <i>0.02</i>	3.86 <i>0.02</i>	0.30 <i>0.05</i>	0.02 <i>0.01</i>	100.5	0.13	100.4
1	AB90+13-18	37.0 <i>0.12</i>	5.18 <i>0.38</i>	14.6 <i>0.23</i>	0.16 <i>0.08</i>	15.2 <i>0.41</i>	0.08 <i>0.03</i>	13.8 <i>0.13</i>	0.06 <i>0.07</i>	0.04 <i>0.02</i>	0.15 <i>0.08</i>	9.36 <i>0.10</i>	0.10 <i>0.02</i>	3.82 <i>0.02</i>	0.35 <i>0.05</i>	0.07 <i>0.01</i>	99.8	0.17	99.7
1	AB90+13-41	36.9 <i>0.38</i>	6.32 <i>0.41</i>	14.1 <i>0.22</i>	0.15 <i>0.03</i>	15.9 <i>0.52</i>	0.07 <i>0.03</i>	12.8 <i>0.56</i>	0.07 <i>0.09</i>	0.07 <i>0.03</i>	0.18 <i>0.06</i>	9.46 <i>0.09</i>	0.07 <i>0.01</i>	3.90 <i>0.02</i>	0.21 <i>0.06</i>	0.07 <i>0.02</i>	100.3	0.11	100.2
2	AB90+13-56	37.3 <i>0.23</i>	3.58 <i>0.09</i>	14.6 <i>0.09</i>	0.21 <i>0.05</i>	14.8 <i>0.22</i>	0.10 <i>0.02</i>	15.1 <i>0.22</i>	0.05 <i>0.05</i>	0.03 <i>0.01</i>	0.11 <i>0.05</i>	9.39 <i>0.03</i>	0.07 <i>0.02</i>	3.87 <i>0.01</i>	0.27 <i>0.03</i>	0.06 <i>0.01</i>	99.6	0.13	99.5
2	AB90+13-61	37.7 <i>0.21</i>	3.31 <i>0.11</i>	14.8 <i>0.12</i>	0.33 <i>0.20</i>	14.4 <i>0.49</i>	0.09 <i>0.03</i>	15.4 <i>0.26</i>	0.05 <i>0.08</i>	0.03 <i>0.02</i>	0.16 <i>0.07</i>	9.46 <i>0.07</i>	0.08 <i>0.01</i>	3.92 <i>0.02</i>	0.24 <i>0.03</i>	0.04 <i>0.01</i>	100.0	0.11	99.9
3	AB90+13-86	36.8 <i>0.19</i>	3.98 <i>0.18</i>	14.6 <i>0.14</i>	0.11 <i>0.03</i>	18.7 <i>0.36</i>	0.18 <i>0.04</i>	12.2 <i>0.27</i>	0.08 <i>0.07</i>	0.02 <i>0.01</i>	0.21 <i>0.04</i>	9.31 <i>0.08</i>	0.07 <i>0.01</i>	3.90 <i>0.01</i>	0.12 <i>0.02</i>	0.05 <i>0.01</i>	100.3	0.06	100.2
3	AB90+13-170	37.0 <i>0.26</i>	3.16 <i>0.12</i>	14.7 <i>0.14</i>	0.06 <i>0.02</i>	18.3 <i>0.40</i>	0.15 <i>0.04</i>	13.2 <i>0.31</i>	0.07 <i>0.08</i>	0.05 <i>0.02</i>	0.12 <i>0.05</i>	9.15 <i>0.12</i>	0.10 <i>0.02</i>	3.90 <i>0.03</i>	0.13 <i>0.02</i>	0.05 <i>0.02</i>	100.2	0.07	100.1
3	AB90+13-244	36.7 <i>0.24</i>	3.71 <i>0.15</i>	14.6 <i>0.15</i>	0.07 <i>0.03</i>	18.7 <i>0.29</i>	0.20 <i>0.04</i>	12.4 <i>0.14</i>	0.08 <i>0.07</i>	0.06 <i>0.03</i>	0.17 <i>0.06</i>	9.19 <i>0.14</i>	0.08 <i>0.02</i>	3.92 <i>0.02</i>	0.09 <i>0.02</i>	0.01 <i>0.01</i>	100.1	0.04	100.1
3	AB90+13-287	36.4 <i>0.24</i>	3.53 <i>0.14</i>	14.5 <i>0.11</i>	0.06 <i>0.02</i>	18.4 <i>0.25</i>	0.21 <i>0.03</i>	12.8 <i>0.13</i>	0.07 <i>0.08</i>	0.03 <i>0.02</i>	0.15 <i>0.06</i>	9.28 <i>0.09</i>	0.10 <i>0.02</i>	3.90 <i>0.02</i>	0.09 <i>0.02</i>	0.01 <i>0.01</i>	99.6	0.04	99.5
3	AB90+13-381	36.3 <i>0.23</i>	3.23 <i>0.07</i>	14.6 <i>0.10</i>	0.07 <i>0.03</i>	19.6 <i>0.27</i>	0.16 <i>0.04</i>	12.2 <i>0.08</i>	0.08 <i>0.01</i>	0.03 <i>0.01</i>	0.17 <i>0.07</i>	9.23 <i>0.09</i>	0.07 <i>0.01</i>	3.88 <i>0.02</i>	0.07 <i>0.02</i>	0.04 <i>0.01</i>	99.7	0.04	99.7
3	AB90+13-594	37.4 <i>0.16</i>	3.74 <i>0.30</i>	14.8 <i>0.14</i>	0.13 <i>0.03</i>	16.5 <i>0.60</i>	0.15 <i>0.03</i>	13.7 <i>0.45</i>	0.06 <i>0.02</i>	0.04 <i>0.02</i>	0.09 <i>0.05</i>	9.19 <i>0.14</i>	0.08 <i>0.02</i>	3.88 <i>0.02</i>	0.26 <i>0.04</i>	0.07 <i>0.02</i>	100.2	0.13	100.0

1σ standard deviation in italics. Metamorphic zones: 1, dehydration zone; 2, transition zone; 3, amphibolite facies zone.

*Distance from the contact with the marble. †Total Fe as FeO. ‡Calculated according to equation (1) of Tischendorf *et al.* (1999). §Calculated assuming the (F,Cl,OH) site is filled.

Table 3b: Fluid composition recorded in biotite in metatonalites from the Seward Peninsula

Zone	Sample (cm)*	Munoz (1984)			Munoz (1992)		
		log($f\text{H}_2\text{O}/f\text{HF}$)	log($f\text{H}_2\text{O}/f\text{HCl}$)	log($f\text{HF}/f\text{HCl}$)	log($f\text{H}_2\text{O}/f\text{HF}$)	log($f\text{H}_2\text{O}/f\text{HCl}$)	log($f\text{HF}/f\text{HCl}$)
1	AB90 + 13-10	4.30 0.03	1.23 0.06	-3.07 0.07	4.57 0.03	4.56 0.06	-0.58 0.07
1	AB90 + 13-15	4.32 0.07	1.76 0.18	-2.56 0.20	4.59 0.07	4.92 0.18	-0.17 0.20
1	AB90 + 13-18	4.28 0.07	1.09 0.08	-3.19 0.10	4.55 0.07	4.36 0.07	-0.74 0.10
1	AB90 + 13-41	4.51 0.12	1.17 0.15	-3.33 0.16	4.78 0.12	4.38 0.12	-0.92 0.15
2	AB90 + 13-56	4.44 0.04	1.07 0.05	-3.37 0.06	4.70 0.04	4.44 0.06	-0.85 0.07
2	AB90 + 13-61	4.52 0.05	1.26 0.09	-3.25 0.11	4.78 0.05	4.65 0.09	-0.72 0.11
3	AB90 + 13-86	4.67 0.07	1.41 0.10	-3.25 0.12	4.95 0.07	4.53 0.09	-0.90 0.12
3	AB90 + 13-170	4.67 0.08	1.29 0.11	-3.38 0.14	4.95 0.08	4.49 0.11	-0.98 0.14
3	AB90 + 13-244	4.83 0.11	2.11 0.25	-2.72 0.26	5.11 0.11	5.24 0.25	-0.36 0.26
3	AB90 + 13-287	4.86 0.10	2.11 0.27	-2.75 0.23	5.14 0.10	5.28 0.27	-0.37 0.23
3	AB90 + 13-381	4.94 0.14	1.48 0.07	-3.46 0.17	5.23 0.14	4.59 0.07	-1.11 0.17
3	AB90 + 13-594	4.41 0.05	1.12 0.11	-3.29 0.11	4.68 0.05	4.37 0.10	-0.85 0.11

1 σ standard deviation in italics. Metamorphic zones: 1, dehydration zone; 2, transition zone; 3, amphibolite facies zone.

