

Mineral chemistry of Ti-rich biotite from pegmatite and metapelitic granulites of the Kerala Khondalite Belt (southeast India): Petrology and further insight into titanium substitutions

BERNARDO CESARE,^{1,2,*} MADHUSOODHAN SATISH-KUMAR,³ GIUSEPPE CRUCIANI,⁴ SHABEER POCKER,³ AND LUCA NODARI⁵

¹Dipartimento di Geoscienze, Università di Padova, Via Giotto 1, Padova, 35137, Italy

²C.N.R., Istituto di Geoscienze e Georisorse, Sezione di Padova, Corso Garibaldi 37, Padova, 35137, Italy

³Institute of Geosciences, Shizuoka University, Oya 836, Shizuoka, 422-8529, Japan

⁴Dipartimento di Scienze della Terra, Università di Ferrara, Via Saragat 1, Ferrara, 44100, Italy

⁵Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, Padova, 35131, Italy

ABSTRACT

Precise chemical composition, including Fe³⁺ and H, of biotite from a pegmatite dike and its host granulite from the Kerala Khondalite Belt of SE India has been determined using a multi-technique approach involving EMP, SIMS, Mössbauer, and C-H-N elemental analysis. Biotite in these rocks formed at $T > 800\text{--}850^\circ\text{C}$ and $P = 5 \pm 1$ kbar.

The full analyses were normalized on the basis of $[\text{O}_{12-(x+y+z)}(\text{OH})_x\text{Cl}_y\text{F}_z]$. Biotite in the pegmatite is Ti-, F-, and Cl-rich (0.33, 0.46, and 0.16 apfu, respectively), H₂O-poor (OH = 0.86 pfu), has $X_{\text{Mg}} = 0.49$ and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}} \leq 3\%$. The low octahedral vacancies (0.06 pfu) and the high oxygen content in the hydroxyl site (OH + F + Cl = 1.49 pfu) confirm the role of the Ti-oxy substitution as a major exchange vector in these high- T biotites.

In the host granulite, fine-grained biotite is Fe³⁺-free, has low Cl (0.03 apfu), and more variable composition, with Ti, F, and X_{Mg} in the ranges 0.26–0.36, 0.52–0.67, and 0.67–0.77, respectively. The number of octahedral vacancies is relatively large (0.10–0.18 pfu) and the sum of volatiles (OH + F + Cl) varies from 1.71 to 2.06 pfu. Systematic variations of X_{Mg} are a function of the microstructural position and are in agreement with retrograde exchange reactions: biotite included in or in contact with garnet has the maximum values, whereas crystals in the matrix have the minima. Titanium has systematic negative correlations with F, X_{Mg} , and (OH + F + Cl), whereas Al and octahedral vacancies are virtually constant.

These trends indicate that the Ti-vacancy, along with substitutions involving Al, cannot explain the observed short-scale variations. Conversely, the Ti-oxy exchange appears to be active, resulting from combination of two vectors: the more conventional hydroxylation $\text{Ti}^{4+} + 2\text{O}^{2-} = (\text{Fe,Mg})^{2+} + 2\text{OH}^-$ and the “fluorination” $\text{Ti}^{4+} + 2\text{O}^{2-} = (\text{Fe,Mg})^{2+} + 2\text{F}^-$. The systematic retrograde redistribution involves not only Fe and Mg as commonly observed, but also Ti, F, and H, in a way such to eliminate the primary Ti-oxy component of biotite.

Keywords: Biotite, crystal-chemistry, granulite, pegmatite, retrograde diffusion, titanium

INTRODUCTION

This paper is a continuation of Charlie Guidotti’s research on metamorphic biotite and is a logical extension of that earlier work to higher grades of granulite metamorphism and partial melting of metapelites. The behavior of Ti in biotite during prograde metamorphism was first summarized by Guidotti (1984): with increasing metamorphic grade Ti is progressively incorporated in biotite, reaching values of ca. 0.3 atoms/22 O atoms (i.e., ca. 2.5 wt% TiO₂) in samples from the “upper sillimanite” zone. Subsequently, Charlie attracted several researchers (including the writers) who focused their efforts on the quantitative aspects of biotite crystal chemistry. The most recent result is the development of the Ti-in-biotite geothermometer (Henry and

Guidotti 2002; Henry et al. 2005) for graphitic metapelites at 4–6 kbar. In the early 1990s, Guidotti and co-workers (in particular Darby Dyar) pioneered the quantification of Fe³⁺ (Dyar 1990) and H in biotite and other minerals from metapelites (Dyar et al. 1991, 1993) showing that the H content of micas is far from stoichiometric, and that direct measurement of H is necessary to properly model mineral formulae. In the case of biotite, Dyar et al. (1991) showed that the Ti increase is mirrored by a continuous decrease of H, suggesting that deprotonation mechanisms may occur during prograde metamorphism.

Based on a series of amphibolite-facies samples from western Maine, the above work did not explore the behavior of biotite at very high temperature (HT) and anatexis, where the possible extent and effects of deprotonation should be maximized. In a previous study of partially melted metapelites, Cesare et al. (2003) showed that deprotonation, by way of the Ti-oxy exchange

* E-mail: bernardo.cesare@unipd.it

($\text{Ti}^{4+} + 2\text{O}^{2-} = \text{Mg}^{2+} + 2\text{OH}^-$) is the main exchange vector for the entrance of Ti in biotite equilibrated at $850 \pm 50^\circ\text{C}$, and outlined the implications of Ti-oxy on HT petrologic processes. The results of Cesare et al. (2003) were obtained from F- and Cl-free biotites from xenoliths in lavas, therefore they may not represent the behavior of biotite in HT metapelites such as granulites and migmatites. In these rocks, biotite typically has high F and Cl contents (e.g., Kamineni et al. 1982; Motoyoshi and Hensen 2001; Cenki et al. 2002; Bose et al. 2005). To extend our investigation to halogen-rich biotites, we have conducted the present study on micas from the metapelitic granulites of the Kerala Khondalite Belt (KKB) of southern India, one of the best exposed and studied examples of HT metasedimentary lower crust. After selection and detailed petrography of two lithologies (pegmatite and host granulite) from the same quarry, we have performed the same multidisciplinary approach adopted by Cesare et al. (2003) for the full-chemical characterization of biotite, including Fe^{3+} and H, by means of EMP, SIMS, C-H-N analysis, Mössbauer spectroscopy, and single-crystal XRD. The present paper focuses on the assessment of Ti substitution mechanisms and the discussion of petrological implications.

GEOLOGICAL AND PETROGRAPHIC BACKGROUND

The KKB (Fig. 1) in southern India is a supracrustal terrain, which was metamorphosed to granulite grade (Chacko et al. 1987) during the Pan-African tectonothermal event (~ 530 Ma; Shabeer et al. 2005; Santosh et al. 2006). This terrain is characterized by the occurrence of extensive garnet + biotite + sillimanite + graphite $\pm$ cordierite gneisses (khondalites), garnet-biotite gneiss (leptynites), and orthopyroxene-bearing granulites (charnockites). Less abundant rock types include clinopyroxene granulites, marbles, and calc-silicate rocks. The central region of

the KKB, around Thiruvananthapuram (Trivandrum), attained a peak metamorphic P - T condition of $\sim 950^\circ\text{C}$ and ~ 8 kbar (Chacko et al. 1996; Nandakumar and Harley 2000; Morimoto et al. 2004), was extensively migmatized (Braun et al. 1996), and exhumed along an initial isobaric cooling path followed by near isothermal decompression (Satish-Kumar and Harley 1998, and references therein). High-temperature metamorphic conditions are also supported by the finding of a spinel-quartz association (Braun et al. 1996; Shabeer et al. 2002; Morimoto et al. 2004).

The samples studied were collected from the abandoned quarry at Irinjayam, ca. 30 km NNE of Trivandrum (Fig. 1). Here, migmatitic rocks consisting of Bt-Grt gneiss, incipient charnockites, and Bt-Grt-Sil $\pm$ Crd granulites are cut by a meter-thick pegmatite dike (Fig. 2a). The pegmatite is straight, undeformed, with little internal zoning, and contains quartz, perthitic alkali feldspar, and biotite. The grain size of minerals in the pegmatite may reach 10 cm, and biotite crystals are subhedral, in plates up to 2 cm thick. The country rocks are fine- to medium-grained, with a marked migmatitic layering consisting of alternating Grt-bearing leucosomes and Bt-rich melanosomes (Fig. 2b). The sample of host migmatite is a fine-grained, Crd-free, Bt-Grt-Sil gneiss consisting of quartz, perthitic alkali feldspar, garnet, biotite, sillimanite, and ilmenite (Fig. 2c). Biotite is relatively abundant in the melanosomes, and very rare in the leucosomes, where garnet forms crystals up to 5 mm in diameter. Biotite rarely exceeds 0.5 mm in size, and occurs in several textural settings: in the rock matrix, as inclusions in garnet, and as crystals in contact with garnet. In the latter case, embayments of garnet boundaries suggest that some biotite grew replacing garnet, probably by back reaction with melt (Kriegsman and Hensen 1998) according to the model reaction $\text{Grt} + \text{melt} \pm \text{Kfs} = \text{Bt} + \text{Sil} + \text{Qtz}$ (e.g., Spear et al. 1999; Waters 2001). The same reaction could be responsible for the formation of fine-grained vermicular intergrowths of biotite and quartz, which form in places, both at the contact with garnet and partly replacing sillimanite and perthitic K-feldspar (Fig. 3). Also these microstructures are interpreted as indicating retrograde net transfer reactions ("ReNTRs" of Kohn and Spear 2000).

