

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 II: Phosphate Mineral Chemistry

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This study explores the origin and geochemical evolution of apatite, monazite, and xenotime along two metamorphic traverses. The first, from the Kigluaik Mountains, Seward Peninsula, Alaska, consists of a localized (85 cm) orthopyroxene–clinopyroxene-bearing dehydration zone. The second consists of orthopyroxene $\pm$ clinopyroxene-bearing granulite facies metabasite layers interlayered with metapelites over a 3–4 km traverse, along the Val Strona, Ivrea–Verbano Zone, Northern Italy (IVZ). In both dehydration zones small Th- and U-poor inclusions of monazite and/or xenotime occur in the apatite. These inclusions are metasomatically induced and nucleated within the apatite via the coupled substitutions $\text{Na}^+ + (\text{Y} + \text{REE})^{3+} = 2 \text{Ca}^{2+}$ and $\text{Si}^{4+} + (\text{Y} + \text{REE})^{3+} = \text{P}^{5+} + \text{Ca}^{2+}$. These are not present in apatite from the original amphibolite facies gneiss. Apatite, in both dehydration zones, also shows a relative increase in both F and Cl compared with apatite from the amphibolite facies zone. Granulite facies metabasites in the IVZ also contain isolated monazite grains, which range from uniform to complexly zoned in Th (13–30.1 mol % ThSiO_4). These are the product of the breakdown and subsequent mobilization of the lanthanides and actinides from monazite-(Ce) in the metapelitic layers into the metabasite layers at the start of granulite facies metamorphism.

KEY WORDS: apatite; monazite; xenotime; KCl–NaCl brines; metasomatism; phosphate minerals; charnockite–enderbite; granulite facies metamorphism

INTRODUCTION

Fluorapatite, $[\text{Ca}_5(\text{PO}_4)\text{F}]$, is a common accessory mineral in most amphibolite and granulite facies, metapelitic to metabasic rocks. The Cl–F–OH chemistry of apatite can be used to fingerprint the volatile composition of fluids present in these rocks under high-grade conditions (e.g. Nijland *et al.*, 1993). In this respect, apatite can play an important role in understanding the history of fluid–rock interaction during the formation and subsequent evolution of either facies. Both Nijland *et al.* (1993) and Bisanz *et al.* (2000) have compared the apatite Cl–F–OH chemistry of a granulite facies zone with its neighbouring and genetically related amphibolite facies zone. Whereas the Bisanz *et al.* (2000) study examined a specific *PT* traverse and recognized some regional trends in $\log(f\text{H}_2\text{O}/f\text{HF})$ and $\log(f\text{H}_2\text{O}/f\text{HCl})$, no regional trends were discerned in the Nijland *et al.* (1993) study, as a result of the lack of a distinct temperature and/or obvious fluid-induced transition from amphibolite to the granulite facies.

In contrast to apatite, monazite $[(\text{Ce}, \text{La}, \text{Nd}, \text{Th})\text{PO}_4]$ and xenotime $[(\text{Y}, \text{HREE})\text{PO}_4]$ are chiefly found in metamorphic rocks of pelitic or granitic origin (e.g. Bingen *et al.*, 1996; Franz *et al.*, 1996). In addition to serving as a geochronometer, monazite coexisting with xenotime has been both empirically and experimentally calibrated as

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

a geothermometer (Gratz & Heinrich, 1997, 1998; Heinrich *et al.*, 1997; Andrehs & Heinrich, 1998). Although chemical relationships between apatite, monazite, and xenotime, as a function of pressure and temperature, are not completely understood, all three either directly or indirectly influence the (Y + REE) chemistry of metamorphic rocks, depending on which silicate phases are present, by acting as a reservoir for these elements.

In this study we expand our comparison of two amphibolite–granulite facies traverses, the Seward Peninsula, Alaska (SP) (metatonalites) (Todd & Evans, 1994) and the Val Strona di Omegna, Ivrea–Verbano Zone, Northern Italy (IVZ) (specifically the metabasite layers) (Franz & Harlov, 1998) begun in Part I (Harlov & Förster, 2002), to include apatite, monazite, and xenotime. Both terranes experienced a high-grade dehydration event transforming a section of either traverse from amphibolite facies to orthopyroxene-bearing granulite facies rock at about 800°C and 7–8 kbar. The principal difference is that for the SP metatonalites the dehydration zone is only 85 cm thick, whereas for the IVZ it extends over a 3–4 km thick section consisting of metabasites interlayered with metapelites. Either traverse can be divided into three principal zones (Todd & Evans, 1994; Harlov & Förster, 2002). The zone closest to the fluid and/or heat source consists of a dehydration zone made of orthopyroxene $\pm$ clinopyroxene–Ti-enriched biotite–plagioclase–K-feldspar–quartz with a near to total absence of hornblende. This is followed by a transition zone, which for the IVZ, consists of orthopyroxene-out in the metabasites and a continuation of granulite facies conditions in the metapelites. For the SP, the transition zone consists of coexisting orthopyroxene, clinopyroxene, and hornblende. Either transition zone is followed by an amphibolite facies zone in which hornblende has replaced orthopyroxene as the dominant Fe–Mg silicate mineral.

Part I of this investigation focuses on silicate mineral chemistry and petrography. This includes feldspar–quartz reaction textures as well as biotite and hornblende mineral chemistry. Microprobe analysis of biotite allows for HF and HCl fugacities relative to H₂O to be estimated, which gives insight into the nature of the metamorphic fluids present shortly after the dehydration event as well as how these fluids evolved as they migrated through either traverse. Part II concentrates on the phosphate mineralogy of both traverses, specifically with respect to apatite, monazite, and xenotime composition, their morphological relationship to each other, and the genesis and subsequent metasomatic alteration of these minerals.

Analytical techniques

Microscopic investigation of the samples was carried out using back-scattered electron (BSE) imaging as well as

transmitted light optical microscopy under crossed polars. BSE pictures were taken using a Zeiss DSM 962 digital scanning electron microscope with either 15 or 20 kV acceleration voltage.

Analyses of monazite and xenotime were performed using a CAMECA SX-50 electron microprobe operating in the wavelength-dispersive mode, employing a PAP correction procedure (Pouchou & Pichoir, 1985). Operating conditions included an accelerating potential of 20 kV, a beam current of 50 nA (measured on the Faraday cup), and a beam diameter of 1 μ m. Only grains with sizes of the order of at least 5 μ m were analysed.

Counting times on the peak were 300 s for Pb, 200 s for U, and 60 s for Th and, in each case, half that time for background counts on both sides of the peak. For the (Y + REE) and other elements, counting times were 80 s on the peak. X-ray lines and background offsets were selected to minimize interferences as well as their correction (Exley, 1980; Roeder, 1985). Wavelength-dispersion spectral scans carried out on complex natural monazite and xenotime were used to determine the peak and background positions of each element and to identify overlapping peaks. The interferences of Th M β on U M α and Y L α on Pb M α were eliminated by using the Th M α , U M β and Pb M β lines. Minor interferences of Th M γ on U M β were corrected using the procedure of Åmli & Griffin (1975).

Primary standards included pure metals for Th and U, vanadinite for Pb, synthetic phosphates prepared by Jarosewich & Boatner (1991) for the REE, and natural minerals and synthetic oxides for other elements. Accuracy of the calibration was checked routinely using synthetic ThO₂ and UO₂₋₁₅, synthetic glass SRM 610, which contains some hundred parts per million of Th, U, and Pb, a synthetic glass containing 0.79 wt % PbO, and the REE glasses prepared by Drake & Weill (1972). Reproducibility of the stated compositions in the SRM 610 glass was better than 15%. Reproducibility of the stated compositions in the REE glasses was better than 5–10%. The analytical errors for the (Y + REE) depend on the absolute abundances of each element. Relative errors are estimated to be <1% at the >10 wt % level, 5–10% at the 1 wt % level, 10–20% at the 0.2–1 wt % level, and 20–40% (or 10% for U, Th, and Pb) at the <0.1 wt % level. Detection limits were $\sim$ 200–300 ppm for all elements monitored except lead ($\sim$ 100 ppm). Representative analyses of monazite from the IVZ granulite facies metabasites and metapelites are contained in Tables 1–3. Representative analyses of monazite and xenotime from the SP metatonalites are contained in Table 4.

Apatite was analysed using either a raster scan over an approximately 80 μ m $\times$ 100 μ m area or a 15 μ m beam spot. Operating conditions included an accelerating potential of 20 kV and a beam current of 20 nA. Extra

Table 1: Representative EMP analyses of monazite in granulite facies metabasites from the Irea-Verbano Zone

| Host mineral: | garnet | plagioclase | |
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 | biotite
 | quartz | K-feldspar | | ilmenite

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| | | VS24 | VS30 | VS30*
 | VS30*
 |
 | | IV94-15 | IV94-15* |

 | |
| Sample: | VS24 | VS30 | VS30 | VS30*
<td>VS30*<td>VS30*<td>IV94-15</td><td>VS30</td><td>IV94-15</td><td>IV94-15*<td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</td><td>IV94-15</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*Analyses from zoned grains.

Table 2: Representative EMP analyses of monazite in apatite or on apatite grain rims in granulite facies metabasites from the Ivrea–Verbano Zone

Sample:	IV97-1a	IV97-1a	VS24	IV97-2	IZ96-181	IZ93-61	IZ93-63	IV94-15
P ₂ O ₅	30.0	29.9	30.5	30.2	30.4	29.9	30.4	30.4
SiO ₂	0.26	0.33	0.22	0.28	0.25	0.29	0.26	0.22
ThO ₂	0.00	0.38	0.00	0.14	0.00	0.00	0.01	0.00
UO ₂	0.00	0.00	0.00	0.13	0.04	0.00	0.06	0.14
Y ₂ O ₃	0.00	0.51	0.12	1.09	0.03	0.00	0.28	0.00
La ₂ O ₃	17.0	17.3	13.6	16.4	13.5	18.5	13.6	14.4
Ce ₂ O ₃	34.5	34.1	32.7	33.0	34.2	34.8	34.3	34.9
Pr ₂ O ₃	3.52	3.44	3.82	3.29	3.98	3.27	3.80	3.83
Nd ₂ O ₃	13.1	12.6	16.7	12.4	15.2	11.7	14.6	14.2
Sm ₂ O ₃	1.05	1.38	2.39	1.48	1.82	1.04	2.03	1.41
Gd ₂ O ₃	0.09	0.54	0.79	0.99	0.56	0.18	0.83	0.46
Tb ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dy ₂ O ₃	0.00	0.03	0.00	0.22	0.00	0.00	0.04	0.00
Ho ₂ O ₃	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00
Er ₂ O ₃	0.00	0.01	0.03	0.10	0.00	0.00	0.00	0.00
Yb ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lu ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CaO	0.20	0.25	0.14	0.40	0.46	0.25	0.31	0.13
FeO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
PbO	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.8	100.7	101.0	100.2	100.4	99.9	100.5	100.2

care was taken to avoid any monazite and/or xenotime inclusions. No discernible difference, i.e. within microprobe error, can be seen between the two approaches. Both techniques gave an accurate and reproducible F analysis when tested using the Durango apatite. Elements analysed included P, Si, Y, La, Ce, Nd, Sm, Gd, Dy, Yb, Ca, Mn, Fe, Sr, Ba, Na, F, and Cl, with counting times of 20–120 s depending on the relative amount of the element. Standards and counting times for the (Y + REE) were the same as used for monazite and xenotime. Anywhere from five to 25 apatite grains were analysed per sample, generally in a relatively even sampling over the entire breadth and length of the thin section. If possible, both the core and rim were sampled. However, as it was necessary to use either a raster scan or a broad beam spot, any contrast between the rim and core composition is, at best, vague and thus will not be considered further in this study. Representative analyses of apatite from the IVZ granulite facies metabasites and metapelites and from the SP metatonalites are contained in Tables 5 and 6, respectively. The full dataset representing all individual monazite, xenotime, and apatite analyses taken from the SP and IVZ traverses may be

downloaded from the *Journal of Petrology* Web site at <http://www.petrology.oupjournals.org>.

Microprobe traverses up to monazite or xenotime inclusions in apatite were made for Ce, Y, Cl and Si (elemental wt %) using a 40 nA, 20 kV, 5 µm beam spot along with standards. Each spot was measured for 300 s using fixed spectrometers. Backgrounds on either side of the peak were counted for 150 s. Long counting times were necessary because of the relatively low abundances of Ce, Y, Cl and Si (hundreds to thousands of ppm) in the apatite. Traverses were made in 5 µm increments and normally involved anywhere from five to 50 points. Si was measured mostly as a control, i.e. those points enriched in Si were generally associated with cracks or pits and consequently were discarded.

