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

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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 > 800–850 °C and P = 5 ± 1 kbar.

The full analyses were normalized on the basis of [O12–(x+y+z)(OH)xClyFz]. 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 XMg = 0.49 and Fe3+/Fetot ≤ 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 XMg 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 XMg 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, XMg, 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 Ti4++2O2– = (Fe,Mg)2++2OH– and the “fluorination” Ti4++2O2– = (Fe,Mg)2++2F–. 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
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 (i.e., ~530 Ma; Shabeer et al. 2005; Santosh et al. 2006). This terrain is characterized by the occurrence of extensive garnet + biotite + sillimanite + graphite ± 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 ~950°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, magmatic rocks consisting of Bt-Grt gneiss, incipient charnockites, and Bt-Grt-Sil ± 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 subrounded, in plates up to 2 cm thick. The country rocks are fine- to medium-grained, with a marked magmatic 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 Grt + melt ± Kfs = Bt + Sil + 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 × 3 × 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 feldspar 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), MnTiO3 (Mn, Ti), chromite (Cr), hematite (Fe), barite (Ba), apatite (F), and vanadinite (CI). 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 × 30 µm each, so that an overall surface of up to 200 × 180 µm2 was analyzed and the bulk composition

![Diagram](https://example.com/diagram.png)

**Figure 1.** Geological Sketch map of KKB in southern India, with location of the outcrop of Irinjayam, where the studied rocks were collected.
Lithium was analyzed on one mica separate by atomic absorption spectroscopy (AAS) and is 292 ppm, equivalent to 627 ppm Li₂O.

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% H₂O) 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 ~5·10⁻⁶ Torr prior to analysis. ¹H and ³¹Si were analyzed using a 10 kV, 10 nA, O-primary beam. The secondary ions were analyzed using an offset of 120 ± 20 eV. The H₂O 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 ±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 C₈H₉NO 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 Ab₂₈An₂½ Kfs₆₉. The exsolved plagioclase lamellae are oligoclase—Ab₇₇An₂₂Kfs₄ and Ab₈₀An₁₆Kfs₄ in vein and host, respectively, whereas the host K-feldspar is Ab₁₅–₁₆An₁Kfs₈₃–₈₄. 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 Al₉₀₂Pₐ₉₃5 [Xₘ₉ = 0.36, where Xₘ₉ = Mg/(Mg+Fe)] throughout most of the crystals, and by small areas, in the vicinity of biotite, where Mg decreases and Fe increases to Al₉₅₂Pₐ₉₂ (Xₘ₉ = 0.22) at the outermost rims.
Rimward decrease of Mg is absent where garnet is in contact with phases other than biotite.

**Biotite**

**H$_2$O contents.** The H contents measured by SIMS, converted to H$_2$O, are reported in Table 2. In the two biotite crystals selected from the pegmatite, H$_2$O is 1.64 ± 0.07 and 1.67 ± 0.12 wt%. Comparison with analysis of NBS303 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.

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 Ti$_2$O$_3$ (5.6 wt%), F (1.9 wt%), and Cl (1.2 wt%), and low in Al$_2$O$_3$ (14.7 wt%). The anhydrous total is very high (>98%) for a “common” EMP analysis of biotite, and the totals with added H$_2$O (99.1–99.3 wt%) suggest that the quality of analyses is good. Calculated average atomic proportions give can uncertainties about cation/anion charges and cation numbers be resolved (see discussion in Waters and Charnley 2002).

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

**Major-element composition**

Table 3 reports the complete chemical analyses and recalculated formulae of biotites made on the basis of [O$_{12-3x+y+z}$ (OH)$_x$Cl$_y$F$_z$] and integrated using the major element, H, and Fe$^{3+}$/Fe$_{tot}$ contents determined by EMP, SIMS, and Mössbauer, respectively. In fact, only with measured values of H and Fe$^{3+}$ can uncertainties about cation/anion charges and cation numbers be resolved (see discussion in Waters and Charnley 2002).