*Distance from the contact with the marble.

Table 4a: Average composition of biotite in metabasites and metapelites from the Ivrea–Verbano Zone

Zone	Sample	Distance (m)*	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeOt	MnO	MgO	Li ₂ O†	CaO	BaO	K ₂ O	Na ₂ O	H ₂ O‡	F	Cl	Sum	O=(F+Cl)	Total	
Metabasites																					
1	IV97-1a	5	37.4 0.64	6.40 0.41	14.1 0.13	0.03 0.02	12.4 0.68	0.02 0.02	14.6 0.77	0.05 0.05	0.02 0.03	0.65 0.29	9.47 0.20	0.08 0.01	3.67 0.07	0.74 0.20	0.06 0.01		99.7	0.32	99.4
1	IV97-1c	10	37.4 0.36	6.01 0.26	14.1 0.22	0.02 0.01	12.5 0.69	0.03 0.02	15.3 0.47	0.05 0.06	0.10 0.06	0.44 0.09	9.23 0.27	0.09 0.02	3.62 0.04	0.86 0.07	0.05 0.01		99.8	0.37	99.4
1	IZ93-61	1560	37.2 0.56	6.22 0.53	13.9 0.10	0.09 0.04	13.1 0.76	0.02 0.02	14.3 0.78	0.06 0.05	0.06 0.04	0.52 0.19	9.35 0.15	0.09 0.02	3.77 0.07	0.41 0.13	0.16 0.02		99.3	0.21	99.1
1	IV97-2	1560	37.0 0.35	5.90 0.17	13.5 0.10	0.54 0.11	12.5 0.40	0.03 0.02	15.4 0.32	0.05 0.04	0.01 0.01	1.15 0.22	9.28 0.07	0.07 0.02	3.67 0.05	0.67 0.10	0.10 0.01		99.8	0.30	99.5
1	IZ96-181	1560	37.5 0.23	6.17 0.39	14.1 0.13	0.04 0.03	11.2 0.42	0.03 0.02	15.7 0.30	0.04 0.04	0.07 0.06	0.69 0.10	9.36 0.10	0.09 0.02	3.64 0.05	0.76 0.09	0.08 0.01		99.6	0.34	99.2
1	IZ93-63	2240	37.3 0.25	6.52 0.29	14.0 0.11	0.13 0.04	11.0 0.66	0.02 0.01	15.9 0.50	0.04 0.05	0.03 0.02	0.25 0.07	9.65 0.07	0.05 0.01	3.76 0.07	0.56 0.15	0.10 0.01		99.4	0.26	99.1
1	IZ94-15	3020	37.0 0.14	6.51 0.52	15.0 0.19	0.09 0.04	11.5 0.47	0.02 0.02	15.0 0.37	0.05 0.06	0.05 0.02	0.52 0.07	9.37 0.09	0.13 0.22	3.79 0.03	0.50 0.06	0.11 0.03		99.7	0.23	99.4
1	VS30	3120	36.7 0.37	4.08 0.24	15.7 0.21	0.13 0.05	15.8 0.64	0.02 0.02	13.5 0.38	0.06 0.14	0.05 0.04	0.46 0.09	9.13 0.13	0.22 0.03	3.89 0.03	0.22 0.03	0.02 0.01		100.0	0.09	99.9
2	VST19	4540	35.7 0.28	4.61 0.34	15.1 0.21	0.09 0.05	22.1 0.74	0.18 0.03	8.78 0.25	0.14 0.08	0.05 0.03	0.12 0.06	9.32 0.10	0.13 0.04	3.86 0.02	0.07 0.02	0.03 0.02		100.3	0.04	100.3
3	IZ93-67	5220	36.6 0.26	2.49 0.24	16.3 0.15	0.11 0.04	18.2 0.48	0.18 0.03	12.4 0.37	0.08 0.06	0.06 0.02	0.10 0.06	9.23 0.19	0.17 0.05	3.97 0.02	<0.01 0.01	0.01 0.01		99.8	0.00	99.8
3	IZ93-68	5980	36.9 0.27	2.36 0.32	18.3 0.12	0.11 0.04	15.8 0.17	0.07 0.03	13.67 0.27	0.06 0.03	0.03 0.03	0.39 0.06	7.88 0.07	0.95 0.04	4.08 0.01	<0.01 0.01	0.01 0.01		100.5	0.00	100.5
Metapelites																					
1	VS19	180	38.1 0.26	5.06 0.26	14.9 0.41	0.05 0.03	9.05 0.94	0.02 0.02	17.8 0.56	0.03 0.04	0.02 0.02	0.19 0.08	9.54 0.10	0.18 0.03	3.11 0.07	2.09 0.12	0.01 0.01		100.1	0.88	99.2
1	VST21	740	37.5 0.35	5.54 0.28	14.9 0.17	0.04 0.02	11.1 0.33	0.01 0.01	16.1 0.43	0.04 0.03	0.05 0.02	0.25 0.07	9.43 0.17	0.14 0.01	3.21 0.04	1.81 0.09	0.02 0.01		100.1	0.76	99.3
1	VST22	2030	38.0 0.37	5.44 0.49	14.8 0.21	0.10 0.03	8.76 0.51	0.02 0.02	17.8 0.54	0.03 0.03	0.03 0.08	0.46 0.08	9.54 0.13	0.14 0.04	3.23 0.08	1.80 0.15	0.12 0.01		100.3	0.79	99.5
2	VST20	3980	37.2 0.28	5.65 0.85	16.5 0.43	0.12 0.03	8.27 0.63	0.01 0.01	17.3 0.53	0.03 0.01	0.01 0.01	0.31 0.09	9.40 0.12	0.14 0.03	3.82 0.06	0.60 0.10	0.07 0.03		99.5	0.27	99.2

1σ standard deviation in italics. Metamorphic zones: 1, granulite facies zone (dehydration zone); 2, transition zone; 3, amphibolite facies zone.

*Distance from the contact with the Mafic Formation. †Total Fe as FeO. ‡Calculated according to equation (1) of Tischendorf *et al.* (1999). §Calculated assuming the (F,Cl,OH) site is filled.