Samples and analytical techniques

One sample of pegmatitic vein and one of its host granulite were selected, and polished thin sections were prepared for EMP and SIMS analysis. In addition, two large crystals ($2 \times 3 \times 1$ cm) were separated from the pegmatite and powdered for C-H-N and AAS analysis, and some large (1 cm across) plates were used as single crystals for Mössbauer spectroscopy and as naturally polished (001) surfaces for further EMP and SIMS analysis.

EMP. Electron-microprobe (EMP) analyses of coarse biotite and alkali feldspar from the pegmatitic vein, and of biotite, garnet, and feldspars from the host rock were obtained with a Cameca SX50 of C.N.R.-I.G.G., Padova, using an accelerating voltage of 15 kV and a sample current of 15 nA. The natural and synthetic standards used were albite (Na), periclase (Mg), corundum (Al), wollastonite (Ca, Si), orthoclase (K), MnTiO_3 (Mn, Ti), chromite (Cr), hematite (Fe), barite (Ba), apatite (F), and vanadinite (Cl). The beam was, where possible, expanded to a diameter of ca. 10 μm , and data correction was performed using a PAP routine. Analytical errors (1σ) on all analyses were 1–2% (relative) for major elements (Si, Al, Mg, Fe, Ti) depending on the abundance of the element. Errors on F and Cl were within 8% (relative) and 3% (relative), respectively. Along with exsolved albite lamellae and host K-feldspar, the primary, pre-unmixing composition of perthitic feldspars was retrieved by integration of analyses in raster mode. Owing to the coarse size of exsolution lamellae and to technical limitations in raster size, it was necessary to perform an automated matrix of up to 8×6 rasters of $25 \times 30 \mu\text{m}$ each, so that an overall surface of up to $200 \times 180 \mu\text{m}^2$ was analyzed and the bulk composition

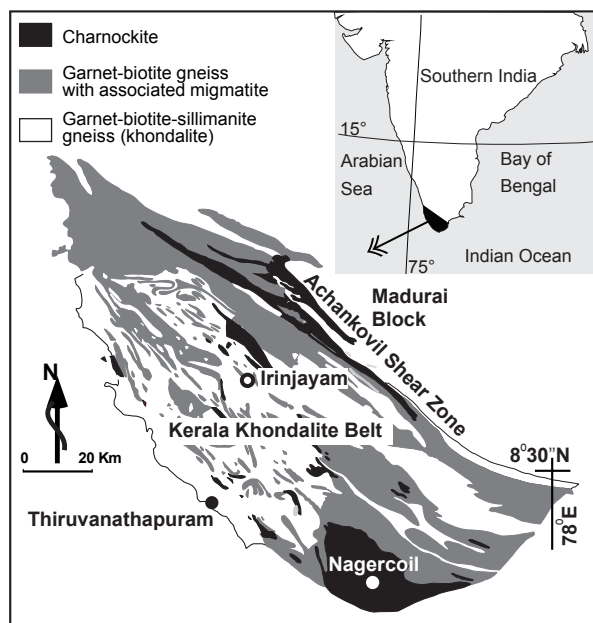


FIGURE 1. Geological Sketch map of KKB in southern India, with location of the outcrop of Irinjayam, where the studied rocks were collected.

assumed as the average of the raster analyses.

Lithium was analyzed on one mica separate by atomic absorption spectroscopy (AAS) and is 292 ppm, equivalent to 627 ppm Li_2O .

SIMS. Analysis of H by SIMS was performed with a Cameca ims-4f ion microprobe at the Department of Geology and Geophysics, University of Edinburgh, using NIST NBS30-Biotite (3.51 wt% H_2O) as a standard. The samples (single coarse lamellae from vein and thin sections of vein and host rock) and NBS30 standard were cleaned, coated with Au, and then stored in the ion microprobe for 3 days at a

vacuum of $\sim 5 \cdot 10^{-8}$ Torr prior to analysis. ^1H and ^{30}Si were analyzed using a 10 kV, 10 nA, O-primary beam. The secondary ions were analyzed using an offset of 120 ± 20 eV. The H_2O content was then calculated using the H/Si ratio relative to the standard (NBS30) that was measured throughout the analytical period. Repeated analyses of the standard suggest that the calculated relative error in the H content is within $\sim 10\%$. Possible contamination by inclusions or foreign minerals was minimized by selection of analysis sites using back-scattered electron imaging.

C-H-N elemental analysis. Analysis of bulk H of ~ 20 mg biotite aliquots from coarse pegmatitic crystals was performed with an EA 1108 elemental analyzer of CE Instruments at C.N.R.-I.G.G., Padova, calibrated with NBS30-Biotite and Acetanilide $\text{C}_8\text{H}_9\text{NO}$ standards.

SEM. SEM X-ray elemental maps of garnet in physical contact with biotite were obtained with a Camscan MX2500 equipped with a tungsten cathode, a four quadrant solid-state BSE detector, and an EDX-EDAX system for microanalysis. The analytical conditions were accelerating voltage = 20 kV; filament emission = ~ 160 nA; working distance = 35 mm; and 1024×800 pixel matrix size.

RESULTS

Alkali feldspar

The composition and unmixing mode of alkali feldspars is virtually identical in pegmatite dike and host granulite (Table 1). The primary composition of feldspar, back calculated from the average of raster-mode analyses, is in both cases $\text{Ab}_{28}\text{An}_{25}\text{Kfs}_{69}$. The exsolved plagioclase lamellae are oligoclase— $\text{Ab}_{77}\text{An}_{22}\text{Kfs}_1$ and $\text{Ab}_{80}\text{An}_{16}\text{Kfs}_4$ in vein and host, respectively, whereas the host K-feldspar is $\text{Ab}_{15-16}\text{An}_1\text{Kfs}_{83-84}$. Compositions of single rasters, averages, and spot analyses on exsolved phases are plotted in the Or-Ab-An ternary diagram, along with relevant solvi in the ternary feldspar system (Fig. 4, see discussion below).

Garnet

Garnet in the host granulite is essentially a pyrope-almandine binary solution, with only 1% spessartine and 2% grossular components (Table 1). As shown by the X-ray elemental map of Figure 5, crystals are zoned in Fe and Mg contents, whereas Ca and Mn are constant. The zoning pattern is characterized by a homogeneous composition $\text{Alm}_{63}\text{Pyp}_{35}$ [$X_{\text{Mg}} = 0.36$, where $X_{\text{Mg}} = \text{Mg}/(\text{Mg}+\text{Fe})$] throughout most of the crystals, and by small areas, in the vicinity of biotite, where Mg decreases and Fe increases to $\text{Alm}_{75}\text{Pyp}_{22}$ ($X_{\text{Mg}} = 0.22$) at the outermost rims.

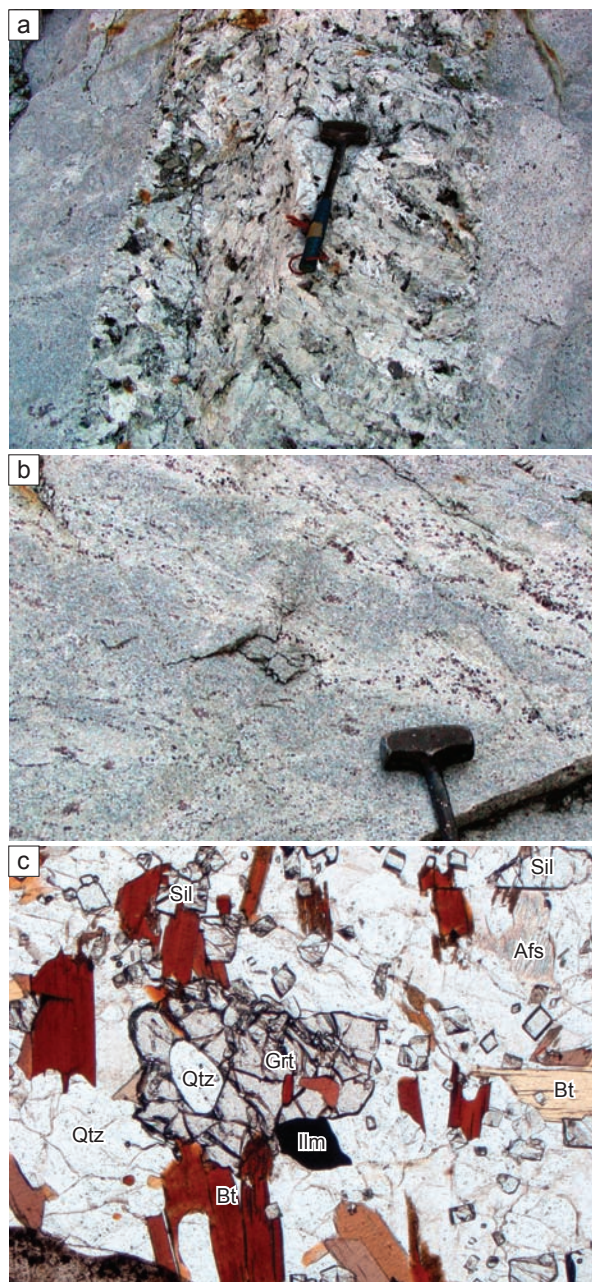


FIGURE 2. (a) Field occurrence of pegmatite dike (vertical at center of image) in medium-grained migmatitic granulites at Irinjayam. Black areas are biotite megacrystals; (b) typical appearance of medium-grained migmatitic host granulites; (c) plane-polarized light photomicrograph of a typical medium-grained dark layer from the metapelitic granulite hosting the pegmatite. The mineral assemblage is Grt-Bt-Sil-Qtz-Afs-Ilm (Afs = alkali feldspar), and garnet shows embayments and replacement by biotite. Width of view = 3 mm.