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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\(_{iv}\) (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 \(\mu\)m of crystals at the contact with garnet. Along with the rimward increase of \(X_{Mg}\) 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 Kohl 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\(^{IV}\) + Si = 2A1) does not account for an average of 0.13 \(^{IV}\)Al atoms (Table 3). Since these biotites are Fe\(^{III}\)-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 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
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

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**Table 2.** Hydrogen contents, converted to H2O values, in biotite from the pegmatite, the host granulite, and from biotite standard NB530, obtained by C-H-N elemental analysis and by SIMS

<table>
<thead>
<tr>
<th>Technique</th>
<th>Pegmatite-1</th>
<th>Pegmatite-2</th>
<th>Host Granulite</th>
<th>NB5 30 (3.51 wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H-N</td>
<td>1.59 (5)</td>
<td>1.64 (10)</td>
<td>3.58 (2)</td>
<td>3.57 (5)</td>
</tr>
<tr>
<td>SIMS</td>
<td>1.47 (5)</td>
<td>1.67 (10)</td>
<td>0.01</td>
<td>0.13</td>
</tr>
<tr>
<td>SIMS</td>
<td>0.07</td>
<td>0.12</td>
<td>2.56 (24)</td>
<td>3.50 (10)</td>
</tr>
</tbody>
</table>

**Table 3.** Chemical composition of biotite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pegmatite</th>
<th>Host Granulite</th>
<th>All data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Si</strong></td>
<td>2.814</td>
<td>2.802</td>
<td></td>
</tr>
<tr>
<td><strong>MgO</strong></td>
<td>10.06</td>
<td>10.08</td>
<td></td>
</tr>
<tr>
<td><strong>FeO</strong></td>
<td>19.32</td>
<td>19.25</td>
<td></td>
</tr>
<tr>
<td><strong>CaO</strong></td>
<td>0.001</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td><strong>K2O</strong></td>
<td>0.038</td>
<td>0.038</td>
<td></td>
</tr>
<tr>
<td><strong>Li2O</strong></td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>H2O</strong></td>
<td>7.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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. 

* Analyzed by AAS. 
† Not measured in this crystal, and assumed as the average value.
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

**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
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 granulate 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 granulate. Another consequence is that the seemingly isothermal trend at $T > 800 \degree C$ 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 $\degree C$ (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.

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; Pátiño Douce et al. 1993) and $X_{Mg}$ increases, both in Grt-Bt-Sil-melt (e.g., Pátiño 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$_4$ 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 $\degree C$ at $T > 800 \degree C$) 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 $X_{\text{Mg}}$, 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 $X_{\text{Mg}}$ (compare also Usuki 2002), in the biotites from the host granulite the $X_{\text{Mg}}$ 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 $X_{\text{Mg}}$ 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-temperature 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-$X_{\text{Mg}}$ 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 $X_{\text{Mg}}$. In none of these studies, however, had F and H been quantified and their variations correlated with those of Ti and $X_{\text{Mg}}$.

The trends in Figure 12 can be also interpreted on the basis of the already mentioned universal rules, namely the “inverse Ti-$X_{\text{Mg}}$ 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 $X_{\text{Mg}}$) 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 $X_{\text{Mg}}$ 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 $X_{\text{Mg}}$ (due to the universal inverse Ti-$X_{\text{Mg}}$ 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 $X_{\text{Mg}}$) 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-$X_{\text{Mg}}$ 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, $^{3}$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...
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) Ti⁴⁺ + 2O₂⁻ = (Mg,Fe)²⁺ + 2OH⁻ and the “fluorination” Ti⁴⁺ +2O₂⁻ = (Mg,Fe)²⁺ + 2F⁻. 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 Ti + Fe + 2O is replaced by 2Mg + OH + F.

Moreover, as seen in Figure 7, excess IVAl 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 Mg₂⁺Fe⁻¹⁻¹Ti⁻¹⁻¹, 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.

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 oxysubstitution 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 (H₂O, 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 13](image-url)  
**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).

![Figure 14](image-url)  
**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 CI for possible halogen-hydroxyl exchange during metamorphism. Owing to the availability of H, F, and CI data, the method of Muñoz (1984, 1992) has been utilized to infer the relative fugacities of H2O 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 Xf \[ F/(OH + F + CI) \] is 0.31–0.32. Had H not been measured, and the (OH + F + CI = 2) normalization scheme been used, a largely underestimated and erroneous Xf of 0.22–0.23 would have been obtained. Such an error propagates in the calculations of the fluorine intercept value [IV(F), 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\( \text{H}_2\text{O} \)/f\( \text{HF} \)] 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(f\( \text{OH} \))/f(f\( \text{HF} \))] 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 granulate have similar Xf 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 Xf).

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 this phenomenon is of greatest importance in slowly cooled HT conditions 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 exchange temperature to be considered, that is 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 thermometer. 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 granulate, produces dramatic effects, such as increasing of 0.9 and 0.5 log units the ratios log [f(f\( \text{OH} \))/f(f\( \text{HF} \))] and log [f(f\( \text{OH} \))/f(f\( \text{Cl} \))] fluids, 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 granulate 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.

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