RESULTS

Occurrence and composition of monazite-(Ce) and xenotime-(Y)

In the IVZ, monazite-(Ce) constitutes a widespread accessory phase in the granulite facies metabasites [this

Table 3: Representative EMP analyses of monazite in granulite facies metapelites from the Ivrea–Verbano Zone

Host mineral:	garnet		feldspar		quartz	
Sample:	IZ96-182	IZ96-182	IZ96-182	IZ96-180	IZ96-182	IZ96-180
P ₂ O ₅	29.4	29.3	29.3	29.5	29.7	28.8
SiO ₂	0.57	0.66	0.68	0.50	0.42	1.11
ThO ₂	2.54	4.13	3.13	6.16	4.87	8.09
UO ₂	0.05	0.40	0.07	0.07	0.16	0.06
Y ₂ O ₃	0.01	1.27	0.00	0.15	0.13	0.00
La ₂ O ₃	18.3	14.9	15.8	15.6	14.6	15.6
Ce ₂ O ₃	31.3	30.6	32.9	30.1	30.5	30.0
Pr ₂ O ₃	2.89	3.13	3.30	2.97	3.13	2.98
Nd ₂ O ₃	12.8	11.6	13.0	11.7	12.5	11.6
Sm ₂ O ₃	1.79	1.56	1.18	1.34	2.02	1.06
Gd ₂ O ₃	0.33	1.13	0.16	0.75	1.02	0.30
Tb ₂ O ₃	0.00	0.04	0.00	0.00	0.00	0.04
Dy ₂ O ₃	0.00	0.30	0.00	0.00	0.00	0.00
Ho ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00
Er ₂ O ₃	0.00	0.08	0.00	0.00	0.00	0.00
Yb ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00
Lu ₂ O ₃	0.00	0.00	0.00	0.00	0.01	0.00
CaO	0.31	0.64	0.31	1.10	0.88	0.89
FeO	0.00	0.00	0.00	0.00	0.01	0.00
PbO	0.03	0.05	0.05	0.09	0.07	0.09
Total	100.3	99.7	100.0	100.1	100.1	100.6

study and Förster & Harlov (1999)] and in both the granulite facies and amphibolite facies metapelites [this study; see also Schnetger (1994) and Bea & Montero (1999)]. In contrast, it is absent in the amphibolite facies metabasites. In the granulite facies metabasites, monazite is associated with a variety of minerals (apatite, garnet, K-feldspar, plagioclase, biotite, quartz, ilmenite, and pyrite) either as inclusions or along grain rims. In the metapelites, it takes the form of anhedral grains hosted in garnet, plagioclase or quartz. Monazite also occurs along grain boundaries or at triple junctions. Although xenotime was not detected in this particular sample set, it has been reported to occur in the amphibolite facies metapelites and, more rarely, in granulite facies metapelites (Bea & Montero, 1999). In the SP, monazite and xenotime occur only associated with apatite as inclusions as well as rim grains. They are present only in samples from the dehydration zone.

For the metabasite rocks in the dehydration zone from either traverse the (Y + REE) phosphate minerals can be divided into two principal population groups. Population I is only found in the IVZ metabasites. They

consist of isolated monazite grains that usually have medium to high contents of Th and are not associated with apatite. Population II occurs in both traverses and consist of small (1–10 µm), Th-poor grains in close association with apatite, either as inclusions or rim grains. In the IVZ they consist only of monazite. In the SP these inclusions and/or rim grains typically consist of coexisting monazite and xenotime.

Population I monazite

Population I monazite (monazite-I) in the dehydrated IVZ metabasites is distinguished by a large compositional diversity in terms of the contents of both the (Y + REE) [34.5 < Σ(Y₂O₃ + REE₂O₃) < 70.1 wt %] and Th (0.00 < ThO₂ < 38 wt %). This compositional diversity can range from the scale of the thin section down to the scale of a single grain. Moreover, monazite-I displays heterogeneity with respect to the proportions between the individual REE, in particular the light REE (LREE). This can be illustrated by the La_N/Sm_N ratio, expressing

Table 4: Mean EMP analyses of monazite and xenotime in apatite from the Seward Peninsula*

	apatite interior		apatite rim	
	monazite	xenotime	monazite	xenotime
P ₂ O ₅	30.3	34.7	29.5	33.2
SiO ₂	0.18	0.17	0.82	1.18
ThO ₂	0.00	0.00	2.99	0.48
UO ₂	0.09	0.04	0.42	3.08
Y ₂ O ₃	6.38	42.3	2.54	39.6
La ₂ O ₃	5.75	0.02	11.5	0.01
Ce ₂ O ₃	20.1	0.27	26.1	0.09
Pr ₂ O ₃	3.40	0.11	3.14	0.16
Nd ₂ O ₃	18.3	1.44	14.4	0.95
Sm ₂ O ₃	5.32	1.33	3.23	0.88
Gd ₂ O ₃	5.33	6.11	2.84	5.49
Tb ₂ O ₃	0.52	1.02	0.19	0.96
Dy ₂ O ₃	1.57	5.92	0.69	5.90
Ho ₂ O ₃	0.21	1.25	0.07	1.25
Er ₂ O ₃	0.56	3.52	0.26	3.24
Tm ₂ O ₃ †	0.05	0.40	0.00	0.34
Yb ₂ O ₃	0.06	1.48	0.00	1.31
Lu ₂ O ₃	0.00	0.14	0.00	0.19
CaO	0.10	0.00	0.00	0.00
FeO	0.22	0.06	0.33	0.03
PbO	0.03	0.02	0.04	0.02
Total	98.4	100.3	99.1	98.4
Temperature (°C)‡	920		695	

*Monazite and xenotime analyses are taken from sample AB90 + 13-18.

†Calculated (see Förster, 1998b).

‡Estimated using the monazite–xenotime thermometer of Gratz & Heinrich (1997).

the slope of the chondrite-normalized LREE patterns (Fig. 1), which here spans an interval from 4.5 to 18.9. In marked contrast, variability in U ($0.04 < \text{UO}_2 < 1$ wt %) and HREE [$\Sigma(\text{Gd}_2\text{O}_3 - \text{Lu}_2\text{O}_3 + \text{Y}_2\text{O}_3) = 0.1\text{--}2.9$ wt %] is small.

Monazite-I grains on the 5–10 µm scale are relatively homogeneous in composition, specifically with respect to ThO₂. Larger grains exhibit a wide range of textures ranging from relatively homogeneous (Fig. 2a) to grains with some indications of zoning (Fig. 2b and c) to large (30–200 µm) grains, which indicate much more complex growth histories (Fig. 2d–f; see also Förster & Harlov, 1999). Such intensively zoned grains occur preferentially as inclusions in metamorphic garnet or are embedded along its grain boundaries (Fig. 2d–f; see also Förster & Harlov, 1999). They are limited in occurrence to the

samples IZ96-181, IZ94-15 and VS30, where they are also observed, though less commonly, in biotite, plagioclase and K-feldspar (see Table 1). The zonation patterns are a reflection of the differences in the Th/REE ratio, with incorporation of Th into the monazite structure mainly according to the substitution reaction $\text{Th}^{4+} + \text{Si}^{4+} = \text{P}^{5+} + \text{REE}^{3+}$. Within a single grain, ThO₂ abundances may range from 7.2 to 38 wt % (Fig. 2e). Zonation is non-systematic. The Th-richest domains may be observed either at or close to the rims (Fig. 2d and f; fig. 3b of Förster & Harlov, 1999) or both in the interior and at the rim of a single grain (Fig. 2e). Monazite-I grains in the remaining metabasite samples resemble those seen in Fig. 2a–c and contain low to moderate amounts of ThO₂ (0.3–10 wt %).

Population II monazite and xenotime

Population II monazite (IVZ metabasites and SP metatonalites) and xenotime (SP metatonalites) grains (monazite-II and xenotime-II) are typically associated with apatite either as small inclusions within the apatite grain and/or along the apatite grain rim (Figs 3–5). Also in the IVZ, monazite grains, which compositionally resemble monazite-II grains, are found in subordinate amounts in plagioclase, K-feldspar, biotite, quartz, ilmenite, and pyrite grains spatially closely associated with the apatite grains. In the IVZ, monazite-II occurs in ~50–70% of the apatite grains in each sample (Table 2) and tends to range in size from single grains of the order of 5–20 µm (Fig. 3a) to clusters of very small grains of the order of 1–5 µm in size (Fig. 3b). Monazite-II can also be found growing along apatite grain boundary rims either singly (Fig. 3c) or coexisting with interior monazite-II inclusions (Fig. 3d). In a subset of the apatite grains, the monazite-II inclusions are systematically arranged parallel to each other, taking the form of long rods when the cross-section of the apatite grain is approximately parallel to the *c*-axis (Fig. 4a and b). In apatite grains, whose cross-section is approximately perpendicular to the *c*-axis, these inclusions appear as small dots or cross-sections of these monazite rods (Fig. 4c and d). In the SP sample suite, monazite-II, along with coexisting xenotime-II, is relatively scarce. Both occur as 1–5 µm size inclusions or rim grains in a scattering (10–20%) of the apatite grains (Table 4; Fig. 5).

Chemically, monazite-II is characterized by uncommonly low contents of Th ($0.00 < \text{ThO}_2 < 0.7$) and U ($0.00 < \text{UO}_2 < 0.2$ wt %) (e.g. Tables 2 and 4). The only one notable exception is monazite-II occurring along apatite rims in some dehydrated SP metatonalites, which contains 3 wt % ThO₂ and 0.4 wt % UO₂ (Table 4). In contrast to consistently low abundances in the actinides, monazite-II is variable with respect to the La_N/Sm_N ratio

Table 5: Representative EMP analyses of apatite in metamorphic rocks from the Ivrea–Verbano Zone

Zone	Sample	Distance (m)*	P ₂ O ₅	SiO ₂	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Gd ₂ O ₃	Dy ₂ O ₃	Yb ₂ O ₃	CaO	MnO	FeOt	SrO	BaO	Na ₂ O	F	Cl	H ₂ O†	Sum	O = (F+Cl)	Total
<i>Mafic Formation</i>																								
<i>Metabasites</i>																								
1	IV97-1a	5	41.3	0.32	0.02	0.05	0.31	0.43	0.02	0.03	0.10	0.00	54.1	0.00	0.19	0.04	0.05	0.02	3.31	0.14	0.16	100.6	1.42	99.1
			40.9	0.36	0.14	0.11	0.45	0.26	0.11	0.11	0.15	0.02	54.4	0.01	0.21	0.04	0.02	0.04	3.61	0.15	0.02	101.2	1.55	99.6
			41.4	0.33	0.00	0.04	0.31	0.28	0.18	0.09	0.00	0.00	55.0	0.02	0.18	0.06	0.01	0.01	3.81	0.14	0.00	101.8	1.63	100.2
1	IV97-1c	10	41.6	0.13	0.09	0.02	0.00	0.18	0.00	0.00	0.04	0.00	55.3	0.00	0.07	0.00	0.00	0.04	3.70	0.01	0.02	101.2	1.56	99.7
1	VS24	720	41.7	0.02	0.06	0.00	0.03	0.12	0.05	0.03	0.10	0.02	54.7	0.00	0.16	0.00	0.00	0.05	2.15	0.25	0.69	100.2	0.96	99.2
			41.9	0.38	0.01	0.05	0.01	0.21	0.14	0.05	0.09	0.00	54.3	0.03	0.48	0.00	0.03	0.03	1.77	0.86	0.73	101.1	0.94	100.1
1	IZ93-61	1560	41.9	0.29	0.00	0.12	0.24	0.17	0.04	0.00	0.00	0.00	55.0	0.04	0.15	0.03	0.06	0.03	3.38	0.31	0.12	101.8	1.49	100.3
1	IZ96-181	1560	41.7	0.09	0.00	0.03	0.18	0.12	0.06	0.00	0.00	0.00	55.0	0.01	0.19	0.07	0.00	0.05	3.45	0.17	0.10	101.2	1.49	99.7
1	IV97-2	1560	41.5	0.34	0.20	0.05	0.21	0.07	0.10	0.00	0.00	0.02	55.0	0.00	0.07	0.00	0.00	0.01	3.65	0.07	0.03	101.3	1.55	99.8
1	IZ93-63	2240	42.0	0.10	0.00	0.12	0.22	0.12	0.16	0.10	0.02	0.00	54.9	0.02	0.21	0.06	0.00	0.05	3.14	0.29	0.23	101.7	1.39	100.4
1	IZ94-15	3020	41.9	0.15	0.00	0.05	0.03	0.14	0.03	0.00	0.00	0.00	55.4	0.01	0.15	0.02	0.01	0.04	3.45	0.23	0.10	101.7	1.51	100.2
			41.4	0.20	0.00	0.11	0.55	0.40	0.13	0.18	0.00	0.04	53.9	0.03	0.38	0.04	0.00	0.15	2.73	0.52	0.35	101.1	1.27	99.8
1	VS30	3120	41.9	0.07	0.03	0.04	0.00	0.00	0.00	0.00	0.04	0.00	55.7	0.06	0.06	0.00	0.00	0.05	2.88	0.14	0.39	101.3	1.24	100.1
2	VST19	4540	42.3	0.04	0.00	0.00	0.01	0.13	0.07	0.10	0.00	0.00	55.7	0.06	0.03	0.00	0.00	0.01	2.86	0.05	0.43	101.9	1.22	100.7
2	IV97-3	4570	42.0	0.02	0.00	0.02	0.02	0.06	0.00	0.07	0.00	0.00	54.9	0.03	0.14	0.07	0.00	0.03	1.98	0.01	0.84	100.2	0.84	99.3
3	IZ93-67	5220	42.1	0.02	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	55.8	0.00	0.11	0.00	0.00	0.01	2.06	0.01	0.82	100.9	0.87	100.1
3	IZ97-4	5980	42.0	0.02	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	55.6	0.03	0.17	0.04	0.01	0.01	2.73	0.01	0.49	101.2	1.15	100.0
3	IZ93-96	6370	41.5	0.05	0.00	0.04	0.01	0.00	0.03	0.00	0.00	0.00	55.7	0.06	0.11	0.00	0.00	0.00	2.55	0.05	0.56	100.7	1.08	99.6
3	IZ93-98	7100	42.9	0.01	0.00	0.03	0.03	0.07	0.04	0.00	0.05	0.01	55.5	0.02	0.10	0.00	0.00	0.01	2.65	0.06	0.51	101.0	1.13	99.9
3	IZ93-99	7720	41.9	0.05	0.00	0.02	0.06	0.00	0.00	0.00	0.00	0.00	55.4	0.07	0.19	0.00	0.00	0.01	2.98	0.05	0.36	101.1	1.26	99.8
3	IZ94-17a	8110	42.3	0.00	0.00	0.08	0.07	0.05	0.06	0.00	0.00	0.00	56.0	0.01	0.11	0.04	0.00	0.00	3.53	0.01	0.13	102.4	1.49	101.0
3	IV97-5	8300	42.3	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.00	55.7	0.05	0.08	0.00	0.10	0.01	1.91	0.00	0.89	101.0	0.80	100.2
3	IZ93-102	11220	42.3	0.00	0.00	0.00	0.02	0.04	0.00	0.03	0.00	0.00	55.7	0.05	0.01	0.00	0.00	0.00	2.45	0.00	0.63	101.2	1.03	100.2
3	IZ93-105	13240	42.1	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	55.4	0.04	0.07	0.00	0.01	0.00	2.54	0.02	0.58	100.8	1.07	99.7
<i>Metapelites</i>																								
1	IZ96-182	1800	40.8	0.30	0.00	0.12	0.27	0.34	0.00	0.03	0.00	0.00	55.6	0.00	0.00	0.00	0.11	0.00	3.69	0.01	0.02	101.3	1.56	99.7
1	IZ93-62	2240	42.0	0.03	0.00	0.08	0.07	0.11	0.00	0.00	0.00	0.00	55.2	0.01	0.25	0.04	0.00	0.04	3.46	0.11	0.13	101.6	1.48	100.1
3	IZ93-65	5220	42.4	0.04	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	55.6	0.03	0.11	0.06	0.00	0.05	3.40	0.01	0.19	101.9	1.43	100.5