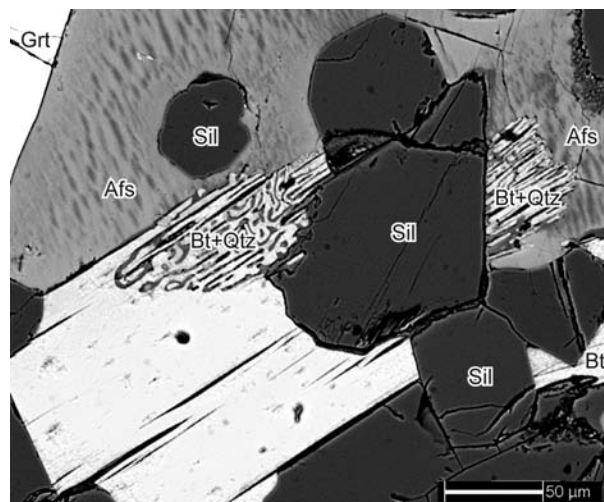


FIGURE 3. Back-scattered electron image (BSE) of vermicular Bt-Qtz intergrowths replacing sillimanite and perthitic alkali feldspar.

TABLE 1. Chemical composition of feldspars and garnet

	Feldspars							Garnet				
	Pegmatite				Granulite			Granulite				
	spot 1	raster 2	Average 3	Average 4	spot 5	spot 6	Average 7	core 8	core 9	rim to Pl 10	rim to Bt 11	rim to Bt 12
Na ₂ O	9.08	1.71	3.04	3.27	1.71	9.26	3.08	0.06	0.00	0.03	0.00	0.00
MgO	0.01	0.00	0.01	0.01	0.02	0.03	0.01	8.66	9.12	8.35	5.46	6.47
Al ₂ O ₃	23.35	18.35	18.78	18.88	18.22	22.08	18.63	21.61	22.03	21.83	21.10	21.64
SiO ₂	63.71	65.61	65.59	66.02	65.46	65.13	65.23	38.87	39.33	38.90	38.01	38.10
K ₂ O	0.12	13.47	11.73	11.71	13.71	0.62	11.76	0.00	0.03	0.00	0.06	0.03
CaO	4.71	0.14	0.55	0.45	0.11	3.41	0.48	0.66	0.70	0.67	0.63	0.69
TiO ₂	0.04	0.01	0.03	0.03	0.02	0.00	0.03	0.10	0.05	0.01	0.10	0.05
Cr ₂ O ₃	0.01	0.00	0.02	0.01	0.11	0.00	0.01	0.03	0.06	0.10	0.06	0.07
MnO	0.00	0.00	0.02	0.01	0.00	0.00	0.01	0.44	0.39	0.40	0.63	0.53
FeO	0.05	0.00	0.02	0.03	0.00	0.00	0.02	30.43	29.28	31.20	33.99	33.21
BaO	0.07	0.02	0.10	0.09	0.48	0.05	0.27					
Total	101.15	99.32	99.91	100.51	99.84	100.57	99.53	100.85	101.00	101.49	100.04	100.80
Si	2.788	3.015	2.989	2.989	3.009	2.857	2.989	2.998	3.007	2.989	3.014	2.983
Ti	0.001	0.000	0.001	0.001	0.001	0.000	0.001	0.006	0.003	0.001	0.006	0.003
Al	1.205	0.994	1.008	1.008	0.987	1.141	1.006	1.964	1.985	1.977	1.972	1.997
Cr	0.000	0.000	0.001	0.000	0.004	0.000	0.000	0.002	0.004	0.006	0.004	0.005
Fe ²⁺	0.002	0.000	0.001	0.001	0.000	0.000	0.001	1.962	1.872	2.005	2.253	2.174
Mn	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.029	0.026	0.026	0.042	0.035
Mg	0.000	0.000	0.001	0.001	0.001	0.002	0.001	0.995	1.039	0.957	0.646	0.756
Ca	0.221	0.007	0.027	0.022	0.005	0.160	0.024	0.054	0.057	0.055	0.054	0.058
Na	0.771	0.153	0.269	0.287	0.153	0.788	0.274	0.009	0.000	0.004	0.000	0.000
K	0.007	0.790	0.683	0.677	0.804	0.035	0.688	0.000	0.003	0.000	0.006	0.003
Ba	0.001	0.000	0.002	0.002	0.009	0.001	0.005					
Total	4.996	4.959	4.981	4.987	4.973	4.983	4.988	8.019	7.997	8.021	7.996	8.014
Ab%	77.2	16.1	27.4	29.1	15.9	80.2	27.8					
An%	22.1	0.7	2.7	2.2	0.6	16.3	2.4					
Or%	0.7	83.2	69.8	68.7	83.6	3.5	69.8					
Alm%								0.65	0.63	0.66	0.75	0.72
Pyp%								0.33	0.35	0.31	0.22	0.25
Sps%								0.01	0.01	0.01	0.01	0.01
Grs%								0.02	0.02	0.02	0.02	0.02

Notes: 1 = spot analysis on plagioclase exsolution; 2 = single 25 × 20 μm raster; 3 = average of 48 rasters 25 × 20 μm; 4 = average of 24 rasters 25 × 20 μm; 5 = spot analysis on exsolved K-feldspar; 6 = spot analysis on plagioclase exsolution; 7 = average of 15 rasters 25 × 20 μm; 8 = garnet core; 9 = garnet core; 10 = garnet rim in contact with plagioclase; 11 = garnet rim in contact with biotite; 12 = garnet rim in contact with biotite.

Rimward decrease of Mg is absent where garnet is in contact with phases other than biotite.

Biotite

H₂O contents. The H contents measured by SIMS, converted to H₂O, are reported in Table 2. In the two biotite crystals selected from the pegmatite, H₂O is 1.64 ± 0.07 and 1.67 ± 0.12 wt%. Comparison with analysis of NBS30 standard and with C-H-N-S elemental analysis on the same crystals (1.59 and 1.47 wt%, respectively) suggests that in this analytical session, H measurement may have been slightly overestimated.

In the host granulite, H₂O contents of biotite vary in the range 2.12–3.09 wt%, with an average value of 2.56 ± 0.24 wt%. This average value has been used in the recalculation of formulae for data points where direct H₂O measurement had not been performed.

Fe³⁺/Fe_{tot}. Mössbauer spectroscopy shows that the large crystals of biotite from the pegmatite contain very small but detectable quantities of Fe³⁺, assumed as 3% of the total Fe owing to the uncertainty of the method. Biotite from the host migmatitic gneiss is Fe³⁺-free.

Major-element composition

Table 3 reports the complete chemical analyses and recalculated formulae of biotites made on the basis of [O_{12-(x+y+z)}(OH)_xCl_yF_z] and integrated using the major element, H, and

Fe³⁺/Fe_{tot} contents determined by EMP, SIMS, and Mössbauer, respectively. In fact, only with measured values of H and Fe³⁺ can uncertainties about cation/anion charges and cation numbers be resolved (see discussion in Waters and Charnley 2002).

The accuracy of the calculated number of atoms per formula unit (apfu) were estimated by propagating the analytical errors on oxide wt%. The estimated errors are between ±0.03 and ±0.04 apfu for the major elements (Si, Mg, Al, Fe, Ti), and within ±0.03 apfu for OH and F.

In the pegmatite, biotite is fairly homogeneous, and the average compositions of the two crystals overlap within uncertainty. The biotite is rich in TiO₂ (5.6 wt%), F (1.9 wt%), and Cl (1.2 wt%), and low in Al₂O₃ (14.7 wt%). The anhydrous total is very high (>98%) for a “common” EMP analysis of biotite, and the totals with added H₂O (99.1–99.3 wt%) suggest that the quality of analyses is good. Calculated average atomic proportions give small amounts of octahedral Al (0.16–0.18 apfu), which are similar to the excess tetrahedral Al (^{iv}Al – 1, that is 0.18–0.20 apfu), Ti contents of 0.32 apfu, an almost filled interlayer site (K + Na = 0.99 apfu), low octahedral vacancies (0.06 apfu), and a high deficiency in the hydroxyl site, where OH + F + Cl sum at 1.49 apfu. The *X*_{Mg} of the biotite from the pegmatite is 0.49.