Table 4b: Fluid composition recorded in biotite in metabasites and metapelites from the Ivrea–Verbano Zone

Zone	Sample	Distance (m)*	Munoz (1984)		Munoz (1992)			
			log(<i>f</i> H ₂ O/ <i>f</i> HF)	log(<i>f</i> H ₂ O/ <i>f</i> HCl)	log(<i>f</i> HF/ <i>f</i> HCl)	log(<i>f</i> H ₂ O/ <i>f</i> HF)	log(<i>f</i> H ₂ O/ <i>f</i> HCl)	log(<i>f</i> HF/ <i>f</i> HCl)
Metabasites								
1	IV97-1a	5	4.00	1.03	−2.97	4.25	4.45	−0.39
			0.12	0.07	0.18	0.12	0.11	0.20
1	IV97-1c	10	3.93	1.04	−2.89	4.18	4.50	−0.29
			0.03	0.06	0.06	0.03	0.05	0.06
1	IZ93-61	1560	4.35	0.84	−3.52	4.64	4.06	−1.19
			0.14	0.09	0.10	0.14	0.06	0.11
1	IV97-2	1560	4.15	0.96	−3.20	4.44	4.27	−0.81
			0.06	0.05	0.06	0.06	0.04	0.05
1	IZ96-181	1560	4.11	1.06	−3.05	4.39	4.40	−0.65
			0.05	0.05	0.06	0.05	0.04	0.06
1	IZ93-63	2240	4.33	1.11	−3.22	4.64	4.36	−0.97
			0.12	0.05	0.11	0.12	0.04	0.11
1	IZ94-15	3020	4.37	1.25	−3.12	4.71	4.35	−1.03
			0.05	0.13	0.13	0.05	0.13	0.13
1	VS30	3120	4.62	2.06	−2.56	4.96	5.02	−0.52
			0.06	0.15	0.16	0.06	0.17	0.17
2	VST19	4540	5.05	2.64	−2.40	5.45	4.97	−0.88
			0.11	0.35	0.35	0.11	0.33	0.34
3	IZ93-67	5220	>6.10	3.05	<−3.51	>6.54	5.51	<−2.08
				0.29			0.28	
3	IZ93-68	5980	>6.24	3.11	<−3.23	>6.70	5.66	<−1.80
				0.20			0.20	
Metapelites								
1	VS19	180	3.59	1.62	1.98	3.83	5.24	0.71
			0.03	0.18	0.21	0.03	0.16	0.19
1	VST21	740	3.64	1.53	2.11	3.91	4.95	0.39
			0.02	0.15	0.14	0.02	0.15	0.14
1	VST22	2030	3.82	0.83	2.98	4.12	4.23	−0.64
			0.04	0.05	0.05	0.04	0.04	0.04
2	VST20	3980	4.42	1.44	2.98	4.79	4.64	−0.91
			0.06	0.19	0.20	0.07	0.22	0.21

1 σ standard deviation in italics. Metamorphic zones: 1, granulite facies zone (dehydration zone); 2, transition zone; 3, amphibolite facies zone.

*Distance from the contact with the Mafic Formation.

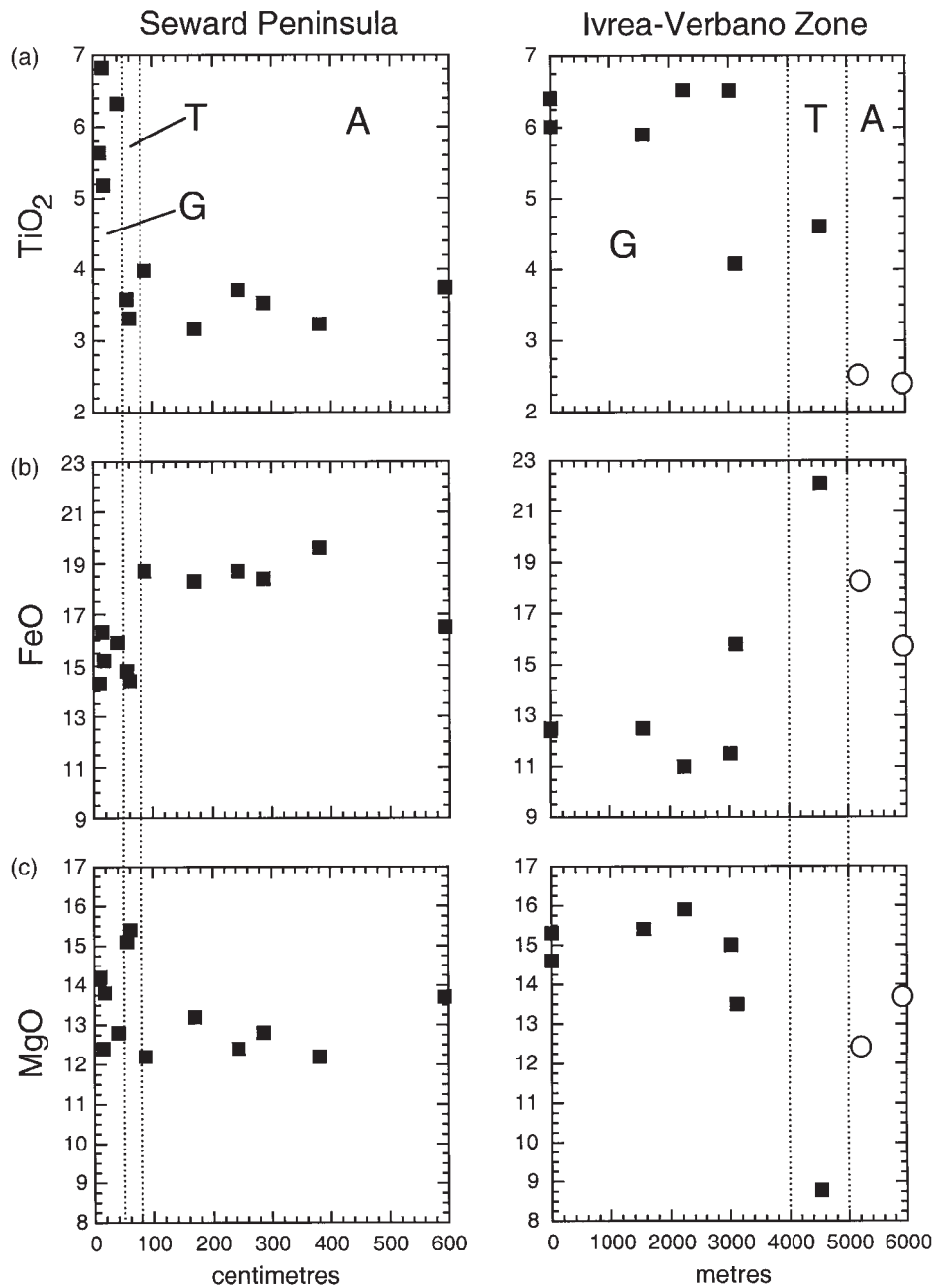


Fig. 8.

who argued that Na is highly mobile in halogen-bearing fluids under granulite facies conditions. However, because not all dehydrated metabasites so far examined contain these albitic rim intergrowths, Na infiltration from the stronalites into the metabasites was neither universal nor of the same order of magnitude over the extent of the dehydration zone. This assumption of an external metapelitic source for Na also explains the lack of albitic rim intergrowths in K-feldspar micro-veins from the SP

dehydration zone, as the marble would have been a negligible source for Na.

Voll (1960) has observed similar albitic rim intergrowths along microcline–microcline grain boundaries, which he termed ‘Wechselsäume’ or swapped rims, in metagranites from the Bavarian Oberpfalz, Germany. Their approximate temperature and pressure of formation was estimated by Voll (1960) to correspond to epidote–amphibolite facies conditions, i.e. 450–550°C