Metamorphic zones: 1, dehydration zone; 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.

Table 6: Representative EMP analyses of apatite in metatonalites from the Seward Peninsula

Zone	Sample-(cm)*	P ₂ O ₅	SiO ₂	Y ₂ O ₃	La ₂ O ₃	Ce ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Gd ₂ O ₃	Dy ₂ O ₃	Yb ₂ O ₃	CaO	MnO	FeO†	SiO	BaO	Na ₂ O	F	Cl	H ₂ O‡	Sum	O = (F + Cl)	Total
1	AB90 + 13-10	41.7	0.16	0.17	0.00	0.19	0.26	0.16	0.03	0.06	0.02	54.4	0.02	0.30	0.04	0.00	0.07	3.01	0.21	0.30	101.1	1.31	99.8
1	AB90 + 13-15	41.6	0.18	0.18	0.00	0.04	0.21	0.07	0.09	0.00	0.00	55.0	0.00	0.17	0.00	0.00	0.08	2.96	0.04	0.37	101.1	1.26	99.8
		42.2	0.07	0.06	0.06	0.00	0.14	0.00	0.00	0.00	0.00	55.3	0.02	0.12	0.00	0.00	0.06	2.90	0.07	0.40	101.4	1.24	100.1
		42.1	0.06	0.00	0.10	0.23	0.10	0.00	0.00	0.00	0.00	55.3	0.06	0.16	0.00	0.03	0.03	2.41	0.18	0.60	101.3	1.05	100.3
1	AB90 + 13-18	41.6	0.08	0.18	0.11	0.14	0.22	0.05	0.04	0.12	0.00	54.2	0.06	0.19	0.05	0.00	0.11	2.87	0.32	0.33	100.7	1.28	99.4
		41.8	0.08	0.00	0.11	0.24	0.08	0.02	0.13	0.00	0.00	54.4	0.08	0.19	0.00	0.03	0.08	2.76	0.28	0.38	100.6	1.23	99.4
1	AB90 + 13-41	41.9	0.03	0.04	0.01	0.07	0.16	0.00	0.05	0.04	0.00	54.7	0.04	0.05	0.03	0.00	0.07	2.99	0.09	0.34	100.6	1.28	99.3
		41.6	0.02	0.11	0.08	0.13	0.09	0.00	0.08	0.00	0.00	54.8	0.04	0.11	0.03	0.03	0.09	2.96	0.26	0.31	100.7	1.31	99.4
2	AB90 + 13-56	41.6	0.08	0.04	0.05	0.20	0.15	0.09	0.00	0.03	0.00	54.7	0.05	0.12	0.02	0.00	0.07	2.61	0.31	0.45	100.6	1.17	99.4
2	AB90 + 13-61	42.3	0.02	0.00	0.00	0.10	0.05	0.00	0.00	0.00	0.00	55.5	0.08	0.12	0.00	0.00	0.06	2.15	0.25	0.71	101.4	0.96	100.4
3	AB90 + 13-86	41.9	0.08	0.00	0.09	0.20	0.09	0.00	0.01	0.00	0.00	55.4	0.08	0.13	0.00	0.01	0.02	2.31	0.19	0.64	101.1	1.01	100.1
3	AB90 + 13-170	42.0	0.03	0.00	0.00	0.07	0.06	0.00	0.00	0.00	0.00	55.3	0.11	0.10	0.00	0.00	0.05	2.03	0.23	0.76	100.7	0.91	99.8
3	AB90 + 13-244	41.6	0.07	0.00	0.13	0.07	0.01	0.00	0.00	0.00	0.00	55.4	0.13	0.14	0.00	0.02	0.05	2.35	0.59	0.52	101.1	1.12	100.0
		41.9	0.01	0.00	0.06	0.11	0.10	0.00	0.00	0.00	0.00	55.5	0.06	0.08	0.00	0.00	0.03	2.14	0.03	0.77	100.8	0.91	99.9
3	AB90 + 13-287	41.7	0.06	0.00	0.15	0.15	0.12	0.00	0.01	0.00	0.00	55.4	0.07	0.11	0.00	0.01	0.00	2.19	0.23	0.68	100.8	0.97	99.8
		42.1	0.09	0.00	0.02	0.13	0.07	0.00	0.00	0.00	0.00	55.0	0.07	0.28	0.00	0.00	0.04	2.06	0.05	0.80	100.7	0.88	99.8
3	AB90 + 13-381	41.7	0.06	0.00	0.07	0.13	0.13	0.00	0.00	0.00	0.00	54.7	0.10	0.18	0.06	0.00	0.03	2.16	0.23	0.69	100.3	0.96	99.3
		41.8	0.09	0.00	0.08	0.18	0.14	0.00	0.00	0.00	0.00	55.4	0.13	0.06	0.00	0.02	0.03	2.17	0.03	0.75	100.9	0.92	100.0
3	AB90 + 13-594	41.8	0.05	0.00	0.05	0.05	0.08	0.00	0.00	0.00	0.00	55.3	0.01	0.06	0.03	0.00	0.04	3.42	0.21	0.11	101.2	1.49	99.7

Metamorphic zones: 1, dehydration zone; 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.

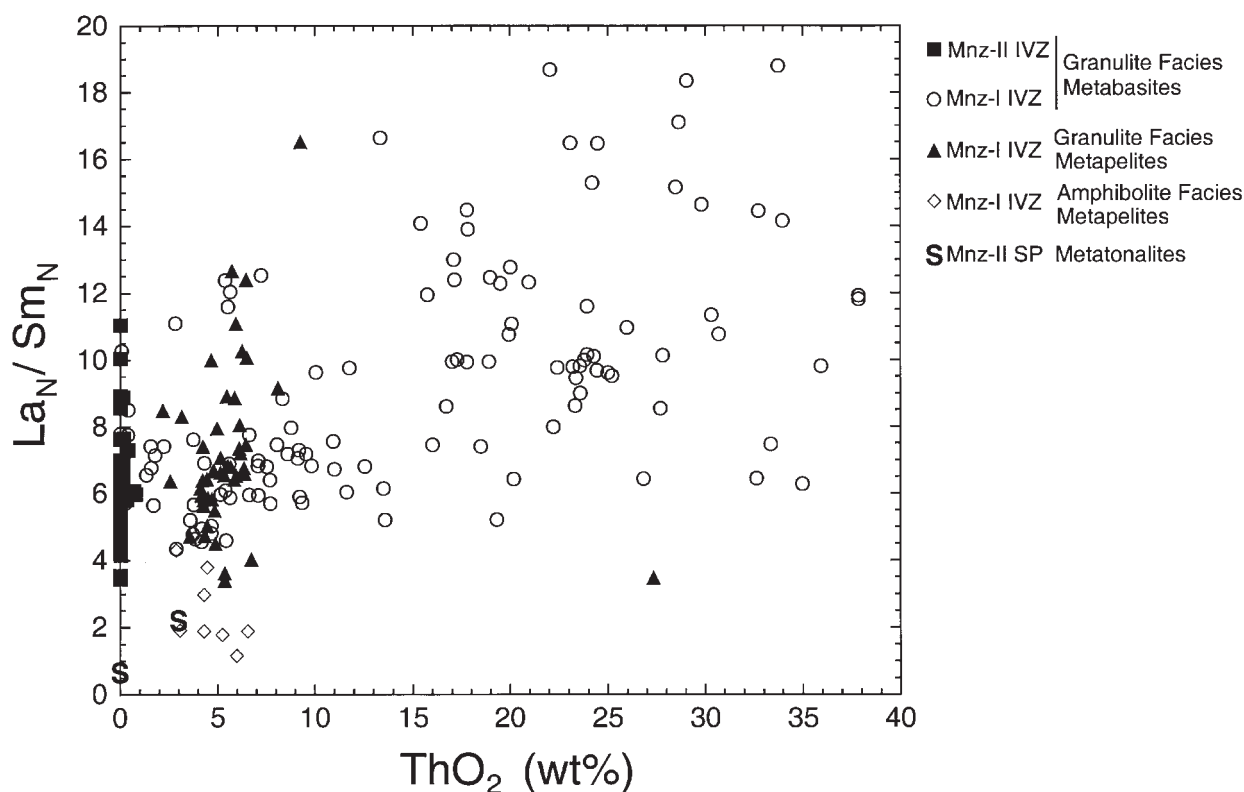


Fig. 1. Plot of La_N/Sm_N (as monitor of the slope of the chondrite-normalized LREE patterns) vs ThO_2 (wt %) in monazite-I and monazite-II. The amphibolite facies metapelite monazite data are taken from Bea & Montero (1999).

(Fig. 1). This ratio ranges from 3.4–11 in IVZ monazite-II to 0.7–2.2 in SP monazite-II. In addition to differences in the LREE pattern, monazite-II from the SP metatonalite differs from that formed in the IVZ metabasites by having significantly higher (Y + HREE) contents. Whereas $\Sigma(\text{Gd}_2\text{O}_3 + \text{Lu}_2\text{O}_3 + \text{Y}_2\text{O}_3)$ is low and ranges from 0.1 to 2.6 wt % in IVZ monazite-II, it is unusually high in monazite-II from the SP depending on whether the monazite formed inside the apatite grain (14.7 wt %) or at its rim (6.6 wt %) (see Table 4).

To investigate the behaviour of the LREE and (Y + HREE) in the apatite in the immediate vicinity of the monazite-II and xenotime-II inclusions or rim grains, microprobe traverses of Ce and Y were performed. These traverses between inclusion-free areas and one larger monazite-II inclusion or a field of tiny inclusions indicate what appear to be consistent trends. Namely, in the immediate neighbourhood of a monazite-II inclusion or rim grain (Figs 5a and 6), or in the midst of a field of small inclusions (Fig. 7), there is an obvious depletion in Ce relative to the rest of this cross-section of the apatite, which does not contain monazite-II. Depletion in Ce is usually counterbalanced by enrichment in Y. The same systematic, but opposite, behaviour is observed for Ce

and Y abundances along traverses approaching xenotime-II inclusions in the SP apatite grains. Here Y tends to be depleted in the vicinity of the xenotime grain, whereas Ce is enriched (Figs 5b and 8).