In the host granulite, biotite compositions are more variable, especially for TiO₂, FeO, and MgO that range from 4.7 to 6.4, 9.0 to 13.0, and 14.8 to 17.5 wt%, respectively. Unlike in the biotite from the pegmatite, Cl is very low (0.1–0.3 wt%) and F

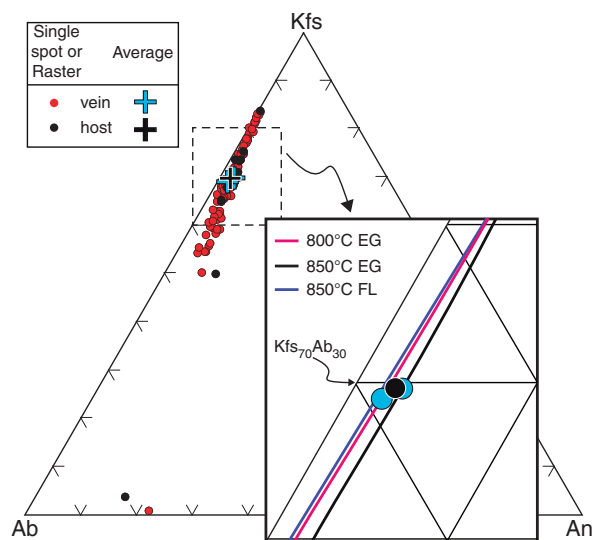


FIGURE 4. Kfs-Ab-An ternary diagram for feldspars, with compositions of spot analyses, single rasters, and averages of raster matrices from a pegmatite vein sample and its host granulite. The enlarged field illustrates the averages of rasters, assumed as the back-calculated composition of primary feldspars, along with the traces of the solvi after Fuhrman and Lindsley (1988, abbreviated FL), and Elkins and Grove (1990, abbreviated EG), as calculated at 6 kbar by García-Casco (personal communication) and plotted with CSpace (Torres-Roldán et al. 2000).

contents are higher (2.2–2.8 wt%). Octahedral Al (0.03–0.16 apfu) is well below the excess tetrahedral Al (0.15–0.23 apfu), and the interlayer site has 0.05 to 0.11 vacancies pfu. The amount of octahedral vacancies is relatively large (0.10–0.18 pfu) and the (OH + F + Cl) content is variable (1.71–2.06 pfu). The X_{Mg} ranges between 0.67 and 0.78.

Systematic chemical patterns in biotite from host granulite

Chemical variations of biotite in the host granulite display some systematic patterns as a function of the microstructural position. Concerning X_{Mg} , biotite inclusions in garnet have the maximum value (0.78), biotite touching garnet has $X_{Mg} > 0.72$, and biotite in the matrix ranges from 0.67 to 0.76 (Fig. 6). Inclusions in garnet also have the highest contents of Na (0.03 apfu) and Al_{tot} (1.3 apfu), and define a separate cluster in compositional plots. This behavior is similar to that reported in high-grade metapelites in the Isle of Pines Terrane, Cuba, by García-Casco et al. (2001). Biotite may show a very subtle zoning, characterized by an increase of X_{Mg} in the outermost 50 μm of crystals at the contact with garnet. Along with the rimward increase of X_{Fe} in adjacent garnet (see above), these zoning features are fully consistent with those described by Tracy et al. (1976) and indicate the progress of retrograde Fe-Mg exchange by intracrystalline diffusion between garnet and biotite (“ReERs” of Kohn and Spear 2000).

There is an excess of Al with respect to the annite-phlogopite join: Al enters primarily the tetrahedral site, and the Al-Tschermak substitution ($R^{2+} + Si = 2Al$) does not account for an average of 0.13 ^{IV}Al atoms (Table 3). Since these biotites are Fe^{3+} -free, this excess of ^{IV}Al can only be accommodated by the entrance of Ti.

There are systematic inverse variations of Ti with F, X_{Mg} (Fig. 6), and the sum (OH + F + Cl). The latter is of particular

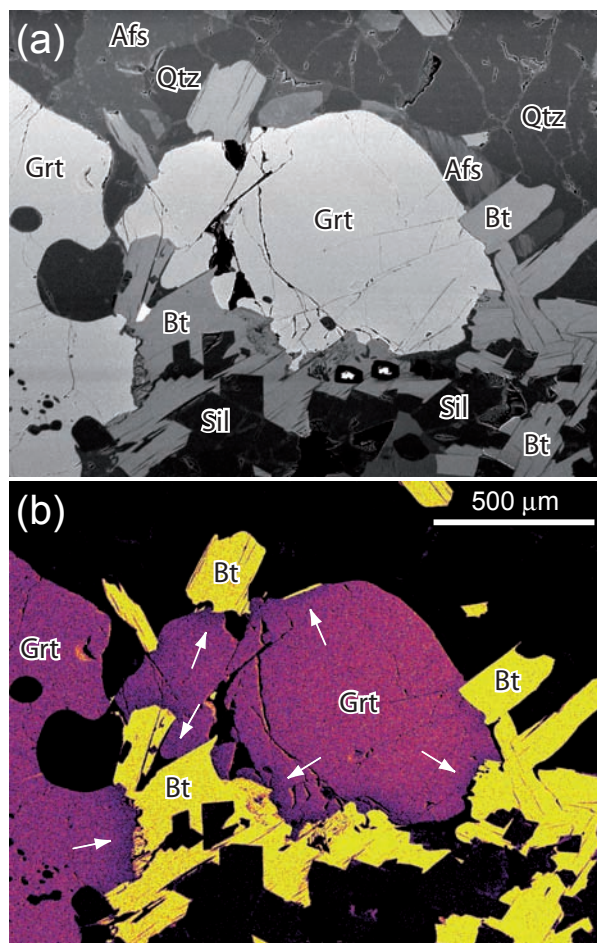


FIGURE 5. (a) BSE image of Grt-Bt relationships in the host granulite. (b) X-ray map of Mg in the same area as a, manipulated to enhance the compositional zoning of Grt. Arrows point to portions of Grt rims depleted in Mg (and enriched in Fe).

interest, especially when compared to the Ti vs. octahedral occupancy relationships: the plot of Figure 7 shows that octahedral occupancy is virtually constant with increasing Ti.

The (OH + F + Cl) vs. Ti trend of host-rock biotites appears to be consistent with the Ti-oxy substitution (Fig. 8, in which only analyses with measured H are plotted), although it should be noted that biotites at the Ti-poor end of the array are virtually devoid of Ti-oxy component.

As noted above, F is inversely correlated with Ti and Fe but co-varies with Mg and X_{Mg} (Fig. 9). As discussed below in more detail, these trends can be interpreted as related to the “Fe-F avoidance” (Muñoz 1984), “Ti-F avoidance” (Grew et al. 1990) and “Mg-F affinity” rules (e.g., Mason 1992; Icenhower and London 1995), which are commonly reported for high- T biotites. Conversely, there is no systematic relationship between Fe or Mg and Cl (Fig. 7), the latter being constant and low, possibly because of Cl undersaturation during biotite crystallization.

Temperature conditions

The minimum temperature of pegmatite crystallization, as well as of equilibration of the host granulites, can be estimated

TABLE 2. Hydrogen contents, converted to H₂O values, in biotite from the pegmatite, the host granulite, and from biotite standard NBS30, obtained by C-H-N elemental analysis and by SIMS

Technique	Pegmatite-1		Pegmatite-2		Host Granulite				NBS 30 (3.51 wt%)	
	Average	st. dev.	average	st. dev.	average	st. dev.	max.	min.	average	st. dev.
C-H-N	1.59 (5)	0.10	1.47 (5)	0.07					3.58 (2)	0.01
SIMS	1.64 (10)	0.07	1.67 (10)	0.12					3.75 (5)	0.13
SIMS					2.56 (24)	0.24	3.09	2.12	3.50 (10)	0.19