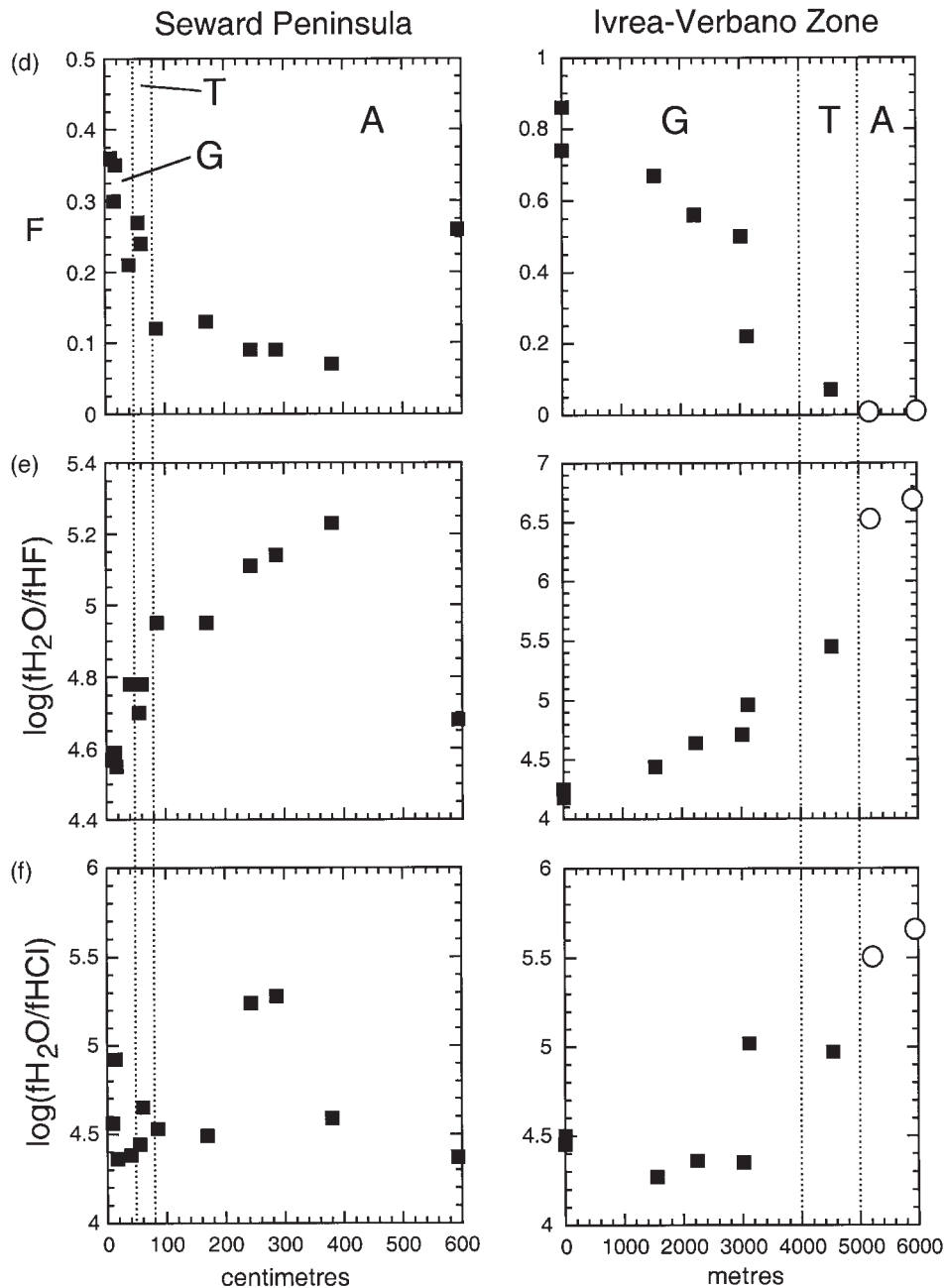


Fig. 8. Plots comparing selected element (mean oxide wt %) or relative element abundances in biotite as a function of distance from the contact with the marble for the SP metatonalites (Table 3a) and from the contact with the Mafic Formation for the IVZ metabasites (Table 4a) for (a) TiO_2 , (b) FeO , (c) MgO , (d) F , (e) $\log(f\text{H}_2\text{O}/f\text{HF})$, and (f) $\log(f\text{H}_2\text{O}/f\text{HCl})$. Error in distance is equal to the width of the symbol in either set of plots. The dotted vertical lines designate divisions between the dehydration zone (granulite facies) (G), the transition zone (T), and the amphibolite facies zone (A) as described in the text. ○ (in plots for the IVZ sample suite), low-Ti biotite. Biotite from samples IZ93-61 and IZ96-181 is not plotted because of anomalous Cl and Cr contents, respectively.

and 4–6 kbar in conjunction with a possible fluid phase. Unfortunately, the one-step ordering of albite from a high-temperature disordered ‘high albite’ to a low-temperature ordered ‘low albite’, upon cooling to

temperatures below $700 \pm 40^\circ\text{C}$, is continuous and reversible such that no intermediate partially ordered state like that for K-feldspar is preserved in nature (Deer *et al.*, 1993; p. 401). As a consequence the albitic rim

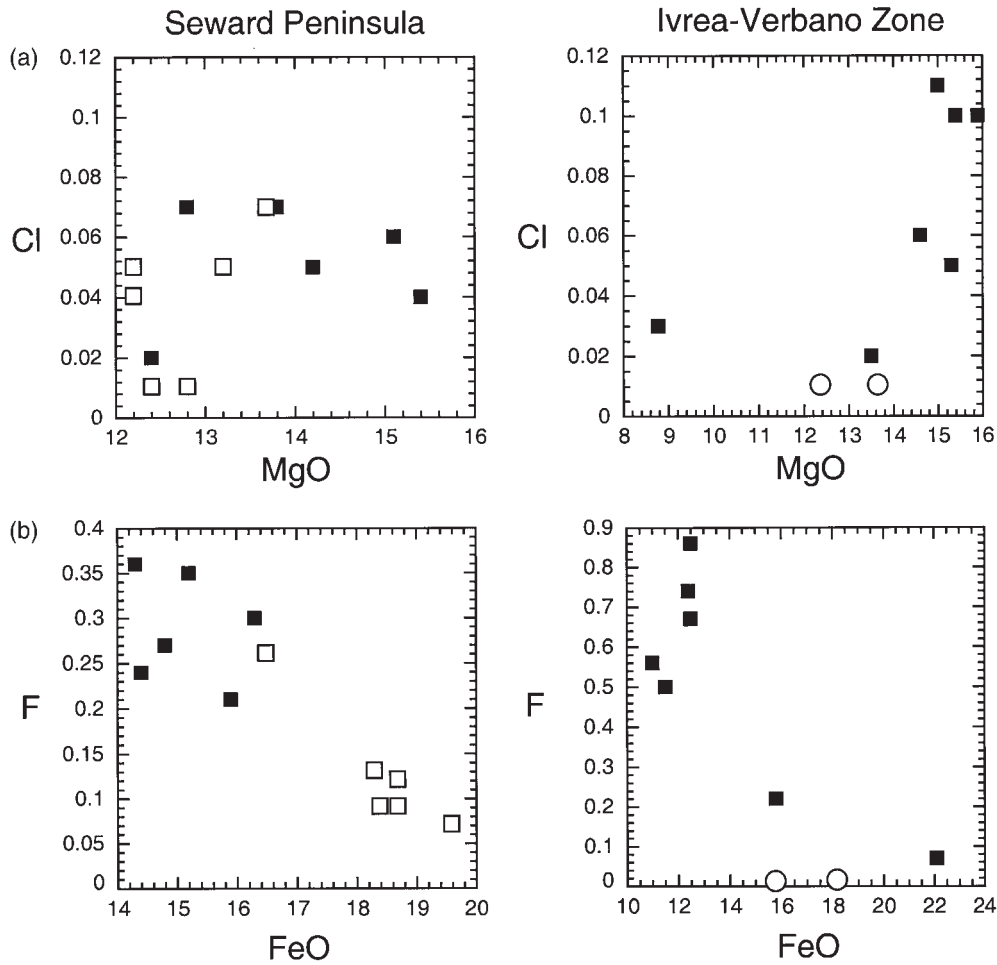


Fig. 9. Plots of (a) Cl vs MgO and (b) F vs FeO, for biotite (mean oxide wt %) from the SP metatonalites (Table 3a) and the IVZ metabasites (Table 4a). ○, low-Ti biotite with a negligible F content for the IVZ sample suite; □ (in plots for the SP), purely non-orthopyroxene-bearing samples.

intergrowths are 'low albite' with no preserved cooling history as seen in the case of the K-feldspar micro-veins (Harlov & Wirth, 2000).