Apatite

In both the SP metatonalites and the IVZ metabasites, apatite is by far the most common phosphate mineral. It tends to occur as 50–500 μm , semi-euhedral to anhedral grains, evenly distributed within the general petrological fabric of the rock. In the IVZ sample suite, it can also occur as inclusions in both garnet and ilmenite. In either case, the apatite shows no signs of corrosion or of being newly grown when compared with apatite grains in the amphibolite facies zone. In contrast to the metabasites, apatite in the IVZ metapelites, which experienced partial melting during granulite facies metamorphism, is both extremely rare and, when found, often shows definite signs of corrosion.

To look for possible changes in the (Y + REE) abundances in apatite related to the dehydration of the amphibolite facies rocks, the oxides of Y and Ce in apatite are plotted as a function of their distance from

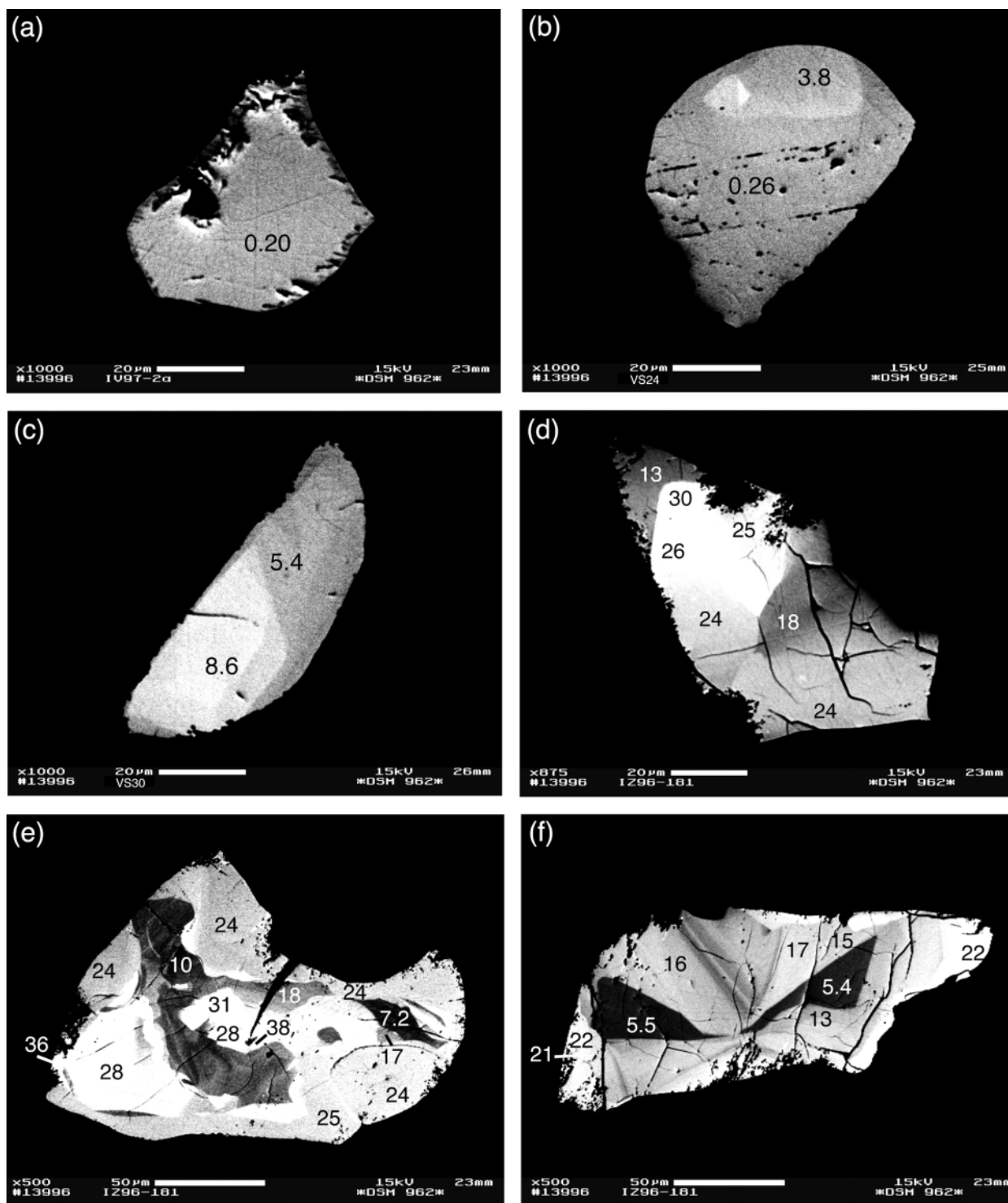


Fig. 2. High-contrast BSE images of various monazite-I grains as seen in the metabasite samples, which show a variety of different zonings with respect to Th. The numbers refer to ThO_2 concentrations (oxide wt %) at these locations as measured by EMP. (a) IV97-2a, a relatively homogeneous monazite-I surrounded by quartz. (b) VS24, a slightly zoned monazite-I located along the rim of a quartz grain in plagioclase. (c) VS30, a moderately zoned monazite-I surrounded by biotite. (d) IZ96-181, a zoned monazite-I located along the side of a garnet grain and surrounded on the remaining three sides by quartz. (e) IZ96-181, a complexly zoned monazite-I located along one side a garnet grain in plagioclase. (f) IZ96-181, a complexly zoned monazite-I surrounded on three sides by garnet and on the remaining side by plagioclase.

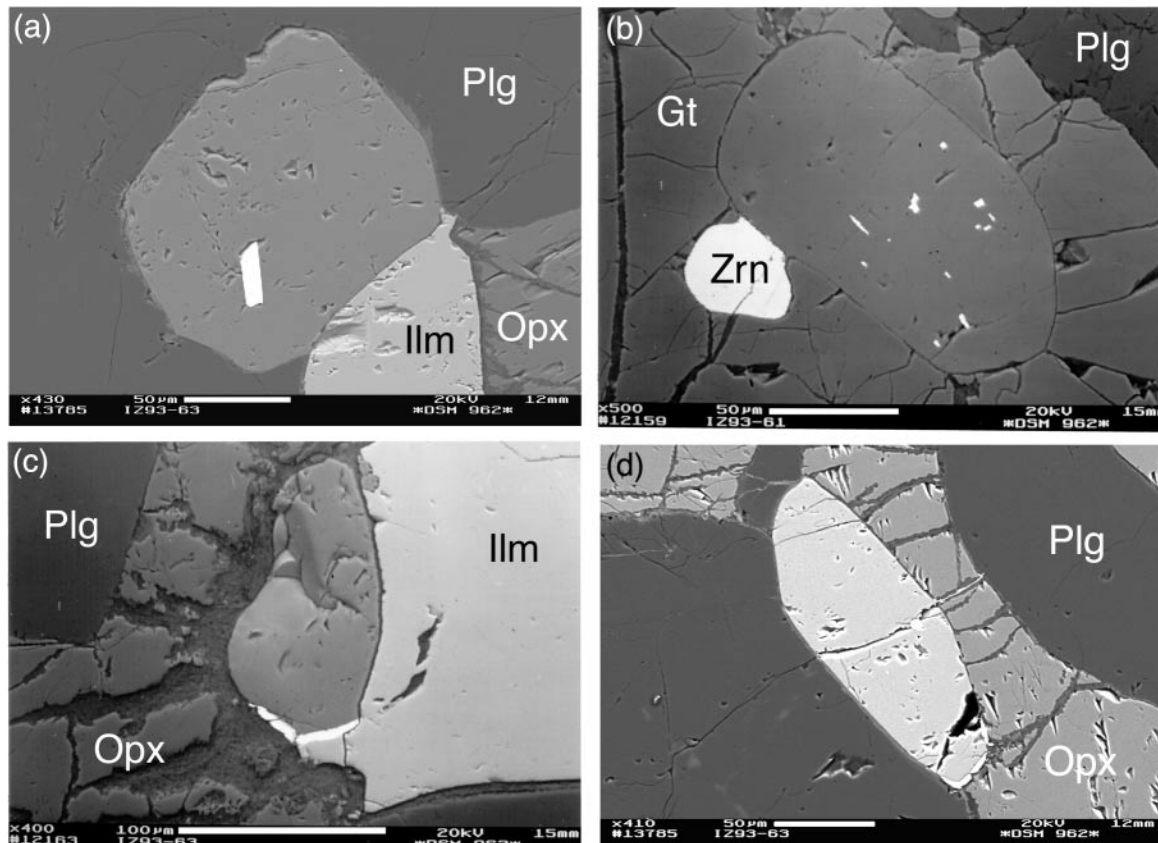


Fig. 3. Examples of different types of monazite-II inclusions in apatite in metabasites from the IVZ dehydration zone: (a) one large monazite-II grain in the interior of the apatite (IZ93-63); (b) a scattering of small monazite-II inclusions in the apatite interior (IZ93-61); (c) a rim monazite-II along the apatite grain boundary (IZ93-63); (d) apatite grains that have both monazite-II inclusions and rim grains (IZ93-63).

the marble layer for the SP and from the Mafic Formation for the IVZ (Fig. 9). Consistency between the two sample suites exists with respect to the behaviour of Y, despite the fact that apatite from the IVZ has less than half the Y content, on average, than apatite from the SP. For either traverse, Y is both more enriched as well as much more variable in apatite from the orthopyroxene-bearing dehydration zone as compared with the transition and amphibolite facies zones (Fig. 9a). In contrast, the behaviour of Ce in apatite differs between the two traverses (Fig. 9b). In the SP, variability in the apatite Ce content, although high, remains relatively constant over the entire length of the 600 cm traverse. In the IVZ, the Ce content in apatite is highly variable per grain in the dehydration and transition zones, but it has both a lower variability as well as a lower abundance in apatite from the amphibolite facies zone. This is in contrast to what was reported by Bea & Montero (1999), who noted a decrease in (Y + HREE) in apatite for both metapelites and metabasites with increasing metamorphic grade, whereas the LREE remained nearly constant. Lastly, if the apatite (Y + REE) component, in atoms per formula unit (a.p.f.u.), is plotted against Na or Si, it becomes apparent that (Y +

REE) displays a positive correlation with respect to both elements (Fig. 10a and b). However, the two traverses differ in which of the two elements is more strongly correlated with (Y + REE). In the SP, Na is the primary cation balancing (Y + REE) (Fig. 10a), whereas in the IVZ, Si is dominant (Fig. 10b).

If the F and Cl contents in apatite are plotted as a function of distance from the marble or the Mafic Formation, respectively, several systematic trends can be established (Fig. 11). Apatite from the SP is higher in F in the dehydration zone than in the amphibolite facies zone (Fig. 11a). One exception is the apatite from the sample furthest away from the contact, i.e. AB90-13+594, which shows a high F content despite having the same Cl content compared with the other apatite grains in the amphibolite portion of the gneiss (Fig. 11a). It should be noted here that biotite and hornblende from this sample show a similar enrichment in F (Harlov & Förster, 2002). Cl shows no easily discernible patterns (Fig. 11b). However, in both the dehydration and transition zones several apatite grains occur that are considerably richer in Cl relative to all apatite grains examined from the amphibolite facies zone. Apatite from