TABLE 3. Chemical composition of biotite

Sample	Pegmatite				Host Granulite								All data	
	Bt1		Bt2		Single spots									
	Average n = 13	St. dev.	Average n = 16	St. dev.	1	2	3	4	5	6	7	8	Average n = 67	St. dev.
SiO ₂	36.17	0.29	35.87	0.31	37.64	38.29	37.58	38.17	37.48	37.51	37.45	38.62	38.03	0.47
TiO ₂	5.37	0.12	5.65	0.08	4.71	5.92	6.22	4.86	6.11	5.84	5.67	5.83	5.51	0.38
Al ₂ O ₃	14.93	0.15	14.75	0.14	14.55	15.11	14.47	14.84	14.61	14.93	14.47	15.06	14.74	0.25
FeO	19.32	0.29	19.25	0.23	11.34	9.09	12.16	10.08	12.75	12.35	11.80	10.20	11.65	0.83
MnO	0.05	0.03	0.04	0.03	0.01	0.06	0.05	0.00	0.02	0.05	0.00	0.00	0.02	0.02
MgO	10.06	0.11	9.95	0.12	16.93	17.53	15.02	17.51	14.91	15.62	15.89	16.88	16.04	0.71
CaO	0.01	0.02	0.01	0.01	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Na ₂ O	0.26	0.07	0.32	0.05	0.05	0.25	0.12	0.09	0.04	0.10	0.09	0.08	0.11	0.04
K ₂ O	9.48	0.17	9.52	0.09	9.83	9.81	9.66	9.60	9.51	9.83	9.75	9.61	9.72	0.15
F	1.94	0.16	1.85	0.16	2.87	2.66	2.43	2.87	2.22	2.48	2.58	2.85	2.57	0.18
Cl	1.20	0.04	1.23	0.02	0.23	0.25	0.20	0.26	0.25	0.20	0.19	0.19	0.23	0.03
EMP Total	98.77	0.58	98.45	0.54	98.17	98.97	97.95	98.26	97.90	98.92	97.90	99.32	98.62	0.54
Li ₂ O*	0.06													
H ₂ O SIMS	1.64		1.67		2.77	2.56†	2.30	2.47	2.33	2.47	2.45	2.56†	2.56	0.24
O = F	0.82		0.78		1.21	1.12	1.02	1.21	0.94	1.05	1.09	1.20	1.08	
O = Cl	0.27		0.28		0.05	0.06	0.05	0.06	0.06	0.05	0.04	0.04	0.05	
Total	99.33		99.06		99.67	100.35	99.18	99.47	99.24	100.30	99.22	100.64	100.05	
Si	2.814		2.802		2.769	2.775	2.805	2.792	2.800	2.769	2.784	2.795	2.795	
^{IV} Al	1.186		1.198		1.231	1.225	1.195	1.208	1.200	1.231	1.216	1.205	1.205	
^{VI} Al	0.183		0.160		0.030	0.066	0.078	0.072	0.087	0.068	0.052	0.080	0.072	
Ti	0.314		0.332		0.261	0.323	0.349	0.267	0.343	0.324	0.317	0.288	0.305	
Fe ²⁺	1.219		1.220		0.697	0.551	0.759	0.617	0.797	0.762	0.734	0.617	0.716	
Fe ³⁺	0.038		0.038		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Mg	1.167		1.159		1.856	1.894	1.671	1.909	1.661	1.719	1.761	1.821	1.757	
Mn	0.003		0.003		0.001	0.003	0.003	0.000	0.001	0.003	0.000	0.000	0.001	
Sum Oct.	2.946		2.934		2.902	2.844	2.865	2.871	2.895	2.876	2.869	2.841	2.858	
Ca	0.001		0.001		0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	
Na	0.039		0.049		0.008	0.035	0.018	0.013	0.006	0.014	0.013	0.012	0.016	
K	0.940		0.949		0.922	0.907	0.919	0.896	0.906	0.926	0.925	0.888	0.911	
Sum W	0.980		0.998		0.930	0.941	0.940	0.909	0.912	0.940	0.938	0.899	0.927	
OH	0.851		0.870		1.359	1.238	1.145	1.249	1.161	1.216	1.215	1.357	1.254	
F	0.478		0.457		0.668	0.609	0.572	0.663	0.525	0.580	0.608	0.652	0.597	
Cl	0.158		0.162		0.029	0.030	0.026	0.032	0.031	0.025	0.024	0.024	0.028	
Sum	1.486		1.490		2.056	1.877	1.743	1.944	1.718	1.821	1.847	2.032	1.880	
X _{Mg}	0.49		0.49		0.73	0.77	0.69	0.76	0.68	0.69	0.71	0.75	0.71	
X _F H ₂ O _{SIMS}	0.32		0.31		0.32	0.32	0.33	0.34	0.31	0.32	0.33	0.34	0.32	
X _F H ₂ O _{ideal}	0.23		0.22		0.33	0.30	0.28	0.33	0.26	0.29	0.30	0.33	0.30	
IV _F	1.035		1.063		1.396	1.425	1.321	1.392	1.352	1.355	1.357	1.369	1.380	
log(f _{H₂O} /f _{H_F})	3.073		3.100		3.359	3.383	3.299	3.349	3.333	3.333	3.327	3.332	3.350	
log(f _{H₂O} /f _{H_{Cl}})	2.578		2.575		3.632	3.582	3.581	3.566	3.496	3.621	3.647	3.682	3.596	
log(f _{H_F} /f _{H_{Cl}})	-0.866		-0.895		-0.326	-0.426	-0.265	-0.407	-0.375	-0.272	-0.255	-0.254	-0.330	

Note: Single spots 1 and 8 = in contact with garnet; 2 = included in garnet; 3 to 7 = in the matrix, not in contact with garnet. log(f_{H₂O}/f_{H_F}), log(f_{H₂O}/f_{H_{Cl}}), log(f_{H_F}/f_{H_{Cl}}) at T = 800 °C, calculated according to Muñoz (1992).

* Analyzed by AAS.

† Not measured in this crystal, and assumed as the average value.

from feldspar compositions which, unlike for garnet and biotite geothermometry, should not be affected by the retrograde exchange (Spear 1993). Figure 4 shows that the back-calculated composition of the feldspars plot within the miscibility gap for ternary feldspars at 800 °C (as defined by Elkins and Grove 1990), or at 850 °C (defined by Fuhrman and Lindsley 1988). As these values represent minimum temperatures of crystallization, it can be concluded that

feldspars indicate T in excess of 800–850 °C. This estimate is in agreement with the data obtained by Shabeer (2004) from rocks of the same outcrop. Because biotite is in textural equilibrium (similar grain-size, shape of phase boundaries, etc.) with feldspars in both rock samples, it follows that biotite was already crystallized in both rocks at T > 800–850 °C.

Application of the Grt-Bt thermometer to mineral pairs in

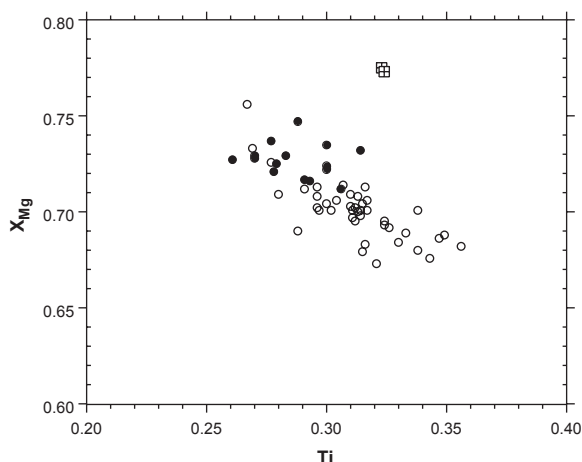


FIGURE 6. X_{Mg} vs. Ti plot for biotite in the host granulite. Filled circles = crystals in contact with garnet; open circles = crystals in the matrix, away from garnet (in 2-D); crossed squares = crystals enclosed in garnet.

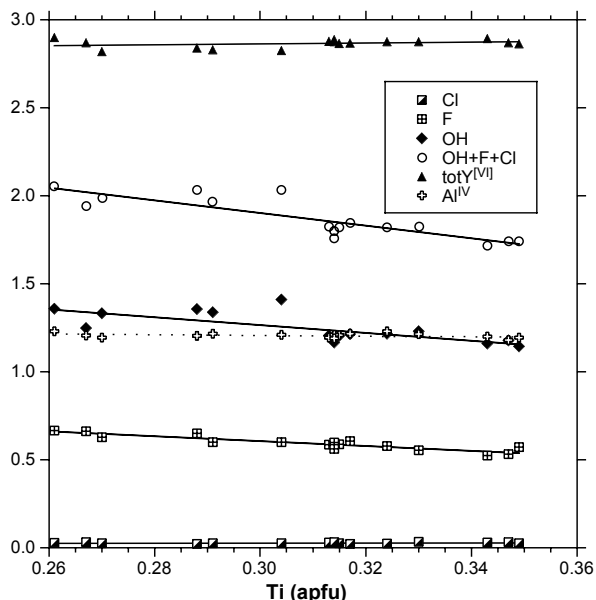


FIGURE 7. Plot of Cl, F, OH, (OH + F + Cl), octahedral occupancy, and ^{IV}Al vs. Ti for biotite in the host granulite. Only crystals where H was directly measured have been used in this plot.

contact, i.e., using the outermost rim composition of garnet in contact with biotite, gave unreasonable temperatures of 450–500 °C. These low temperatures, often found in granulites (e.g., Bose et al. 2005) are in agreement with what should be expected in fine-grained rocks with low modal amounts of biotite, affected by Fe-Mg exchange (ReETRs) during slow cooling (Spear 1991, 1993; Kohn and Spear 2000).