Biotite chemistry

Ti abundance

In both sample suites, biotite in the orthopyroxene-bearing rocks is enriched in Ti compared with biotite from the original hornblende-bearing gneisses (Tables 3a and 4a; Fig. 8a). This correlation between Ti in biotite and the metamorphic 'grade' as it relates to the presence or absence of orthopyroxene agrees well with experiment (e.g. Patiño-Douce, 1993). It also corresponds well to observations from other granulite–amphibolite traverses (Schreurs, 1985; Hansen *et al.*, 1995, 2002). Patiño-Douce (1993) demonstrated experimentally that the solubility of Ti in biotite increases with temperature in a strongly non-linear fashion such that up through to amphibolite

facies conditions, the effect of Ti on the stability of biotite is very small. However, upon the initiation of granulite facies metamorphism, and the dehydration reactions and lower H₂O fugacities that characterize it, Ti in biotite increases markedly, rendering the biotite relatively refractory.

The orthopyroxene-bearing rocks from either the IVZ metabasites (graphite–pyrrhotite–ilmenite–rutile) or the SP metatonalites (graphite–pyrrhotite) must have formed under relatively reducing conditions, i.e. below the quartz–ferrosilite–magnetite oxygen fugacity buffer, as there is no free magnetite. With respect to the IVZ, the presence of both rutile and ilmenite suggests that the formation of Ti-enriched biotite was essentially a back reaction, shortly after the peak of metamorphism ($T < 800^{\circ}\text{C}$), between orthopyroxene, K-feldspar, a TiO₂-bearing phase (rutile, ilmenite) and later-stage OH-bearing fluids along the grain boundaries via the general reactions

Table 5: Average composition of hornblende in metatonalities from the Seward Peninsula

Zone	Sample-(cm)*	SiO ₂	TiO ₂	Al ₂ O ₃	MgO	CaO	MnO	FeOt	Na ₂ O	K ₂ O	Cl	F	H ₂ O†	O = (F + Cl)	Total
2	AB90 + 13-56	45.4	1.09	11.1	12.5	11.3	0.32	14.1	1.26	1.16	0.03	0.06	2.01	0.04	100.3
		0.53	0.05	0.51	0.24	0.12	0.04	0.22	0.05	0.09	0.01	0.02	0.01		
2	AB90 + 13-61	46.5	1.12	10.5	13.1	11.6	0.28	13.2	1.21	1.09	0.03	0.05	2.03	0.03	100.7
		0.54	0.06	0.46	0.26	0.10	0.02	0.18	0.04	0.08	0.01	0.03	0.01		
3	AB90 + 13-86	43.7	1.53	11.6	10.3	11.2	0.37	17.0	1.28	1.34	0.04	0.02	1.99	0.02	100.4
		0.45	0.13	0.33	0.33	0.09	0.05	0.50	0.05	0.07	0.01	0.02	0.01		
3	AB90 + 13-170	44.4	1.10	11.1	11.1	11.3	0.32	16.5	1.22	1.18	0.04	0.00	2.00	0.01	100.2
		0.86	0.08	0.77	0.40	0.11	0.03	0.35	0.08	0.14	0.01		0.01		
3	AB90 + 13-244	43.8	1.43	11.1	10.6	11.4	0.44	17.3	1.28	1.20	0.00	0.00	2.01	0.00	100.5
		0.40	0.05	0.42	0.20	0.09	0.03	0.12	0.04	0.09			0.01		
3	AB90 + 13-287	43.9	1.36	11.1	10.7	11.2	0.48	17.0	1.27	1.22	0.01	0.00	2.01	0.00	100.2
		0.45	0.07	0.38	0.23	0.11	0.03	0.25	0.05	0.09	0.01		0.01		
3	AB90 + 13-381	43.5	1.28	11.3	10.1	11.2	0.37	18.0	1.28	1.25	0.03	0.00	1.99	0.01	100.3
		0.47	0.15	0.40	0.21	0.10	0.04	0.23	0.05	0.10	0.01		0.01		
3	AB90 + 13-594	44.6	1.50	10.9	11.4	11.3	0.34	15.3	1.26	1.20	0.05	0.03	1.99	0.02	100.0
		0.58	0.12	0.53	0.31	0.13	0.03	0.25	0.06	0.12	0.01	0.02	0.01		

1 σ standard deviation in italics. Metamorphic zones: 2, transition zone; 3, amphibolite facies zone.
 *Distance from the contact with the marble. †Total Fe as FeO. ‡Calculated assuming the (F,Cl,OH) site is filled.

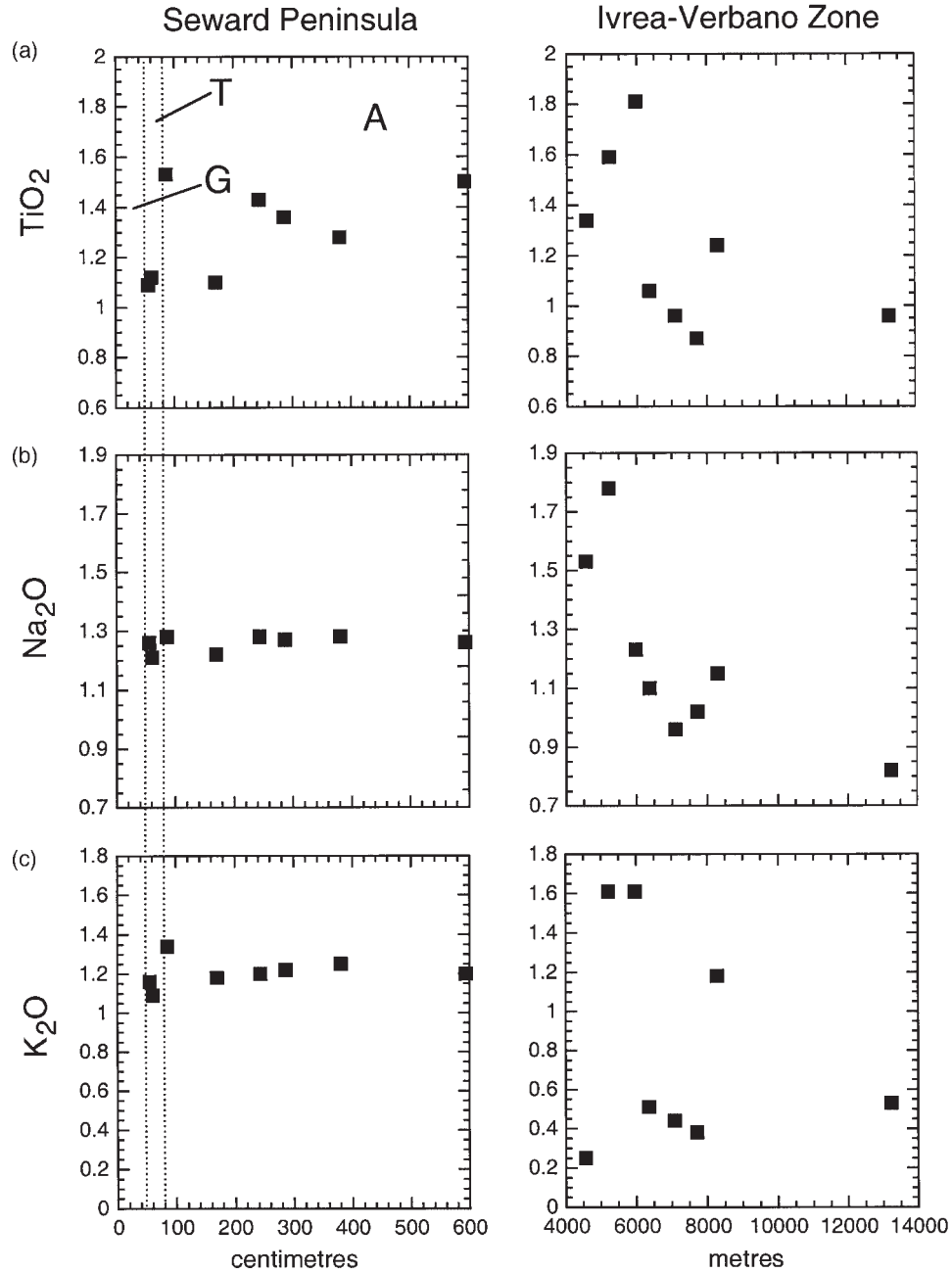
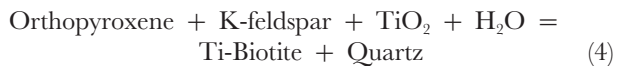
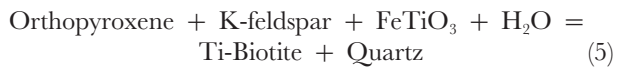