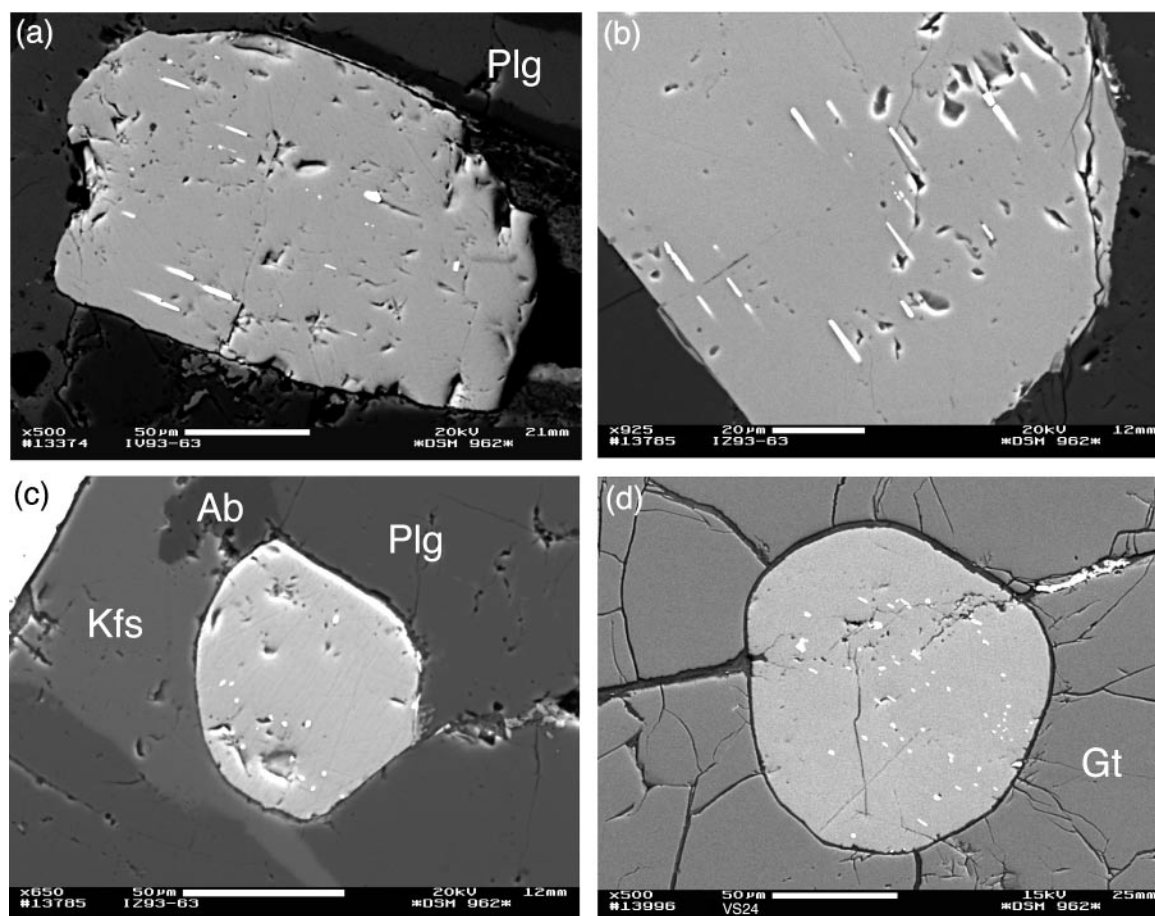


Fig. 4. Examples of monazite-II grains in the form of rods growing preferentially along the c -axis of an apatite grains from sample IZ93-63 (a, b). (c) and (d), apatite from IZ93-63 and VS24 cut nearly perpendicular to the c -axis. Here the monazite-II rods appear in cross-section as small dots coming out of the plane of the photograph.

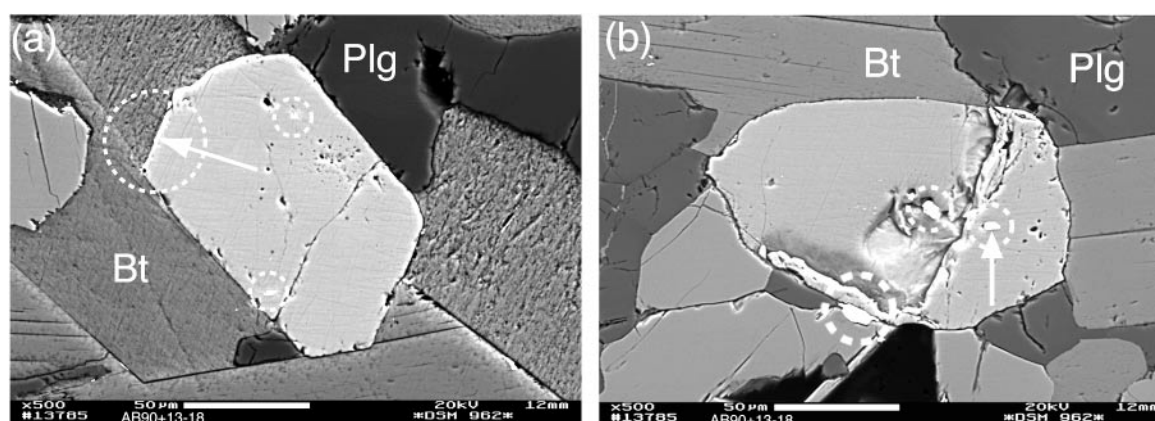


Fig. 5. Examples (circled) of monazite-II and xenotime-II inclusions in apatite from the SP sample AB90+13-18 ranging from a rim monazite-II coupled with two small interior xenotime-II inclusions (a) to two interior xenotime-II inclusions and a rim monazite-II (b). (a) and (b) show the location of the Ce and Y electron-microprobe traverses described in Figs 6 and 8, respectively. Arrow is in the direction of the traverse.

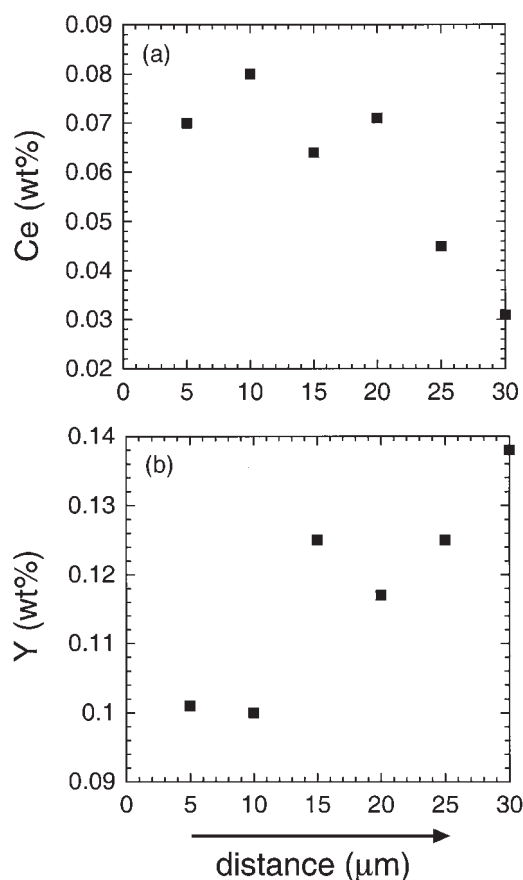


Fig. 6. Ce (a) and Y (b) microprobe traverses (element wt %) in apatite (SP) up to a linear rim monazite-II shown in Fig. 5a.

the IVZ shows both a greater complexity with respect to the pattern of F and Cl as a function of distance as well as slightly higher F and Cl contents in comparison with apatite from the SP (Fig. 11). However, as in the case of the SP, apatite tends to be enriched in both F and Cl in the dehydration zone relative to the amphibolite facies metabasites. It should be noted, nevertheless, that some samples do not follow this general trend. This is seen especially in the IVZ amphibolite facies zone, where differences in the mean F content for apatite in samples from two consecutive metabasite layers can be fairly large (Fig. 11a).

DISCUSSION

Origin of (Y + REE) phosphate minerals

Population-I monazite

The formation of monazite-I in the IVZ metabasites as a primary (igneous) phase is incompatible with the mafic nature of its host rock, in which major silicate minerals

and apatite normally account for the bulk of the lanthanides and actinides (e.g. McKay, 1989). If the decomposition of basaltic minerals were able to deliver sufficient elements to form monazite-I, these should, in general, be more commonplace in those metabasites affected by granulite facies metamorphism, which is not the case. In reality, only a few other occurrences of monazite in mafic to ultramafic rocks are known. In all these cases, their presence is always proposed to be associated with high-grade metamorphic and metasomatic processes involving external sources for the (Y + REE) (Rudnick *et al.*, 1993; Liou & Zhang, 1996; Bea *et al.*, 1999). This implies that monazite-I must be secondary. Given the absence of monazite-I in the amphibolite facies metabasites, their formation probably is linked to contact metasomatic overprinting during the partial melting of the metapelites, which has been proposed to have affected the mafic rocks during emplacement of the Mafic Formation and subsequent granulite facies metamorphism (Harlov & Förster, 2002).

There are two potential sources for the (Y + REE) and the actinides responsible for the formation of monazite-I. These include pre-existing (Y + REE)-bearing minerals within the original amphibolite facies metabasite itself and (Y + REE)-bearing minerals within the interlayered metapelites. With respect to the first potential source, minerals present in the amphibolite facies rocks, but absent in the granulite facies rocks (hornblende and titanite) have to be considered first. However, although amphiboles from mafic rocks (Bottazzi *et al.*, 1999; Cortesogno *et al.*, 2000; Dalpé & Baker, 2000) as well as titanite in general (Exley, 1980; Bea, 1996) can be important reservoirs for the (Y + REE) and Th, breakdown of these species is unlikely to account for the genesis of monazite-I. This is because, as both minerals are evenly distributed in the amphibolite facies metabasites, monazite-I should be as well, which is not the case. Furthermore, there is some evidence that titanite was probably not a part of the original mineral assemblage that underwent the dehydration event, but rather was a later-stage reaction product between ilmenite and a Ca-bearing fluid, as titanite is commonly found rimming ilmenite (see Harlov & Förster, 2002, fig. 2b). In the IVZ metabasites, the elements mobilized in the course of hornblende breakdown were either consumed in the newly formed pyroxenes and garnet or were taken up by pre-existing apatite. Apatite itself also can be excluded given that apatite in metabasites from the dehydration zone is usually richer in the (Y + REE) than apatite from the amphibolite facies metabasites (see Fig. 9).

With respect to the second potential source, there are two possible means by which the metapelites may have contributed monazite-I (Table 3). First, the metabasites may have assimilated metapelitic material during emplacement. In this situation, xenocrystic monazite-I would

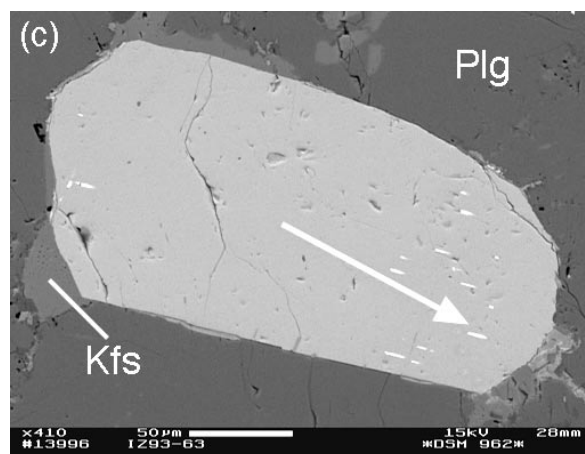
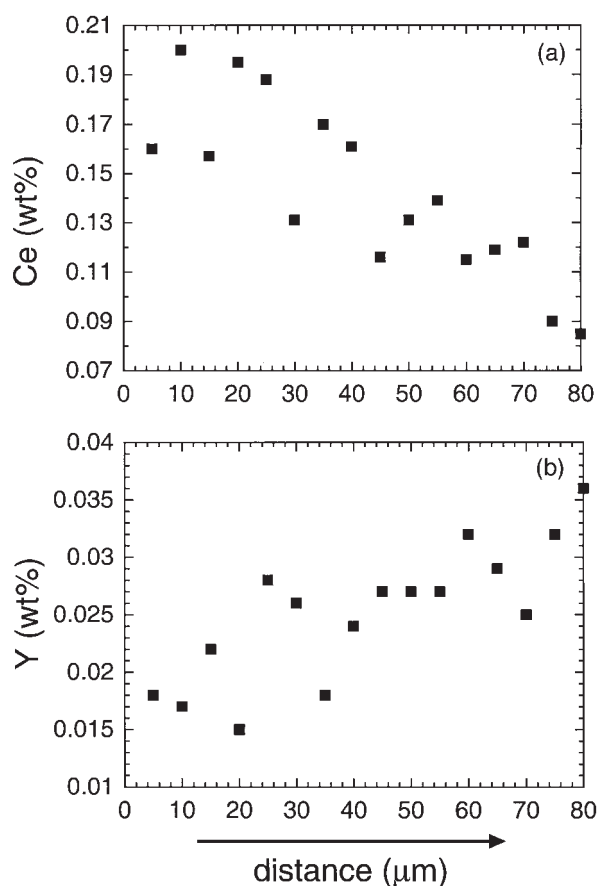


Fig. 7. Ce (a) and Y (b) microprobe traverses (element wt %) in an apatite grain from sample IZ93-63. The traverse goes from the interior of the grain crossing through a field of small monazite-II inclusions (c). Arrow is in the direction of the traverse.

represent a simple mechanical admixture from the metapelites taken up by the original basaltic melts during interaction with the original sedimentary rocks. As the dehydrated metabasite samples included in this study contain a metapelitic component in amounts of 10–30% (unpublished bulk-rock data; Harlov & Förster, 2002), this mode of monazite assimilation must be considered to be plausible. Assuming that such monazite grains have retained their original composition and not re-equilibrated in the basaltic magma, a close similarity in composition should exist between basaltic and metapelitic monazite-I. However, metapelitic monazite-I compositions (Table 3) indicate that this should hold only for monazite grains that contain <8 wt % ThO_2 (e.g. Fig. 2a and b). These are more evenly distributed within the metabasites and could potentially represent metapelitic xenocrysts (Table 1).