Application of the Ti-in-biotite thermometer of Henry et al. (2005) would indicate temperatures in excess of 750 °C for the large crystals in the pegmatite, and in excess of 800 °C for most of the biotites in the host granulite (Fig. 10). Although the latter are in broad agreement with feldspar thermometry, it should be noted that quantitative application of the Henry et al. (2005) model to our rocks is hampered by the absence of graphite and

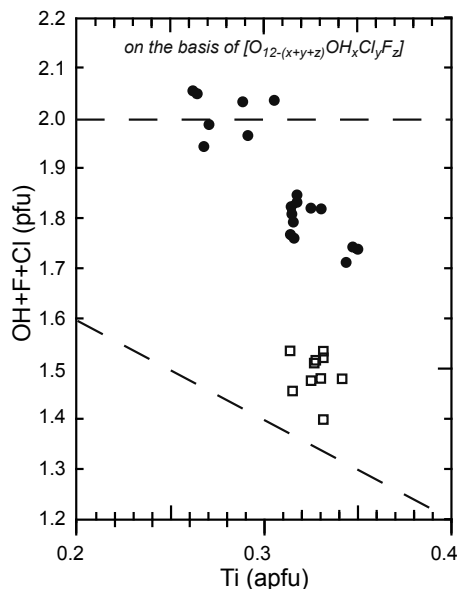


FIGURE 8. Plot of (OH + F + Cl) vs. Ti for biotite in the host granulite. Horizontal and diagonal dashed lines represent the ideal Ti-vacancy and Ti-oxy substitutions, respectively.

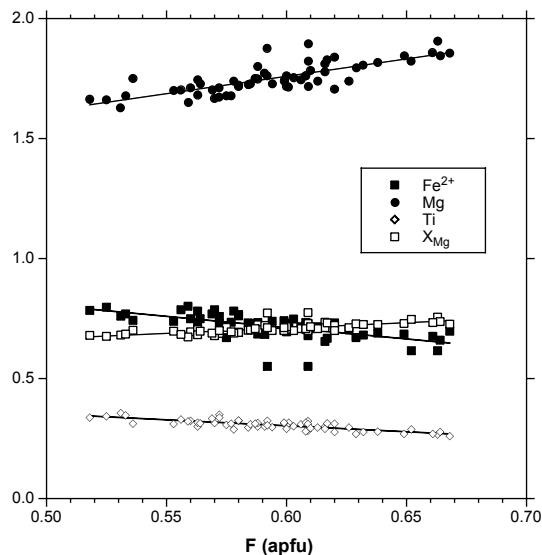


FIGURE 9. Plot of Fe, Mg, Ti, and X_{Mg} vs. F for biotite in the host granulite.

by the different pressure regime. In addition, as suggested above and discussed below in detail, the high temperature obtained from biotite in the host granulite is very likely fictitious, as the Ti and X_{Mg} values are not primary.

DISCUSSION

Interpretation of chemical variations of biotite in the host granulite

Based on the microstructural and chemical data presented above, and on earlier studies of similar rocks in the KKB region (Braun et al. 1996; Shabeer 2004), we can envisage a petrogenetic model (Fig. 11) involving initial biotite growth during prograde

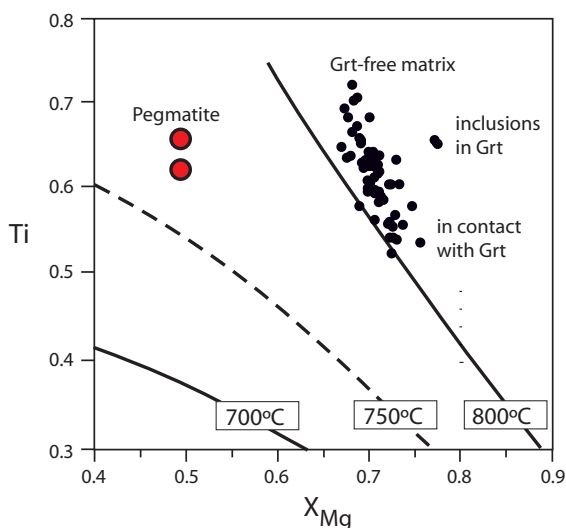


FIGURE 10. Ti vs. X_{Mg} plot for the biotites, with isotherms from Henry et al. (2005). Ti atoms are twice the values in Table 3, for comparison with the thermometer of Henry et al. (2005).

HT metamorphism followed by (1) biotite melting with formation of peritectic garnet; (2) biotite crystallization at slightly lower temperatures, for example by retrograde back-reaction of melt with the Grt-bearing restitic assemblage; (3) formation of Bt-Qtz vermicular intergrowths locally replacing garnet, K-feldspar and sillimanite; and finally (4) Grt-Bt exchange reactions during cooling. Although there is microstructural evidence that some biotite grew replacing K-feldspar and sillimanite (Fig. 3), it is not clear if these net-transfer reactions (ReNTRs) occurred before or during chemical re-equilibration by exchange reactions (ReERs), i.e., if the stages 3 and 4 are sequential or coeval.

As discussed in detail by Spear (1993) and Kohn and Spear (2000), the increase of X_{Mg} in biotite and of X_{Fe} in garnet observed in the host granulite indicate the occurrence of ReERs. In fact, ReNTRs, like back-reactions both with melt and at subsolidus conditions, should move biotite to Fe-richer composition. Therefore, the preferred interpretation is that stages 3 and 4 are sequential, i.e., after reaching the final microstructural configuration and positioning of grain boundaries, phase compositions were further modified by retrograde diffusion. As a consequence, the composition of biotite in contact with garnet is not primary, but has been reset toward Mg-richer compositions during the retrograde evolution of the granulite. Another consequence is that the seemingly isothermal trend at $T > 800^\circ\text{C}$ in the Ti- X_{Mg} plot of Figure 10 is fictitious, as the biotite with the highest X_{Mg} values are likely to have attained their compositions at the closure temperatures of the intercrystalline exchange of ca. 500°C (Spear 1993).

The biotite included in garnet (highest X_{Mg} , intermediate Ti, highest Na and Al) represents a distinct population and corresponds texturally to a residual prograde biotite stable just before the peak of metamorphism and melting. Also for this biotite, the composition is likely reset by retrograde exchange with garnet (compare García-Casco et al. 2001). This should, however, affect only Fe and Mg since garnet cannot exchange F and Ti.

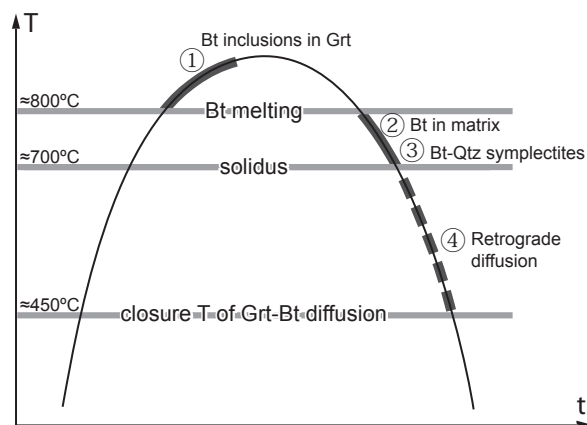


FIGURE 11. Schematic T - t diagram illustrating the behavior of biotite during the HT metamorphism and melting event, and through the subsequent cooling. As discussed in the text, stages 3 and 4 could be (in part) coeval.

In the matrix biotite, a clear negative correlation between Ti and both F and X_{Mg} is observed (Figs. 6 and 7). The Ti- X_{Mg} relationships in biotite from high-temperature metapelites deserve particular attention. Although an inverse relationship has been proposed as universal by Guidotti (1984), and can be observed in granulite-grade rocks (e.g., Motoyoshi and Hensen 2001), positive correlations are present both in nature (e.g., Harlov and Förster 2002) and in experiments (e.g., Stevens et al. 1997), and they are corroborated by phase-petrology considerations. This situation may appear controversial, but actually highlights the presence of different controls on Ti- X_{Mg} relationships: (1) thermodynamics (in the form of temperature) for the positive correlations; and (2) crystal-chemical constraints (typically isothermal) for the negative correlations.

The first control, temperature, is outlined by phase relations in the pelitic system. During melting, Ti in biotite increases with increasing temperature (e.g., Guidotti et al. 1977; Patiño Douce et al. 1993) and X_{Mg} increases, both in Grt-Bt-Sil-melt (e.g., Patiño Douce and Johnston 1991) and in Grt-Bt-Crd-melt assemblages (e.g., Spear et al. 1999; Johnson et al. 2001). Only in the case of a Grt-free Bt-Crd-melt association would a temperature increase be accompanied by a decrease of X_{Mg} (e.g., Spear 1993).