Fig. 10. Plots comparing selected element (mean oxide wt %) abundances in hornblende as a function of distance from the marble for the SP metatonalites (Table 5) and the contact with the Mafic Formation for the IVZ (Table 6) for (a) TiO_2 , (b) Na_2O , and (c) K_2O . The dotted vertical lines for the SP designate divisions between the dehydration zone (granulite facies) (G), the transition zone (T), and the amphibolite facies zone (A) as described in the text. Standard deviations in composition are given in Tables 5 and 6. Error in distance is equal to the width of the symbol in either set of plots.



and/or



(see Patiño-Douce, 1993, fig. 11). The relatively high abundances of orthopyroxene, K-feldspar, rutile and ilmenite in the present samples imply that the amount of biotite produced was limited by the post-peak metamorphic H_2O fugacity. In this respect, reactions (4) and (5) would serve as a means of adjusting (i.e. lowering)

Table 6: Average composition of hornblende from the Mafic Formation and metabasites from the Ivrea–Verbano Zone

Zone	Sample	Distance (m)*	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	MgO	CaO	MnO	FeOt	BaO	Na ₂ O	K ₂ O	Cl	F	H ₂ O†	O = (F + Cl)	Total
<i>Mafic Formation</i>																		
	I293-60	0	41.6 0.46	2.65 0.32	12.5 0.41	0.01 0.02	11.0 0.28	11.8 0.09	0.06 0.02	15.1 0.46	0.08 0.05	1.62 0.09	1.67 0.08	0.06 0.01	0.08 0.03	1.96 0.01	0.04	100.2
<i>Metabasites</i>																		
2	IV97-3	4570	44.5 0.33	1.34 0.10	11.2 0.20	0.01 0.01	11.6 0.29	11.5 0.11	0.38 0.03	15.6 0.46	0.02 0.03	1.53 0.12	0.25 0.02	0.00	0.00	2.02 0.01	0.00	99.9
3	I293-67	5220	40.5 0.39	1.59 0.23	14.6 0.50		8.77 0.32	11.7 0.09	0.27 0.02	17.4 0.32		1.78 0.04	1.61 0.09	0.00	0.00	1.98 0.01	0.00	100.3
3	IV97-4	5980	41.3 0.13	1.81 0.22	12.7 0.23	0.02 0.02	6.60 0.06	11.7 0.06	0.32 0.04	21.1 0.23	0.03 0.04	1.23 0.04	1.61 0.07	0.01 0.01	0.00	1.96 0.01	0.00	100.4
3	I293-96	6370	45.8 0.24	1.06 0.10	11.3 0.36		9.79 0.08	11.2 0.13	0.32 0.05	17.5 0.30		1.10 0.06	0.51 0.02	0.01 0.01	0.00	2.03 0.01	0.00	100.6
3	I293-98	7100	46.2 0.56	0.96 0.14	11.2 0.48		10.3 0.55	11.0 0.36	0.26 0.07	16.9 0.75		0.96 0.15	0.44 0.08	0.01 0.01	0.00	2.04 0.01	0.00	100.2
3	I293-99	7720	45.1 0.48	0.87 0.20	12.2 0.34		9.43 0.28	10.6 0.26	0.16 0.02	18.1 0.32		1.02 0.07	0.38 0.04	0.01 0.01	0.00	2.02 0.01	0.00	99.9
3	IV97-5	8300	44.0 0.31	1.24 0.19	12.5 0.18		8.37 0.17	10.9 0.12	0.26 0.04	18.7 0.26		1.15 0.03	1.18 0.06	0.00	0.00	2.00 0.01	0.00	100.3
3	I293-105	13240	46.0 1.36	0.96 0.19	11.2 1.47		9.69 0.73	11.7 0.47	0.24 0.03	17.0 0.66		0.82 0.10	0.53 0.13	0.01 0.01	0.00	2.03 0.02	0.00	100.2

1σ standard deviation in italics. Metamorphic zones: 2, transition zone; 3, amphibolite facies zone.

*Distance from the contact with the Mafic Formation. †Total Fe as FeO. ‡Calculated assuming the (F,Cl,OH) site is filled.

the H_2O fugacity in these rocks as a function of pressure and temperature during cooling and uplift such that the high-grade mineral assemblage present, i.e. orthopyroxene–K-feldspar–ilmenite–Ti-biotite–quartz, was stabilized. In general, this ‘buffering’ of the H_2O fugacity allows such high-grade ‘dry’ mineral assemblages to be preserved under mid- to upper-crustal PT conditions over long periods of time (Yardley & Valley, 1997).

In the case of the SP dehydration zone, lack of both rutile and ilmenite would suggest that the limited amount of Ti available from the breakdown of the hornblende [Table 5; reaction (1)] went directly into the biotite via the $TiFe_{-2}$ exchange vector (see Patiño-Douce, 1993). Lack of magnetite would imply that excess Fe from the biotite probably went into other Fe–Mg-bearing silicate phases such as the pyroxenes. Evidence for this is seen in the lower Fe content in biotite from the dehydration zone as compared with biotite from the amphibolite facies zone (Fig. 8b). What can be concluded, then, for either traverse, is that an increase in the Ti content of the biotite in the dehydration zones is not only temperature related but must involve other factors such as a lowering of the H_2O activity and consequently the nature of the fluids present both during and shortly after the dehydration event.

Fluid composition in terms of relative HCl and HF fugacities

In both the SP and IVZ dehydration zones, the last fluids in equilibrium with the biotite show virtually identical relative HF and HCl fugacities (compare Tables 3b and 4b). With respect to the SP, whereas the composition of the fluid responsible for the orthopyroxene-bearing zone was principally CO_2 (Todd & Evans, 1994), Tables 3a and 5 and Fig. 8d–f suggest the presence of an additional F–Cl–OH component. In addition to being an obvious source for OH, the very minor Cl component in the hornblende (Table 5) could also serve as a source of Cl as well. This would account for the somewhat erratic and localized Cl content in the biotite from the SP. The systematic decrease of f_{HF} relative to f_{H_2O} away from the contact suggests that some mineral source in the marble was responsible for the F component in the CO_2 -rich fluids percolating through the metatonalites. Todd & Evans (1994) noted the presence of halogen-bearing minerals in the marble such as phlogopite and clinohumite. This behaviour cannot be explained if the former hornblende in the dehydration zone is invoked as the sole source for F, as hornblende deep in what was apparently the original amphibolite gneiss contains negligible amount of F (Table 5). In addition, if hornblende were indeed the primary source of F, the same overall level of enrichment in F in the biotites should be seen throughout the dehydration zone as opposed to the

systematic trend actually observed (Fig. 8e). Proof that this F–Cl–OH component, at least with respect to F and OH, travelled well beyond the dehydration zone in the SP can be seen in the uniform decrease in the HF fugacity relative to H_2O for biotite hundreds of centimetres into the original amphibolite facies gneiss (Fig. 8e).