The second model involves active mass transport of actinides, (Y + REE) and P into the metabasites during granulite facies metamorphism and subsequent partial melting of the metapelite layers. During partial melting of the metapelites, the metabasite layer at the contact with

the metapelite layer presumably would have also been semi-molten to a depth of several centimetres and/or could have been infiltrated by pelite-derived partial melt or associated fluids to some extent. Monazite-I with high concentrations of ThO_2 could have nucleated in these regions, partially or wholly as a result of the breakdown of Th-bearing monazite-(Ce) in the immediate adjacent metapelites and the subsequent large-scale, high-grade redistribution of these now released and subsequently mobile elements. However, mass transfer of these elements must have occurred on a highly localized scale and then only in the immediate vicinity (centimetres) of the boundary between the metapelite and metabasite layers, as whole-rock analysis of the granulite facies metapelites shows no evidence of a wholesale depletion in Th and the LREE, with the exception of U (Schnetger, 1994; Bea & Montero, 1999). This would imply that the three samples (IZ96-181, IZ94-15 and VS30) that contain complexly zoned monazite-I grains probably came from a location within centimetres of the boundary with a metapelite layer. The remaining samples were probably sampled deeper in the metabasite layer beyond this partial melt zone. Un-

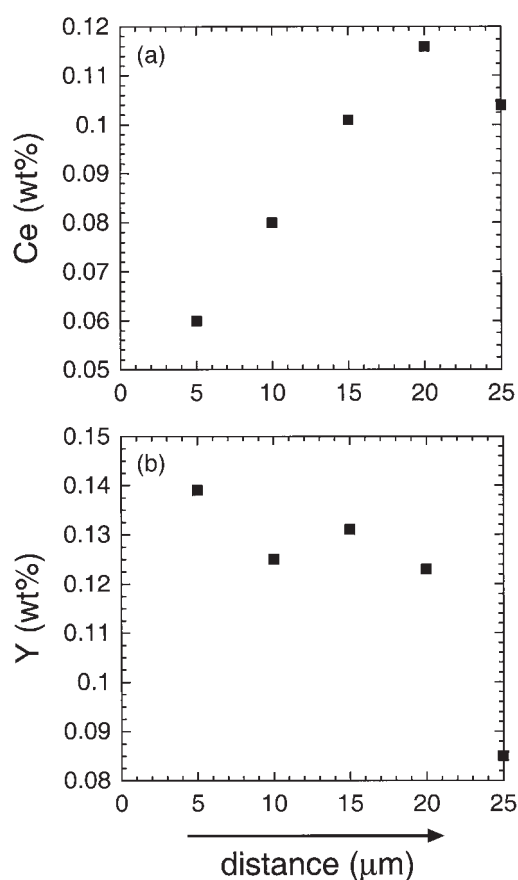


Fig. 8. Ce (a) and Y (b) microprobe traverses (element wt %) in apatite (SP) up to the interior xenotime-II grain shown in Fig. 5b.

fortunately, difficulties in determining the exact location and breadth of a metabasite layer relative to the adjoining metapelite layers in the field did not permit exact definition of the sample position with respect to the neighbouring metapelite layers to test this model. Nevertheless, an external source for the LREE and Th coupled with different sampling localities within the metabasalt layers would easily explain the inhomogeneous distribution of complexly zoned monazite-I within our suite of samples.

Because a number of these Th-rich grains occur as inclusions in garnet (e.g. Förster & Harlov, 1999) as well as being closely associated with garnet as semi-inclusions (e.g. Fig. 2f), their formation must pre-date that of their host. Therefore mass transfer must have taken place close to peak metamorphic conditions, i.e. at temperatures higher than 700–800°C and pressures >6–8 kbar (Henk *et al.*, 1997; Franz & Harlov, 1998). Moreover, their morphology and complex internal textural structure are consistent with the observation that, in many cases, the monazite-I underwent several growth and resorption episodes under high-grade metamorphic conditions (Zhu *et al.*, 1997; Bingen & van Breemen, 1998; Braun *et al.*,

1998; Cocherie *et al.*, 1998; Hawkins & Bowring, 1999). In general, these observations would suggest that both the elevated *PT* conditions required for granulite facies metamorphism, the partial melting and the presence of monazite-bearing metapelites in the immediate contact with metabasites, and the relatively small thickness of the basaltic layers themselves (typically 25–100 cm; Sills & Tarney, 1984) were critical for the formation of monazite-I in the metabasites.

Examples of similarly complex monazite grains are recorded in amphibolite–granulite facies orthogneiss, Rogaland–Vest Agder terrain, SW Norway (Bingen & van Breemen, 1998). Here high-grade metamorphic ‘fluids’ are proposed to have been responsible for Th-enriched embayments along the rims of a selection of monazite grains. These rim embayments are similar to what is seen in monazite from the IVZ metabasites (see Fig. 2d–f). Bingen & van Breemen (1998) interpreted these embayments as inward-directed fronts of secondary replacement resulting from variations in the surrounding fluids to which these monazite grains were exposed. Monazite showing similar Th-enriched embayments has also been observed in leucogneisses from the Brattstrand Bluffs coastline, eastern Antarctica (Watt & Harley, 1993; Watt, 1995). Here the monazite grains are interpreted to have experienced both resorption and subsequent regrowth along the grain rims during anatexis in a partial melt associated with the formation of leucosomes.

Population-II monazite-(Ce) and xenotime

Monazite-II and xenotime-II grains have been observed as inclusions and/or rim grains associated with fluorapatite from a variety of medium- to high-grade ($T > 500^{\circ}\text{C}$) metamorphic rocks (McKeown & Klemeš, 1957; Åmli, 1975; Pan *et al.*, 1993; Hiroi *et al.*, 1997; Pan, 1997). There is no evidence to suggest that they are the result of exsolution in the apatite during cooling or that they represent independent monazite and/or xenotime grains later overgrown or partially overgrown by apatite (e.g. Åmli, 1975). With respect to the SP and IVZ, a series of observations support the conclusions of both Åmli (1975) and Pan *et al.* (1993) that monazite-II and/or xenotime-II nucleated either within the apatite or along the apatite grain rim utilizing the actinide, (Y + REE) and P budgets locally available. For example, monazite-II inclusions in apatite from both the SP and IVZ consistently show evidence of depletion in Ce (monitoring the LREE) in the immediate vicinity of the inclusion or a field of inclusions (Figs 5a, 6 and 7). Depletion in the LREE (Ce) is generally counterbalanced by the enrichment in the (Y + HREE) as reflected by the behaviour of Y. Both groups of (Y + REE) show the exact opposite behaviour in apatite when a xenotime-II

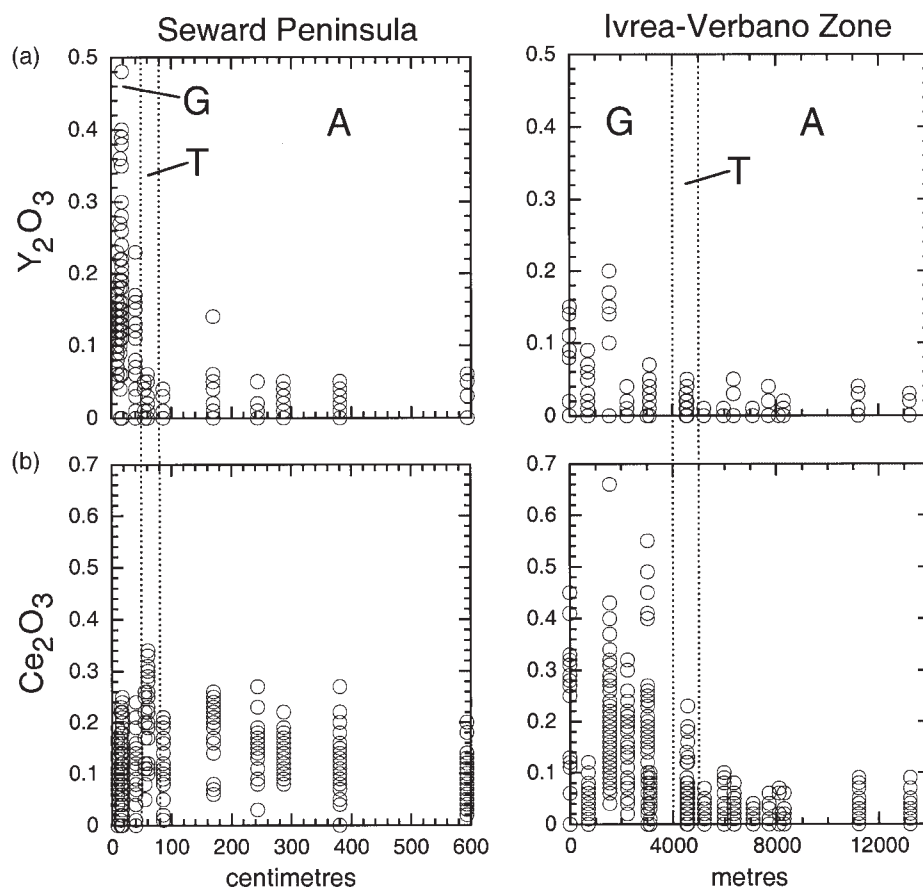
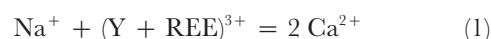


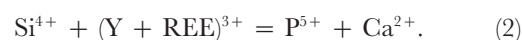
Fig. 9. Y_2O_3 (a) and Ce_2O_3 (b) contents (oxide wt %) in individual apatites plotted as a function of distance from the marble layer for the SP samples and from the Mafic Formation for the IVZ samples.

inclusion is approached. A second argument involves the presence of xenotime-II in apatite from the SP dehydration zone in contrast to its absence in apatite from the IVZ dehydration zone. The simplest explanation would be that apatite from the SP, which on average contains 2–3 times the Y content of that in the IVZ (Fig. 9; Tables 5 and 6) apparently had sufficient quantities of (Y + HREE) to allow xenotime-II to form as opposed to that in the IVZ. The relatively low to non-existent Th and U content in monazite-II or xenotime-II is in itself another strong argument that these grains formed utilizing the actinide budget locally available within the apatite, as apatite does not normally take in large amounts of either element in mafic to intermediate igneous rocks (e.g. Matsumoto *et al.*, 2000). Lastly, the fact that these inclusions are present only in apatite from either the SP (metatonalite) or IVZ (metabasite) dehydration zones and, in the case of the IVZ traverse, show no obvious *PT* dependence, by itself, would suggest that their genesis was induced by fluids of only a specific composition (e.g. low H_2O activity).

These observations are supported by the fact that in the apatite structure trivalent cations such as Y or the REE can substitute for Ca^{2+} and P^{5+} with electrostatic neutrality maintained by the presence of additional Si^{4+} and/or Na^+ . This has been confirmed via detailed investigations of the crystal chemistry of fluorapatite by Fleet & Pan (1995), who have demonstrated that substitution of (Y + REE) for Ca in fluorapatite can be charge compensated equally in tandem by both Na and Si. This is seen for the (Y + REE) content in apatite, which shows a distinct positive correlation with Na + Si (Fig. 10). Either substitution can be expressed in the form of a coupled substitution reaction (Roeder *et al.*, 1987; Rønsbo, 1989; Fleet *et al.*, 2000):



and



In the case of apatite from the SP, the principal coupled substitution reaction is (1), as Na is relatively more

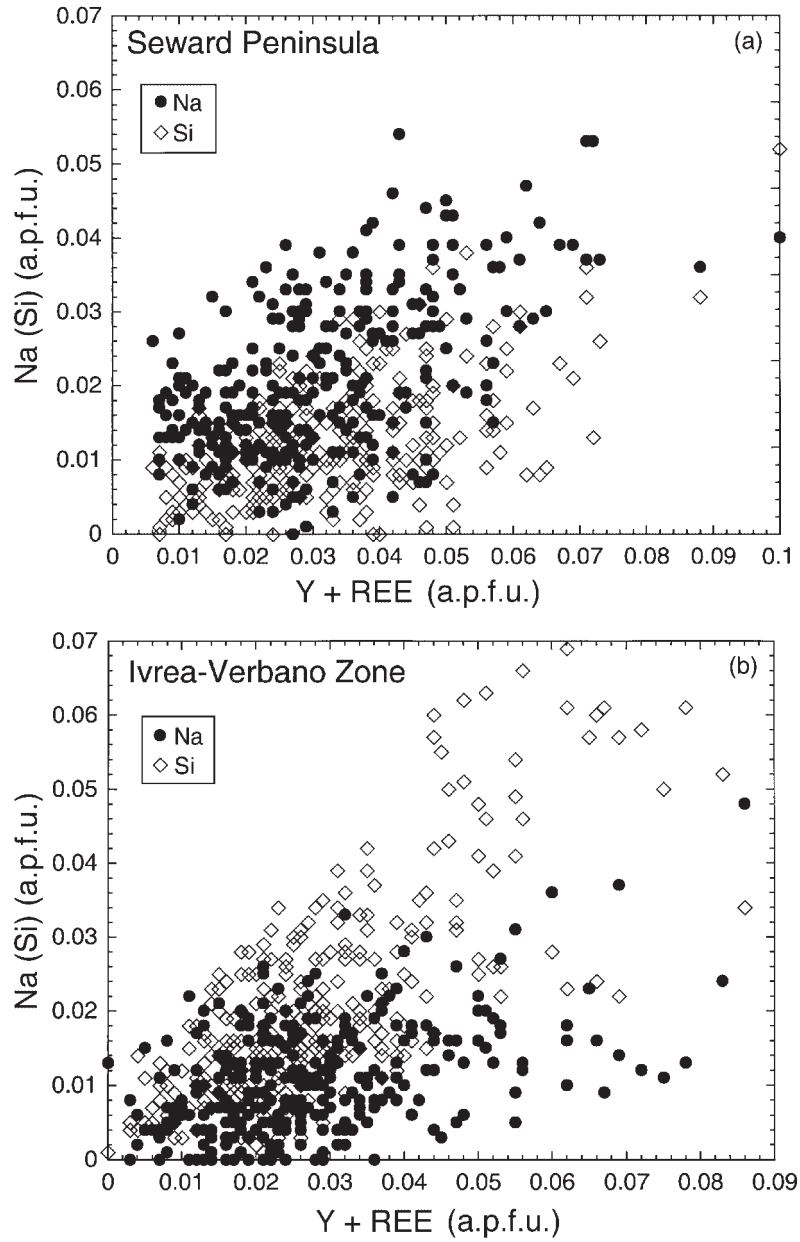
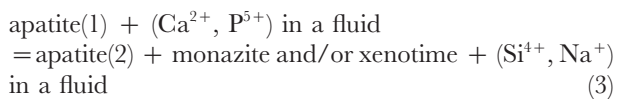
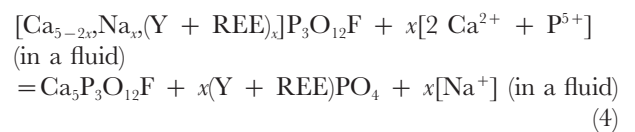