The second, crystal-chemical, control is apparent by inspection of the Ti-saturation surface recently proposed for graphitic metapelites at low pressure, where Henry et al. (2005) outline the importance of the $MgFe_{-1}$ exchange for Ti substitution, showing that, all other factors being constant, a decrease in Ti correlates with higher X_{Mg} . Similar negative correlations in single samples are apparent in biotite from graphite-bearing pelitic schists of Torrox (García-Casco and Torres-Roldán 1996, 1999). Negative Ti- X_{Mg} correlations were also reported by Waters and Charnley (2002); although their biotites span a larger interval of Ti (0 to 5 atoms/22 O atoms), these authors invoked local equilibrium as an explanation. Equilibrium on a millimeter-scale also might be proposed for the chemical variations observed in this study, since our data define a quasi-isothermal trend (an interval $<30^\circ\text{C}$ at $T > 800^\circ\text{C}$) in Figure 10. However, local equilibrium cannot explain the Mg-richer, Ti-poorer composition of biotite touching

Fe-rich garnet, which contrasts with the Fe-richer composition of biotite in Grt-free domains (Fig. 6) and is the opposite of what should be expected in KFMASH system. Since these chemical patterns are indicative of Fe-Mg exchange between garnet and biotite during cooling, the negative correlation between Ti and X_{Mg} , in the present study, is an effect of retrograde diffusion.

Inter- and intracrystalline diffusion during cooling

Although it is commonly reported that retrograde reactions between garnet and biotite only cause variations of X_{Mg} (compare also Usuki 2002), in the biotites from the host granulite the X_{Mg} changes are also correlated with systematic variations of Ti (negatively) and F and OH (positively). This behavior is well illustrated by Figure 12, where the increase of X_{Mg} is considered as a measure of the extent of retrograde diffusion. The good correlations in Figure 12 (slightly scattered for OH) demonstrate that during down- T re-equilibration in natural systems, biotite exhibits intracrystalline diffusion of Ti, F, and H in addition to Fe and Mg. Although Fe-Mg variations could be accommodated solely by Grt-Bt exchange, variations of F and H necessarily require exchange with other phases (solid or fluid/melt) in the adjacent matrix. The decrease of Ti can be balanced by either growing another Ti-bearing phase or by increasing the amount of biotite. The latter possibility would in turn require further exchange with a K-bearing phase. A comprehensive balance of sources and sinks of elements during the retrograde re-equilibration of biotite is beyond the scope of this paper, but it can be noted that micrometer-sized crystals of rutile have been observed in places at the boundaries of biotite.

The mobility of Ti in biotite during retrogression is well documented in previous studies. For example, within-sample negative Ti- X_{Mg} trends are reported from the high-grade rocks

described by Thomson (2001) and discussed by Henry et al. (2005), whereas in the study of García-Casco et al. (2001), within-sample variations of Ti take place at constant X_{Mg} . In none of these studies, however, had F and H been quantified and their variations correlated with those of Ti and X_{Mg} .

The trends in Figure 12 can be also interpreted on the basis of the already mentioned universal rules, namely the “inverse Ti- X_{Mg} relationship” and the “Fe-F avoidance.” Under the reasonable assumption that the retrograde diffusion of Mg and Fe between garnet and biotite (as quantified by X_{Mg}) is the principal (or the only) driving force within the re-equilibration process, we can propose a model that accounts for all chemical variations of biotites in the host granulite. The increase in X_{Mg} intrinsically implies a decreasing content of Fe in biotites. In agreement with the Fe-F avoidance, these Fe-poorer biotites would be more prone to host larger amounts of F. The parallel decrease of Ti with increasing X_{Mg} (due to the universal inverse Ti- X_{Mg} relationship), would explain the progressively larger OH contents in biotite as a function of retrograde re-equilibration. Therefore, we speculate that the decrease in Fe and Ti contents (both inversely related to X_{Mg}), would be directly responsible for larger F and OH contents, respectively, in the hydroxyl site of pre-existing partially dehydrogenated Ti-rich biotites. It should be noted that the above model would explain the positive correlation between F and OH (see Fig. 12), otherwise unexpected on the basis of a direct exchange vector $F(OH)_{-1}$ as caused, for instance, by variations of fluid composition.

Although Figure 12 is also consistent with the “Ti-F avoidance” and “Mg-F affinity” rules, these relationships simply arise from the combined occurrence of the “inverse Ti- X_{Mg} relationship” and “Fe-F avoidance” rules.

Approach to Ti-substitutions

One of the purposes of this research is to explore the exchange vectors that better define the variation of Ti in biotite, i.e., the departure from the “ideal biotite plane” (Guidotti 1984). Such vectors may represent a purely descriptive tool, or the actual process (e.g., intracrystalline diffusion) that brought about the observed chemical differences between biotite crystals. In both cases the definition of the exchange vectors is important, but in the latter case it is also linked to a petrogenetic process.

As it is likely that the observed chemical variations represent the effects of a diffusive process, we can try to model the exchange vectors that describe not only ideally but also actually, the way Ti enters—in this case exits—the structure of biotite.

If the attention is focused on the narrow range of Ti variation (0.26 to 0.35 apfu) and not on the overall departure from the Ti-free ideal biotite plane, it is apparent from Figures 7 and 8 that the major chemical variation correlated to that of Ti is the negative trend of the occupancy of the hydroxyl site ($OH + F + Cl$). Conversely, ^{IV}Al and octahedral occupancy are virtually constant. This implies that a mechanism of Ti-oxy exchange was active in these biotites and that, in contrast, the Ti-vacancy and Ti-Tschermak substitutions did not play a relevant role.

We can speculate on the reason why all the retrograde Ti loss was compensated almost entirely by the incorporation of $OH + F$ (i.e., the reverse Ti-oxy vector). Perhaps it was just a response to an increased supply of OH and F, or it might equally be that

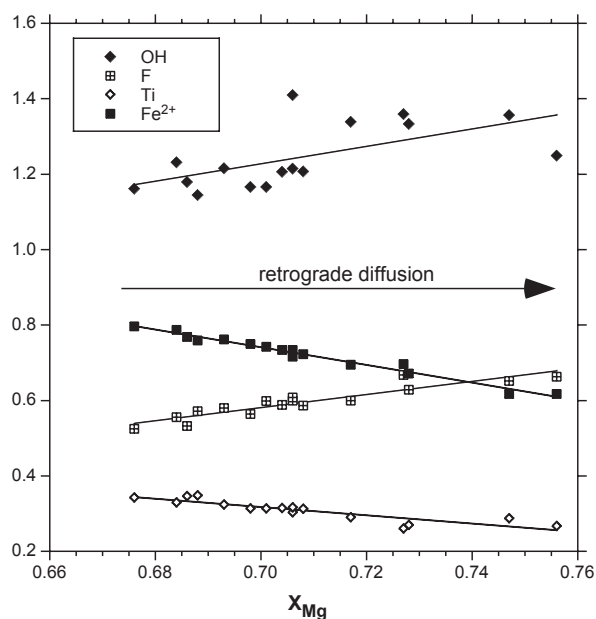


FIGURE 12. Plot of OH, F, Ti, and Fe vs. X_{Mg} for biotite in the host granulite. Only crystals where H was directly measured have been used in this plot.

the resetting of the other two exchange vectors—Ti-vacancy and Ti-Tschermak—was less favored energetically, so that the reverse Ti-oxy was the easiest route. Without entering into a detailed discussion on the thermodynamics and activation energies involved in the above mechanisms, it should be noted that the Tschermak vector requires Al/Si exchange in tetrahedral sites, whereas the vacancy vector requires a net cation transfer within the octahedral sheet. Therefore, the exchange of OH + F through the mica interlayer appears as the less diffusion-limited process.

The Ti-oxy substitution can be further constrained by analyzing separately the variations of F, OH, and Cl, where it is apparent that Cl is low and constant, and that there are negative correlations of Ti with both F (−1.4) and OH (−2.2). Therefore, we can propose that the reverse Ti-oxy exchange in the studied granulitic metapelites is the sum of two components: the more conventional hydroxylation (or protonation) $\text{Ti}^{4+} + 2\text{O}^{2-} = (\text{Mg,Fe})^{2+} + 2\text{OH}^-$ and the “fluorination” $\text{Ti}^{4+} + 2\text{O}^{2-} = (\text{Mg,Fe})^{2+} + 2\text{F}^-$. The latter appears to play a prominent role. The compositional change of biotites in the host-rock is essentially described by a trend in which $\text{Ti} + \text{Fe} + 2\text{O}$ is replaced by $2\text{Mg} + \text{OH} + \text{F}$.

Moreover, as seen in Figure 7, excess $^{\text{IV}}\text{Al}$ and octahedral vacancies may account for fixed amounts of 0.06 and 0.14 atoms Ti, respectively, it appears that (in this sample) the Ti-oxy exchange operates under a fixed extent of long-range Ti-Tschermak and Ti-vacancy substitutions.

Since the octahedral occupancy is constant, replacement of Ti by divalent cations occurs on a 1:1 basis. The plot of Fe and Mg vs. Ti (Fig. 13) allows evaluation of how this octahedral exchange occurs: the linear correlations of Fe and Mg, having slope of −1.1 and +2.1, respectively, indicate that the overall octahedral exchange is $\text{Mg}_{2.1}\text{Fe}_{-1.1}\text{Ti}_{-1}$, and suggest that for each atom of Mg acquired by biotite during Fe-Mg exchange with garnet, another atom of Mg was acquired by Ti loss.