On the basis of the data available, the simplest explanation for the F anomaly seen at ~600 cm into the amphibolite facies gneiss for the SP is that of a local enrichment in F inherited from its progenitor (Fig. 8d and e). This enrichment is also reflected in the F content of the hornblende (Table 5) and apatite (Harlov & Förster, 2002). Although it is possible that the high F content in this sample could represent some sort of fluid ‘spike’ much as that seen in a chromatographic column, lack of samples in the immediate vicinity (± 200 cm) of sample AB90+13-594 does not allow sufficient information to make a more substantive speculation.

In the IVZ sample suite, the fugacity of HCl relative to H_2O is about one order of magnitude lower in the fluids last equilibrated with the biotite in the amphibolite facies metabasites compared with that in the orthopyroxene-bearing dehydration zone (Fig. 8f). This trend is much more obvious for the fugacity of HF relative to H_2O , which is characterized by a smooth decrease of about two orders of magnitude as a function of distance from the Mafic Formation. Although the majority of the F should have been partitioned into the underplating mafic magma at the base of the sequence (e.g. Markl & Piazzolo, 1998), a minority would have been expelled during crystallization, which would have gradually become relatively more diluted with H_2O with increasing distance from the Mafic Formation, as a result of hornblende breakdown. This is seen in the hornblende from the Mafic Formation, which is relatively enriched in F and Cl compared with hornblende in the amphibolite facies metabasite layers, which contains negligible amounts of either element (Table 6).

Additional support for the presence of Cl-bearing fluids in the IVZ includes the presence of NaCl daughter crystals in micron-sized high-grade fluid inclusions in the quartz grains from the granulite facies metapelites (de Negri & Touret, 1979). In addition, using TEM, Harlov & Wirth (2000) have observed the presence of $CaCl_2$ daughter crystals in 50–100 nm size, intact fluid inclusions in the K-feldspar micro-veins, especially along the quartz–K-feldspar phase boundaries.

Hornblende chemistry

Major element patterns in the hornblende are more difficult to interpret. This is especially seen in the SP, where, contrary to the smooth patterns recorded in biotite, the distribution of most of the major components

appears to be relatively constant (Fig. 10). Hornblende near or in the transition zone is relatively enriched in F (see Table 5). However, the F content in the hornblende rapidly decreases further along the traverse into the amphibolite gneiss. This pattern is consistent with the general F pattern seen in biotite (Fig. 8d) as well as apatite (see Harlov & Förster, 2002; fig. 11a). This is further evidence of an F component in the CO₂-rich fluid, originating in the marbles, which moved through these rocks during the dehydration event. This fluid, in addition to enriching biotite and apatite in F, also enriched hornblende nearest the dehydration zone, apparently becoming more diluted with respect to F as it moved further into the amphibolite facies zone. However, these same fluids apparently had no influence in altering the rather uniform cation composition of the hornblende, which reflects the invariant composition rendered the hornblende by the FMASH system at fixed pressure and temperature (Todd & Evans, 1994).

Whereas hornblende from the IVZ shows a higher variability in composition than is seen for the SP, a general pattern for Ti and Na, as a function of decreasing content with increasing distance from the transition zone, can be recognized (Table 6; Fig. 10). With respect to Ti, this pattern may, in part, be a temperature effect, with Ti contents decreasing as a function of falling temperature and increasing distance from the heat source, i.e. the Mafic Formation (e.g. Ernst & Liu, 1998). In the case of Na, its decreasing abundance could reflect a dilution in Na in the proposed fluid front as a result of Na partitioning into the hornblende as the fluid moves further up the rock column. However, an alternative explanation again could be that this variability in composition as well as apparent decreases in both the Ti and Na content only reflect relative varying modal compositions in the metabasites along the traverse, with the composition of the hornblende fixed by the FMASH system at the particular pressure and temperature of each sample location.

FLUID-INDUCED SOLID-STATE HIGH-GRADE DEHYDRATION

Todd & Evans (1994) presented several strong lines of evidence that the 85 cm thick dehydration zone in the SP was probably induced by the infiltration of a CO₂-rich fluid from an underlying marble layer. This limited ability of CO₂ to penetrate rock has been confirmed in fluid-rock experiments along the CO₂-H₂O join involving synthetic dunite and quartzite at 10 kbar and 950–1200°C. Fluids rich in CO₂ have very high wetting angles such that they do not form an interconnected network along grain boundaries but rather isolated pockets of fluid (Watson & Brenan, 1987; Holness, 1997). This behaviour probably encourages their entrapment

as fluid inclusions and could explain the high number of CO₂-rich fluid inclusions generally observed in granulite facies rocks (e.g. Touret, 1985). Experiments looking at CO₂ transport in quartzite at 5–13 kbar and 1050–1200°C have shown that the CO₂ could penetrate the sample only via a macroscopically visible system of transgranular fractures and not along grain boundaries (Brenan & Watson, 1988). Additional support for these observations comes from $\delta^{18}\text{O}$ isotope studies of incipient charnockite formation in southern India, which strongly suggest that high-grade CO₂-rich fluids have a limited infiltration range of <2 m (Harris & Bickle, 1989). With respect to capacity for mass transport, both Walther (1992) and Newton & Manning (2000) have shown that silicates in general have very low solubilities in pure CO₂ under granulite grade conditions. These solubilities only increase with increasing H₂O activity. This would imply that in the case of the SP the mobility of SiO₂, Al₂O₃, and K₂O responsible for the genesis of the K-feldspar micro-veins as well as TiO₂, was probably facilitated by the F-Cl-OH component in the fluid as documented by both biotite and hornblende.

Because of its limited mobility on a regional scale, it is unlikely that a CO₂-rich fluid could have played a significant role in dehydrating the IVZ metabasites. Indeed, in a $\delta^{18}\text{O}$ study of the metabasites and metapelites from the Val Strona di Omegna, Baker (1988) found no evidence of CO₂ infiltration from either the mantle or the Mafic Formation. However, a broad and continuous decrease in the fugacity of HF and HCl relative to H₂O, as recorded in the biotite grains from the metabasite layers in the dehydration and transition zones, supports the existence of a low H₂O activity fluid front, with both a F and Cl component, starting at the location of the present-day Mafic Formation. In such a scenario, with increasing distance from the Mafic Formation, such a fluid front would become increasingly diluted with H₂O, contributed primarily by hornblende breakdown. At some point H₂O activities, as a function of the prevailing *PT* conditions, would be too high to allow for the breakdown of the hornblende to orthopyroxene ($\pm$ clinopyroxene) stopping the dehydration process. The production of such a fluid front would have to have occurred during the latter stages of crystallization of the Mafic Formation when Cl- and F-bearing fluids would have been forced out (see Bailey, 1980; Markl & Piazzolo, 1998). In such a scenario, dehydration of the metabasite layers would then have occurred after the partial melting of the metapelite layers, which is speculated to have occurred during the actual emplacement of the magmas responsible for the Mafic Formation (Schnetger, 1994). Any local fluids contributed by the now granulite facies metapelites and/or fluids passing through the metapelite layers must have had relatively low H₂O activities to allow for the survival

and/or creation of orthopyroxene in the interlayered metabasites.