Fig. 10. Plot of the Na and Si atoms per formula unit (a.p.f.u.) as a function of the total (Y + REE) content (a.p.f.u.) in individual apatites from the SP (600 cm) (a) and the IVZ (14 000 m) (b).

abundant than Si, whereas in the case of the IVZ, the principal coupled substitution reaction is (2). Nucleation of either monazite-II or xenotime-II in apatite then ideally involves the following general mass balance reaction adopted and simplified from Pan *et al.* (1993) and references therein:



where apatite(1) is enriched in (Y + REE), Na and Si relative to apatite(2), which has become depleted in these cations. Reaction (3) can be written more directly in the form of two reactions that take into account coupled substitution reactions (1) and (2) each individually, or



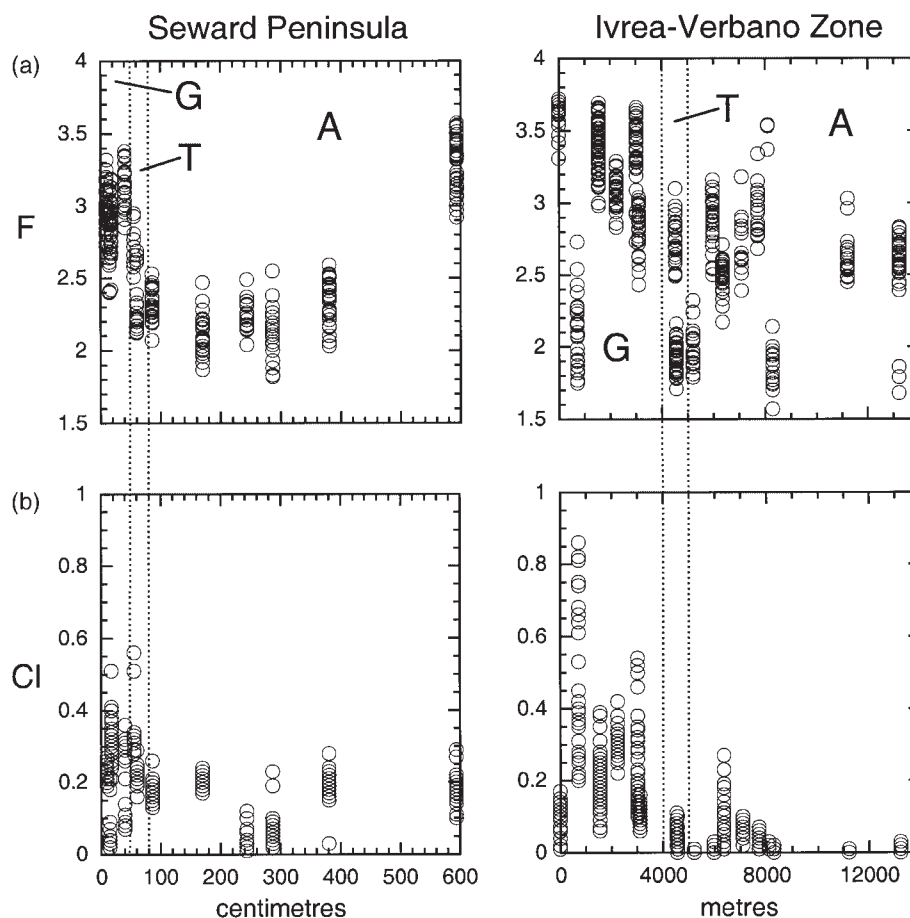
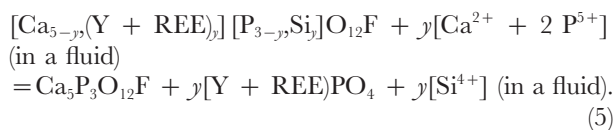


Fig. 11. Plot of F (a) and Cl (b) in individual apatites as a function of distance from the marble layer for the SP samples and from the Mafic Formation for the IVZ samples. On the basis of the data available, the simplest explanation for the F anomaly seen at 600 cm in the SP traverse (AB90+13-594) is that of a local enrichment in F which was inherited from the progenitor of the gneiss for this sample (see also Harlov & Förster, 2002).

and



In either case a fluid phase is required for the transport of Ca^{2+} and P^{5+} as well as removal of Na^+ and/or Si^{4+} . Lastly, recent experimental work has confirmed that monazite and xenotime can be fluid induced to originate as inclusions in both chlorapatite (Harlov *et al.*, 2002) as well as in fluorapatite (Harlov & Förster, in preparation) via reactions (1)–(5).

The presence of elongated monazite-II grains parallel to the *c*-axis in a selection of these apatite grains (Figs 4 and 7) has been described by Pan *et al.* (1993). They demonstrated that the *b*-axis of these inclusions is elongated and parallel to the *c*-axis of the apatite host whereas

the *c*-axis of these inclusions is oriented parallel to the *a*-axis of the apatite. Pan *et al.* (1993) inferred that these orientations reflect a 'topotactic-like' relationship between the monazite inclusions and the apatite crystal matrix. In other words, the monazite grains appear to have grown with this orientation in the apatite so as to minimize the dimensional misfit between the strain-free lattices at the boundary between the two phases.

Temperatures estimated from coexisting monazite-II and xenotime-II inclusions in apatite from the SP using the monazite–xenotime thermometer of Gratz & Heinrich (1997) give a temperature of 920°C (Table 4). In contrast, estimates from coexisting monazite-II and xenotime-II grains located along the apatite grain rim yield a temperature of 695°C. These values are in line with the temperature of 800°C estimated by Todd & Evans (1994). The temperature at ~900°C probably more closely approximates the actual peak metamorphic temperature experienced by these rocks during the de-

hydration event, as both monazite and xenotime are relatively refractory with high stopping temperatures (e.g. Heinrich *et al.*, 1997). The temperature of $\sim 700^\circ\text{C}$ estimated from coexisting monazite-II and xenotime-II grains along the apatite rim is probably due to some resetting of the Ce and Y contents as well as increased Th contents in the monazite (e.g. Viskupic & Hodges, 2001) and U in the xenotime. This probably is the product of an exchange with later-stage grain boundary fluids at temperatures below 800°C during the early stages of isobaric cooling. This resetting of Ce and Y and enrichment in Th, presumably, would also have some effect on the temperature calibration of Gratz & Heinrich (1997), although this has not yet been explored experimentally. Considering the fact that coexisting monazite-II and xenotime-II in the apatite grain interior contain very low to negligible concentrations of Th and U relative to what is usually measured in monazite and xenotime not associated with apatite (Franz *et al.*, 1996; Förster, 1998a, 1998b), such coexisting pairs could represent one of the more accurate applications of the Gratz & Heinrich (1997) monazite–xenotime thermometer to date.

(Y + REE) mobility during fluid–rock interaction

A number of lines of evidence point towards the apatite in the dehydration zone as having interacted with a high-grade fluid. The first of these is that Y is more variable in apatite grains located in the dehydration zone than in those from the amphibolite facies zone (Fig. 9). This is seen particularly for apatite grains from the SP traverse. In contrast, variability in Ce for these apatite grains is relatively low. This is in contrast to the IVZ, where it is relatively high. In this respect, the two dehydration zones differ in which (Y + REE) group was preferentially partitioned into the apatite: (Y + HREE) in the SP and LREE in the IVZ.

Although the origin of excess (Y + REE) in the apatite remains unknown, one likely source was hornblende breakdown. Different levels of LREE and (Y + HREE) enrichment in apatite from the dehydration zone of either traverse could be related to the composition of the presumed hornblende itself: for example, with respect to the SP, it was LREE poor. It could also be a consequence of the presence (IVZ) or paucity (SP) of garnet in the dehydration assemblage. Garnet is an efficient depository for (Y + HREE). In the case of the IVZ, it probably consumed most of the (Y + HREE) released during hornblende decomposition. This then allowed only a small portion to be incorporated into the apatite, which would explain its low Y content in general (compare Tables 5 and 6) as well as the total absence of xenotime-II inclusions. In the SP, (Y + HREE) was free to enter

the apatite structure and thus enrich the apatite up to a level high enough for a limited number of xenotime inclusions to form.

As a result of the greater abundance of Na, (Y + REE) in the structure of apatite from the SP have been stabilized principally via coupled substitution reaction (1) and, to a lesser extent, by coupled substitution reaction (2), suggesting that Na was more mobile than Si (Fig. 10a). This is opposed to what is observed for the IVZ, where the (Y + REE) were stabilized principally by coupled substitution reaction (2), perhaps implying that Si was more mobile than Na (Fig. 10b). In the SP, hornblende constitutes the most probable source for Na, as modal mineral analysis indicates that this was the only phase to break down to orthopyroxene and clinopyroxene during dehydration (Todd & Evans, 1994).

The presence of a marble layer, coupled with stable isotope evidence, points to CO_2 as being a significant component in the dehydrating fluid (Todd & Evans, 1994). Carbon dioxide could constitute a potential complexing ligand for the transport of the (Y + HREE) at low T (Wood, 1990). Synthetic fluid inclusion studies suggest that one possible means of transport for Na in a CO_2 -rich fluid could be as Na_2CO_3 (e.g. Schmidt & Bodnar, 2000). In contrast, Si has a much lower solubility in such fluids (e.g. Walther, 1992; Newton & Manning, 2000).

However, correlation algorithms for REE complexes developed by Haas *et al.* (1995), using experimental data from the literature, suggest that (Y + REE) carbonate complexes would not play a major role at 800°C , although (Y + REE)–Cl and (Y + REE)–F complexes could. The biotite chemistry for either traverse records HCl and HF fugacities that are well within one order of magnitude of each other (Harlov & Förster, 2002, fig. 8e and f). Moreover, the relative fugacities of HF and HCl with respect to H_2O show no substantial difference for either traverse. The implication is that because F and Cl must be considered as components of the fluid phase present both during and shortly after the dehydration event, F and Cl could have facilitated the transport of the (Y + REE) and other mobile elements such as Na and Si. In this respect, concerning the IVZ granulite facies metabasites specifically, transport of Th certainly could have been promoted by fluorine complexes, whereas Cl could have acted as the complexing agent for the LREE (e.g. Haas *et al.*, 1995; Gieré, 1996; Pan & Fleet, 1996).

Apatite halogen chemistry

When comparing the halogen chemistry of apatite as a function of distance from the fluid and/or heat source, it is important to keep in mind that in the case of the SP any compositional variation in the apatite is plotted

over a distance of 600 cm whereas for the IVZ any compositional variation is over a traverse of $\sim 14\,000$ m (Harlov & Förster, 2002). Second, there is no variation in temperature or pressure over the SP traverse, whereas the samples from the IVZ experience a distinct gradation in temperature and pressure ranging from $\sim 800^\circ\text{C}$ and 8 kbar at the contact with the Mafic Formation to $\sim 600^\circ\text{C}$ and 4 kbar at the termination of the traverse (see Harlov & Förster, 2002, fig. 1b). Lastly, whereas the SP represents a compositionally homogeneous tonalitic gneiss, the IVZ consists of a complex series of interlayered metabasites and metapelites.