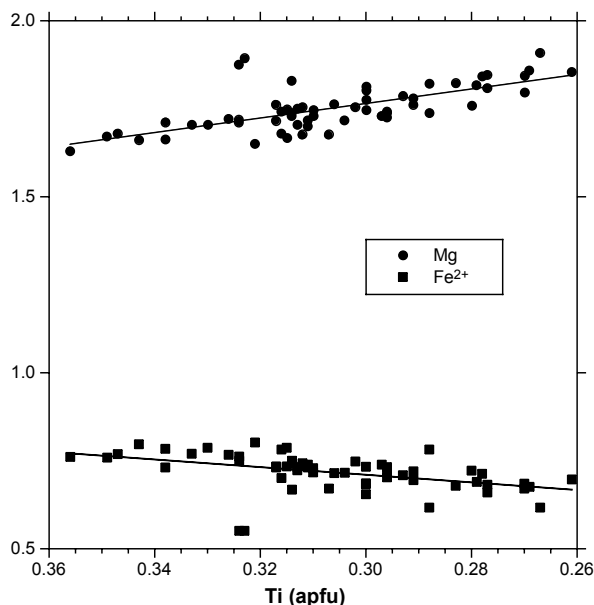


FIGURE 13. Plot of Mg and Fe vs. Ti (in reverse axis direction), with calculated linear fits having slopes of −1.08 (for Fe) and +2.06 (for Mg).

The biotite from the pegmatite shows a much greater dehydroxylation and different OH-F-Cl contents. This may imply a different fluid/melt composition from which it was crystallizing. In this mica, the long-range Ti entrance and departure from the Ann-Phl-Eas-Sid plane can be modeled primarily (80%) by the Ti-oxy exchange, with a moderate involvement (20%) of the Ti-vacancy exchange and absence of Ti-Tschermak.

Integration of results from both the pegmatite and host granulite with data from the xenoliths of El Hoyazo, Spain (Cesare et al. 2003) provides further insight into Ti-substitutions in biotite from high-grade rocks. Figure 14 shows that the extent of oxy substitution is variable, and that in a relatively narrow range of Ti contents an apparent transition exists from almost pure or dominant Ti-oxy exchange (samples from El Hoyazo and pegmatite) to a combination of Ti-vacancy plus Ti-Tschermak (reequilibrated biotite in host granulite). Even if the composition of part (or all) of the biotite in the host granulite is not primary and has been affected by down-*T* hydroxylation and fluorination, these differences remain, and imply that there is no unique mechanism for the intake of Ti in biotite from high-temperature, partially melted metapelites.

Understanding the reason of this behavior requires additional case studies, as well as ad hoc experimental investigation. We can, however, propose two possible explanations: the simplest and always possible, but very difficult to constrain, is differences in the activity of fluid species (H_2O , F, Cl) in the environment of crystallization. The second is the possible crystal-chemical control of X_{Mg} in the type of Ti-exchange, which is suggested by the trend defined in Figure 14, where the greatest extent of Ti-oxy substitution corresponds to the lowest X_{Mg} values, and vice versa.

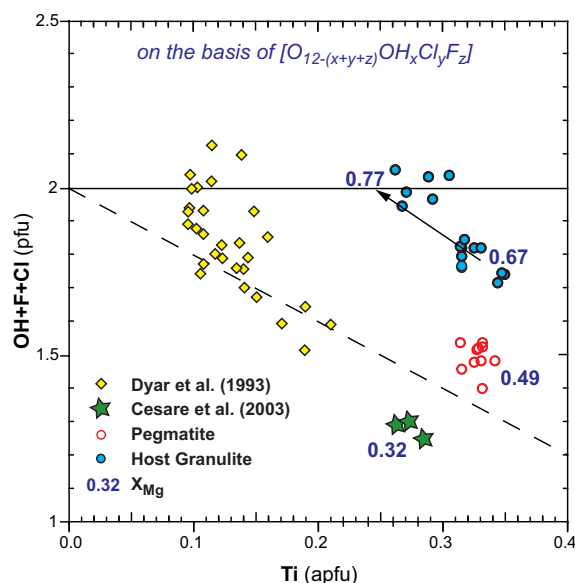


FIGURE 14. Ti vs. (OH + F + Cl) diagram with data from this study, from partially melted metapelitic xenoliths (Cesare et al. 2003) and from greenschist- to amphibolite-facies graphitic metapelites (Dyar et al. 1993). All data points refer to crystals in which H was analyzed. Also reported are the X_{Mg} values of biotite in the HT, granulitic rocks. The arrow represents the re-equilibration trend observed in the biotites from the host granulite in this study.

This is in agreement with the proposal of Henry et al. (2005) that Mg influences the type of Ti substitution mechanism.

F fugacity and errors

The halogen contents of the micas considered here indicate that F is of greater importance than Cl for possible halogen-hydroxyl exchange during metamorphism. Owing to the availability of H, F, and Cl data, the method of Muñoz (1984, 1992) has been utilized to infer the relative fugacities of H_2O and HF in the fluid (Table 3). Note that this approach should not be applied quantitatively to the micas of this study due to their high Ti contents (Muñoz 1984). Therefore the results can only be used for comparative evaluation. In the pegmatite, measured OH is 0.85 pfu, and the resultant $X_F [F/(OH + F + Cl)]$ is 0.31–0.32. Had H not been measured, and the $(OH + F + Cl = 2)$ normalization scheme been used, a largely underestimated and erroneous X_F of 0.22–0.23 would have been obtained. Such an error propagates in the calculations of the fluorine intercept value $[IV(F), \text{Muñoz 1984}]$, which would increase from actual values of 1.03–1.06 to 1.27–1.29. Although it gives rise to differences in $\log[(f_{H_2O})/(f_{HF})]_{\text{fluid}}$ that may appear to be small (3.1 vs. 3.3 adopting the calibration of Muñoz 1992), such 22% relative error of $IV(F)$ is among the highest calculated by Muñoz (1984).

Because dehydroxylation is most common and most extensive in high-Ti biotite from high- T rocks, it follows that estimates of $\log[(f_{H_2O})/(f_{HF})]_{\text{fluid}}$ and $\log[(f_{H_2O})/(f_{Cl})]_{\text{fluid}}$ from granulites and UHT metapelites should generally be (largely) overestimated if H in biotite has not been determined (e.g., Harlov and Förster 2002; Bose et al. 2005).

The data in Table 3 also show that the error associated with calculating OH by difference is unpredictable, as crystals with higher F contents in the host granulite have similar X_F and higher $IV(F)$ when compared with the biotite in the pegmatite. This behavior is contrary to expectation, and is caused by the different extent of dehydroxylation of the two samples (along with their different X_{Mg}).

The present work allows discussion of another problem highlighted by Muñoz (1984), i.e., the low- T hydrothermal overprint on halogen contents, which affects pristine compositions without producing textural evidence. As shown above, this phenomenon is of greatest importance in slowly cooled HT rocks, and implies that in most granulites and migmatites, the halogen (and hydrogen as well) contents of micas are probably not primary. It also implies that the exchange temperature to be used in the calculation of relative halogen fugacities should not be the peak value of biotite crystallization, but a lower value, difficult to constrain. Results reported in Table 3 were obtained for all biotites using an arbitrary T of 800 °C, corresponding to the minimum T estimated from feldspar thermometry. However, this is likely to be a meaningful value only for the biotite from the pegmatite dike. Using a value of 500 °C—assumed as the closure T of retrograde exchange—in the analyses from the host granulite, produces dramatic effects, such as increasing of 0.9 and 0.5 log units the ratios $\log[(f_{H_2O})/(f_{HF})]_{\text{fluid}}$ and $\log[(f_{H_2O})/(f_{Cl})]_{\text{fluid}}$, respectively.

Finally, despite all the sources of error and uncertainty in the application of the approach, we can confidently conclude that the crystallization of biotite in the pegmatite dike and in the

host granulite occurred, although at very similar temperatures, in the presence of fluids with markedly different composition, and that in the pegmatite the relative fugacities of F and Cl were significantly higher.

ACKNOWLEDGMENTS

Our interest for biotite in high-grade rocks has been stimulated by numerous discussions with Charlie Guidotti, who was of great help and to whom we dedicate this paper, hoping that he would agree with our conclusions. We thank Raul Carampin and Filippo Olmi (EMP), John Craven (SIMS), and Aurelio Giaretta (C-H-N) for their patience during analytical sessions, Leonardo Tauro for careful sample preparation and Sandra Primor for SEM image manipulation. Thanks to Ross Angel for hinting the possibility of retrograde diffusion of H, to Antonio García-Casco and Franco Sassi for critical reading of the manuscript, and to Jack Cheney and Dave Waters for their reviews. Thanks to Darby Dyar, Ed Grew, Darrell Henry, and Franco Sassi for their efforts in organising the GSA symposium and editing this volume in honor of Charlie. Financial support from Italian MIUR (PRIN 2005-047810) and C.N.R. (Euromargins ESF Eurocore) to B.C., from the Ministry of Education, Culture, Sports, Science and Technology, Japan (no.18740319) to S.K.

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MANUSCRIPT RECEIVED JANUARY 22, 2007

MANUSCRIPT ACCEPTED JULY 24, 2007

MANUSCRIPT HANDLED BY DARBY DYAR