Studies of high-grade Cl- and F-bearing fluids with respect to their role in granulite facies metamorphism have focused primarily on low H_2O activity, concentrated or supercritical NaCl–KCl brines (e.g. Aranovich *et al.*, 1987; Aranovich & Newton, 1998; Newton *et al.*, 1998). Such fluids have been proposed as a possible initiator of the dehydration reactions required during regional granulite facies metamorphism. In distinct contrast to CO_2 , the mobility of these brines along silicate grain boundaries at granulite grade pressures and temperatures is high (Holness, 1997). This is seen in grain boundary experiments involving quartzite at 10 kbar and 950–1150°C, which indicate that these brines have both a low viscosity and a low wetting angle (Watson & Brenan, 1987). This allows them to form a highly interconnected network along grain edges, thus allowing for the possibility of fluid transport by porous flow over relatively large distances. This feature might explain why brine-rich fluid inclusions are relatively rare in granulite facies rocks (e.g. Touret, 1985), although another possibility is that the isochore for such inclusions can be steep when compared with the retrograde *PT* path. This results in collapsed brine inclusions, which are relatively difficult to detect (e.g. Touret & Huizenga, 1999). In general, brines are well known to have a strong capacity for alkali exchange and mobility (Orville, 1972) as well as a high mobility for metals and silica over a wide range of temperatures and pressures (Helgeson, 1964, 1969; Barnes, 1979; Newton & Manning, 2000). In addition, experiments at granulite grade pressures and temperatures (700–900°C; 6–10 kbar) involving the reversal of the brucite–periclase transition in concentrated and supercritical NaCl–KCl– H_2O brines (Aranovich & Newton, 1996, 1997) or the melting of albite in solutions across the NaCl– H_2O join (Shmulovich & Graham, 1996) indicate that at pressures ≥ 4 kbar, the activity of H_2O goes approximately as $X_{H_2O}^2$ or higher and not as X_{H_2O} . As a consequence, at granulite grade pressures, a fluid can be relatively H_2O rich, i.e. $X_{H_2O} \geq 0.5$ and still have a low H_2O activity. This observation is augmented by additional experiments involving the transition of phlogopite + quartz to enstatite + K-feldspar + H_2O (750–875°C, 2–12 kbar) in the presence of a concentrated KCl brine (Aranovich & Newton, 1998), although similar experiments have yet to be done involving hornblende using reaction (1). These experiments indicate that the stability field of phlogopite + quartz is shifted to lower temperatures, suggesting that the assemblage orthopyroxene–biotite–garnet–K-feldspar–plagioclase–quartz can exist at much higher H_2O activities (0.4–0.6) than estimated previously from the thermodynamic properties of phlogopite. H_2O activities in this range are commonly observed in near-peak metamorphic brine rich fluid

inclusions from granulite facies terranes (Touret, 1985, 1996). With respect to the IVZ, although there is evidence for a large-scale fluid front moving up from the Mafic Formation through the metabasite layers, there is no direct evidence that this front was a concentrated or supercritical brine. All that can be concluded is that this fluid must have had a low H_2O activity and contained a Cl and F component in unknown amounts.

However, some sort of contribution in the form of fluids or even volatile-rich melts to the metabasite layers by the intervening metapelite layers during partial melting cannot be totally ruled out, as whole-rock analysis of each of the metabasite samples indicates a metapelitic component. In addition, evidence outlined by Harlov & Förster (2002) strongly suggests that there was also mixing along the boundary between the metapelite and metabasite layers during partial melting of the metapelites. However, it is highly unlikely that these partial melts could have acted as a dehydrant in the metabasite layers causing the hornblende to break down to orthopyroxene $\pm$ clinopyroxene, as these partial melts would have been enriched in H_2O . In this respect, there is also no evidence to suggest that the K-feldspar micro-veins could have originated from these same partial melts extracted from the surrounding metapelites during granulite facies metamorphism, as such melts would have approximated a granitic composition (Schnetger, 1994). Lastly, even if partial melts from the metapelite layers were somehow responsible for the K-feldspar micro-veins, their crystallization would have released H_2O and, consequently, partially rehydrated the garnet and orthopyroxene in contact with these micro-veins producing reaction rims of biotite and/or hornblende, for which there is no petrographic evidence.

However, increases in the bulk-rock K content need not be limited to either partial melts or mechanical mixing. They could also be metasomatically induced. Some workers, including Korzhinskii (1959) and Perchuk *et al.* (2000), have proposed that, under granulite facies conditions, K is highly mobile in halogen-bearing fluids. This would suggest that enrichment of the metabasite layers in K could also have been, at least in part, a product of the metasomatic event that dehydrated them.

SUMMARY AND CONCLUSIONS

Despite the fact that the dehydration zones in the SP and IVZ possess dramatically different thicknesses (85 cm vs 3–4 km), the stark similarity between the two traverses with respect to their feldspar–quartz textures and biotite chemistry argue for a fluid-induced dehydration of the IVZ metabasite layers. In either traverse, micro-veins of K-feldspar occur along quartz and plagioclase grain boundaries with replacement antiperthite in a random

scattering of plagioclase grains. Modal mineral analysis as well as reintegration using microprobe analysis coupled with transmitted light, BSE and TEM investigations on the micron and sub-micron scale support a high-grade origin for these micro-veins. They also support the proposal that the chief source of K for the K-feldspar resulted from the breakdown of hornblende, rather than biotite, in the presence of quartz, to orthopyroxene, clinopyroxene, plagioclase and H₂O during a melt absent, dehydration event induced by fluid infiltration, although in the case of the IVZ there is evidence for an external source of K as well. Cation (Ti, Fe, and Mg) abundances in the biotite, coupled with HF fugacities relative to H₂O, as a function of distance in either traverse suggest regrowth during the dehydration event and/or exchange with a fluid phase in the dehydration zone at relatively low H₂O activities shortly after the peak of metamorphism.

In the SP, trends in the biotite composition with respect to the HF fugacity relative to H₂O imply that fluid infiltration into the metatonalite occurred over a much larger traverse (≥ 4 m) than indicated by the dehydration zone (85 cm) (Fig. 8e). A similar pattern is seen in the IVZ, although the absence of high-grade biotite in the amphibolite facies metabasites hampers a complete comparison. However, the HCl and HF fugacities relative to H₂O estimated for biotite in the dehydration and transition zones support the presence of a low H₂O activity Cl–F-bearing fluid, which became further diluted with respect to increasing distance from the Mafic Formation and thus acted as a medium of transport for carrying H₂O away from the metabasite layers. Regular patterns in the hornblende compositions in the IVZ suggest that any fluids given off during the underplating event could have influenced the metamorphic column over a distance far beyond the granulite facies zone, although by this time the H₂O activity of these fluids was too high to effect the breakdown of hornblende to orthopyroxene and clinopyroxene. Finally, during the formation of biotite and the K-feldspar micro-veins in the IVZ dehydration zone, no measurable influence from H₂O-rich fluids and/or melts derived during the melting of the metapelites can be recognized. This would then presume that the melting of the metapelites and their transformation to the restitic strombolites occurred before the dehydration of the metabasites and were not directly responsible for their dehydration. In either traverse the one universal feature is that of increasing H₂O content with increasing distance from the fluid and/or heat source. The simplest explanation for this increasing H₂O content is the breakdown of hornblende coupled with a fluid front, initially characterized by a low H₂O activity fluid that, by removing H₂O from the dehydration zone, gradually becomes more diluted with H₂O as it moves away from the fluid source up the rock column.

The remarkable similarities seen between the SP and IVZ dehydration zones with respect to their K-feldspar–plagioclase–quartz textures and biotite chemistry, coupled with evidence of both a Cl and F signal for either traverse, lend additional credence to the idea that high-grade, low H₂O activity fluids, over scales ranging from centimetres to kilometres, can play a crucial role in the dehydration of hornblende + quartz to orthopyroxene $\pm$ clinopyroxene, K-feldspar and plagioclase. This would imply that in general such fluids could serve as a principal instigator in the granulite facies metamorphism of mafic rocks in the middle to lower crust.

ACKNOWLEDGEMENTS

We thank Helga Kemnitz and Ursula Glenz for assistance with the SEM, Dieter Rhede and Oona Appelt for help with the electron microprobe, and Richard Wirth for assistance with the TEM photo. Bernard Evans and Clifford Todd at the University of Washington, Seattle, generously provided the original samples from the SP used by Todd & Evans (1994). Leander Franz, Stefan Teuffel and Onno Oncken are acknowledged for collecting the majority of the samples from the IVZ used in this study for use in an earlier project. Thorough and thoughtful reviews by Bernard Evans, Jacques Touret, Timo Nijland and Ed Hansen were of great help in revising the original manuscript.

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