In the SP dehydration zone, the amount of Cl found in the apatite grains as well as its variability among the apatite grains per sample is almost indistinguishable from what is seen for apatite grains in the amphibolite facies zone. In this respect it resembles the Cl pattern seen in biotite from the SP traverse (Harlov & Förster, 2002). Only a small subset of the apatite in the dehydration zone displays some enrichment in Cl. The principal source for this excess Cl probably was internal, from the hornblende, which contains a minor Cl component (Harlov & Förster, 2002, table 5). In contrast, the regular spatial distribution pattern in F seen for both apatite and biotite, coupled with a substantial increase in F for either mineral in the dehydration zone (see Fig. 11; see also Harlov & Förster, 2002, fig. 8d and e), indicates an external source for F, inasmuch as the original hornblende contains only negligible amounts. Todd & Evans (1994) noted the presence of halogen-bearing minerals in the marble at the contact, such as phlogopite and clinochumite, which could have acted as a reservoir for F.

Both the F and Cl content in apatite from the IVZ tend, on average, to be higher in the dehydration zone, with a systematic gradation that is more obvious for Cl than for F (Fig. 11). Most of the scatter in either pattern is probably a result of the compositional complexity of the traverse, caused by a variable interaction between the interlayered metabasite and metapelite layers and/or a compositional variability in the individual metabasite layers themselves. It is unlikely that hornblende constituted a source for Cl or F, as it contains negligible amounts of either element in the amphibolite facies metabasites (Harlov & Förster, 2002, table 6). The same holds true for biotite. All evidence suggests that it was apparently a stable phase during the dehydration event or else the product of a back reaction between orthopyroxene and residual fluids along grain boundaries shortly after the peak of metamorphism. This implies that the F- and Cl-bearing Ti-enriched biotite abundant in the dehydration zone would have acted as a sink for both Cl and F rather than as a source. This is supported by recent experimental evidence, which has demonstrated that phlogopite can form under relatively dry conditions ($X_{\text{H}_2\text{O}} = 0.3$) in concentrated brines at granulite facies

Table 7: Biotite–apatite temperatures for granulite facies metabasites from the Ivrea–Verbano Zone

Sample	Distance (m)*	T ($^\circ\text{C}$)†	T ($^\circ\text{C}$)‡	T ($^\circ\text{C}$)§
IV97-1a	5	810	578	675
IV97-1c	10	810	577	674
IV97-2	1560	760	621	696
IZ93-63	2240	730	631	702
IZ94-15	3020	720	658	712
VS30	3120	710	578	669
Mean†			607 ± 31	688 ± 16

*Distance from the contact with the Mafic Formation. †Henk *et al.* (1997). ‡Calculated using the expression given by Zhu & Sverjensky (1992). §Calculated using the expression given by Sallet (2000).

†Mean value $\pm 1\sigma$.

conditions (800°C and 10 kbar) (Harlov & Melzer, 2002). Furthermore, each halogen shows a gradient with decreasing abundance as a function of increasing distance from the fluid or heat source (Harlov & Förster, 2002, fig. 8d–f). This would support the idea that any increase in the Cl or F content in both the apatite and biotite came from an external infiltrating fluid. Potential sources could include the Mafic Formation coupled with possible local contributions from the metapelite layers.

Biotite–apatite F–OH thermometry

Utilizing the F–OH biotite–apatite thermometer of Zhu & Sverjensky (1992) gives mean temperatures of 607°C for the IVZ (Table 7) and 623°C for the SP (Table 8). Temperatures estimated using the apatite–biotite thermometer of Sallet (2000), which is based on both experimental data as well as an improved apatite–biotite thermometer grid, are on average closer to 700°C (Tables 7 and 8). Neither thermometer show any real systematic variance for either traverse. Temperatures per sample were estimated using the average biotite composition (Harlov & Förster, 2002, tables 3a and 4a) and the apatite analysis with the lowest F content.

These temperatures are ~ 100 – 200°C below peak metamorphic temperatures measured using other thermometers such as garnet–orthopyroxene (Todd & Evans, 1994; Henk *et al.*, 1997; Franz & Harlov, 1998) or monazite–xenotime (this study). This indicates that they represent a last re-equilibration of both the biotite and apatite with the interstitial grain boundary fluids present after the peak of metamorphism and the presumed dehydration event. That is, they represent the

Table 8: Biotite–apatite temperatures in metatonalites from the Seward Peninsula

Zone	Sample-(cm)*	<i>T</i> (°C)†	<i>T</i> (°C)‡
1	AB90 + 13-10	625	699
1	AB90 + 13-15	664	720
1	AB90 + 13-18	691	723
1	AB90 + 13-41	527	642
2	AB90 + 13-56	634	695
2	AB90 + 13-61	689	718
3	AB90 + 13-86	624	690
3	AB90 + 13-170	669	708
3	AB90 + 13-244	606	680
3	AB90 + 13-287	619	687
3	AB90 + 13-381	556	650
3	AB90 + 13-594	575	665
Mean§		623 ± 49	690 ± 26

*Distance from the contact with the marble. †Calculated using the expression given by Zhu & Sverjensky (1992). ‡Calculated using the expressions given by Sallet (2000). §Mean value ± 1σ.

stopping temperature for F–OH exchange between biotite and apatite, which in this case appears to be in the region of ~600–700°C (Zhu & Sverjensky, 1992).

SUMMARY AND CONCLUSIONS

Apatite in both the SP metatonalites and the IVZ metabasites records the presence of high-grade fluids apparently concurrent with a dehydration event (granulite facies metamorphism) of what formerly were amphibolite facies rocks. One line of evidence includes the presence of monazite-II and/or xenotime-II inclusions in apatite from the dehydration zones, which are proposed to be the product of a fluid-induced metasomatic overprint via two simple coupled substitution reactions. Both high variability in and enrichment of (Y + REE) in the apatite from the dehydration zone in comparison with apatite from the amphibolite facies zone suggest increased mobility for (Y + REE), which could have been accomplished only through a fluid phase and probably involved the breakdown of hornblende. Furthermore, apatite in the dehydration zone, compared with apatite from the amphibolite facies zone, shows a relative increase in F and, at least for the IVZ, a relative increase also in Cl. If the HF fugacity relative to H₂O for biotite (Harlov & Förster, 2002) and apatite from the same sample are both plotted as a function of their distance from the fluid and/or heat source, they show the same basic pattern in

relative abundances for either traverse (Fig. 12). This is a remarkable agreement, considering that these HF fugacities have been estimated independently of each other for two different mineral species using different calibrations. Such consistent patterns are what one would expect if either traverse had experienced a metasomatic event in the form of a uniform fluid flow front through these rocks. In the case of the SP, Todd & Evans (1994) demonstrated that the dehydration zone was induced by the influx of a CO₂-rich fluid from an underlying marble. That the IVZ dehydration zone, when compared with the SP dehydration zone, should show such similar features with respect to both apatite and biotite chemistry as well as the same intimate relationship between apatite and monazite-II (here minus xenotime) strengthens the idea that these features in the IVZ were also fluid induced, although not by a CO₂-rich fluid (see below).

One major difference from the SP traverse is the presence of variably Th-enriched monazite-I grains in the IVZ granulite facies metabasites, which indicate a more complex history for these rocks. Their ubiquitous presence, as well as the complex zoning pattern with a substantial Th enrichment in a subset of these grains, points to an origin concurrent with the partial melting of the neighbouring metapelite layers and the subsequent redistribution of the now apparently mobile actinide elements and (Y + REE) into the metabasites at the boundary between the metapelite and metabasite layers. In this respect, the significant supply of (Y + REE), other high field-strength elements (Th, Nb) and P in most of the granulite facies metabasites in this study and others (e.g. Sills & Tarney, 1984), in comparison with their amphibolite-facies precursors, is suggested to be due to the introduction of those elements from the interlayered metapelites and not to represent a primary signature as proposed by Sills & Tarney (1984).

With respect to the perceived tectonic and magmatic history of the IVZ during granulite facies metamorphism, all lines of evidence presented by Harlov & Förster (2002), coupled with those in this study, point to a two-step process in the chemical evolution of the metabasites. The first step is that of the partial melting of the metapelites, which must have taken place relatively early during the underplating event when the magmas responsible for the Mafic Formation were still in a mostly molten state (e.g. Schnetger, 1994). This would have then allowed for an environment in which the complexly zoned monazite-I grains could have formed at the metapelite–metabasite boundary. The high H₂O activity inherent in the partial melt from the metapelites would have discouraged any breakdown of the hornblende and/or biotite in the metabasites to orthopyroxene and clinopyroxene. Only after this H₂O-rich partial melt had been expelled (presumably via fractures or fault lines in the tectonically thinned crust) leaving behind the present-day restitic and

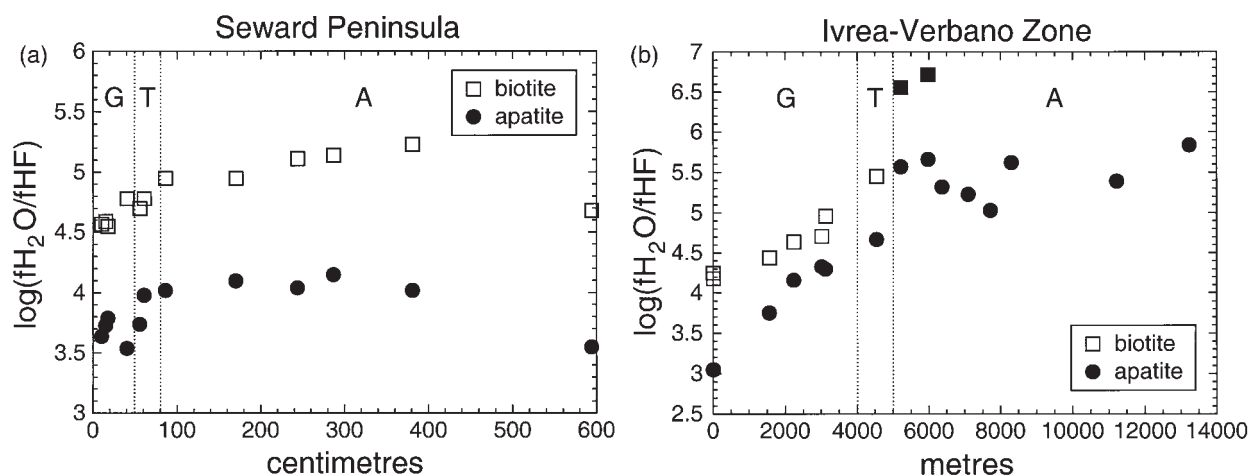


Fig. 12. Plot of $\log(f\text{H}_2\text{O}/f\text{HF})$ for both biotite (Munoz, 1992) and apatite (Korzhinskiy, 1981) as a function of distance from the marble layer for the SP (a) and from the Mafic Formation for the IVZ (b). Temperature and pressure used in the estimation of $\log(f\text{H}_2\text{O}/f\text{HF})$ are 800°C and 8 kbar for the SP and those given by Henk *et al.* (1997) for the IVZ. Mean biotite compositions are taken from Harlov & Förster (2002). Apatite compositions represent those grains from each sample that record the highest biotite–apatite equilibrium temperature and, thus, are the least reset. ■ (for biotite from the IVZ), F-poor low-Ti biotites.

relatively dry metapelites, and only after the majority of magmas responsible for the Mafic Formation were in the latter stages of crystallization, could the high-grade fluid event associated with the dehydration of the metabasites have taken place. This is because plutonic magmas, in general, tend to expel the majority of their fluids during the final stages of crystallization (e.g. Bailey, 1980). It has further been demonstrated that such fluids are capable of penetrating a relatively large volume of the surrounding country rock (e.g. Markl & Piazzolo, 1998).

Franz & Harlov (1998) proposed that successive pulses of a concentrated or supercritical Cl-rich brine, given off by the Mafic Formation during the latter stages of its crystallization, were responsible for the dehydration of a 3–4 km section of metabasite layers in the upper Val Strona in the immediate vicinity of the Mafic Formation. However, from both this study and Harlov & Förster (2002), it is evident that the composition of biotite and apatite, in particular, do not reflect a substantial predominance of HCl over HF in the fluids with which they have equilibrated. Yet, whether HF predominated over HCl or not, the basic conclusions in this study, coupled with those for the silicate minerals outlined in Part I (Harlov & Förster, 2002), still all point to a high-grade, low H_2O activity fluid front with both a F and Cl component and a negligible CO_2 component being responsible for the dehydration of the IVZ metabasites.

In retrospect, if a high-grade, low H_2O activity Cl–F-bearing fluid is capable of dehydrating 3–4 km of magmatic rock, by extension such a fluid could play a major role in dehydrating much larger volumes of the

hornblende–quartz-bearing mafic lower crust to orthopyroxene-bearing rock during granulite facies metamorphism. Similar fluids have been proposed as being the principal instigator of granulite facies metamorphism in the Archaean Eastern Dharwar craton of southern India (Hansen *et al.*, 1995; Harlov *et al.*, 1997). In this regard, then, the importance of low H_2O activity Cl–F-bearing fluids in the evolution and/or stabilization of the mafic lower crust could be enormous.

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