

Hydrogen deficiency in Ti-rich biotite from anatectic metapelites (El Joyazo, SE Spain): Crystal-chemical aspects and implications for high-temperature petrogenesis

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ABSTRACT

Titanium-rich biotites from graphite-bearing metapelitic xenoliths, equilibrated at ca. 850 °C and 7 kbar in the presence of a granitic melt, have been studied through complete chemical analysis and single-crystal XRD refinements. The chemical study combines EMP analyses, hydrogen determination by both SIMS and C-H-N elemental analysis, and Mössbauer spectroscopy. Biotites in the analyzed xenoliths have TiO₂ contents ranging from 4.5 to 4.9 wt% and an X_{Fe} of 0.67. Their F and Cl contents are negligible, and Fe³⁺/Fe_{tot} ranges from 10 to 16%. The H₂O content of the biotites ranges from 2.4 to 2.8 wt%, and a small fraction of H is accommodated in the lattice as NH₄. Based on these full chemical analyses, the calculated OH occupancy is 1.26 to 1.30 groups per formula unit, more than one third less than the stoichiometric value.

The entrance of Ti in the octahedral site of biotite is consistent with the Ti-oxy exchange, whereas Ti-Tschermak or Ti-vacancy substitutions play a very minor role. The Fe³⁺-oxy exchange cannot account for the observed OH deficiency.

From single-crystal XRD, biotites belong to the 1M polytype and contain variable amounts of stacking faults. The *c* cell parameter, K-O4 and <K-O>_{outer} distances provide an independent estimate of the OH content, which agrees with SIMS determinations. The linear relationship between ⁵¹Ti⁴⁺ and the bond-length distortion of the *cis*-M2 octahedron reveals the partitioning of Ti⁴⁺ in M2, and the Ti⁴⁺ off-center shift toward O4 supports the occurrence of the Ti-oxy exchange. The ordering of Ti⁴⁺ over two non-equivalent M2 sites, which would be favored energetically, is in agreement with the evidence for a third octahedral site suggested by Mössbauer spectroscopy. The biotite dehydrogenation combined with the partitioning of Ti⁴⁺ in M2 and the low thermal expansion of Ti⁴⁺-containing octahedra, are the keys to understanding the thermal stabilization of Ti substitution in biotites.

INTRODUCTION

Biotite is the primary H₂O reservoir in high-temperature crustal rocks such as metapelites and metagreywackes (e.g., Grant 1985; Stevens et al. 1997), and is the essential reactant for the formation of S-type granitic melts by fluid absent (“dehydration”) melting at low to medium pressures (e.g., Brown and Fyfe 1970; Vielzeuf and Holloway 1988). Thus, full understanding of the crystal-chemical changes of biotite as a function of pressure, temperature, and other physical-chemical variables is required for a correct modeling of magma generation and mass-transfer processes in the upper crust. Improving knowledge of biotite crystal chemistry can also help to refine the models of biotite thermodynamic properties used in numerical simulations.

In metapelites, biotite shows significant departures from the stoichiometric Annite-Phlogopite (Ann-Phl) binary solution, K(Fe, Mg)₃AlSi₃O₁₀(OH)₂. Some of them, such as the Tschermak exchange [(Fe, Mg)SiAl₂] occur within the model pelitic system KFMASH, i.e., within the “ideal biotite plane”

(Guidotti 1984); many others involve non-KFMASH components and site vacancies. A comprehensive discussion of the crystal-chemical variations and exchange mechanisms in metamorphic biotites can be found in Dymek (1983), Guidotti (1984), Dyar et al. (1991), and Henry and Guidotti (2002). In this paper, we focus on the substitution of Ti in biotite, which is one of the most important, especially because it shows a clear dependence upon temperature (e.g., Guidotti et al. 1977; Patiño Douce et al. 1993).

Chemical analyses from natural metapelites and experimental runs show that at temperatures approaching melting, biotite may contain up to 6 wt% TiO₂ (e.g., Stevens et al. 1997; Cesare 2000). Comparison of the melting behavior of biotite in Ti-free and Ti-bearing experiments (Patiño Douce and Johnston 1991; Stevens et al. 1997), has shown that the presence of Ti increases the upper limit of biotite stability of up to 80 °C, reinforcing the idea that Ti may exert a role on the thermal stabilization of biotite (Dymek 1983; Guidotti 1984).

The possible exchange mechanisms by which Ti enters the biotite lattice have been discussed in detail (review in Waters and Charnley 2002). All of them consider Ti in octahedral coordination, and the most important are:

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Unlike the first two exchanges, with the Ti-oxy exchange (3) the substitution of one divalent cation by Ti in the octahedral site is accompanied by the loss of H from the (OH) groups ["dehydrogenation" or "deprotonation," Dyar et al. (1993)]. The primary consequence of exchange (3) is that the H content of biotite is deficient with respect to stoichiometry.

The missing knowledge of the H content, not obtained by standard EMP analysis, typically hampers the assessment of the operative Ti-substitution mechanism. Thus, the Ti-oxy substitution has been neglected in most works simply because it could not be verified. As in the conclusions of Dymek (1983) and Patiño Douce et al. (1993), Ti is generally modeled by the Ti-vacancy substitution (2), but in none of these studies was H analyzed directly. Dymek (1983), however, noted that his data were fully consistent also with a Ti-oxy substitution, and that the preference for the Ti-vacancy is tentative. Patiño Douce et al. (1993) proposed the Ti-vacancy exchange on the basis of a $TiFe_{-2}$ correlation in biotites of his experimental runs. However, consideration of the whole octahedral cation distribution of his biotites also shows a good $MgFe_{-1}$ correlation, and a poor negative correlation between Ti and total octahedral occupancy. Thus, the Ti-vacancy exchange is not demonstrated by the data of Patiño Douce et al. (1993), but rather derives from the assumption that Ti-oxy components are not present because they cannot be constrained.

With the growing use of ion probes, analysis of H has become easier, and quantitative data show that magmatic biotites are characterized by marked H deficiencies, which correlate with octahedral cations such as Fe^{3+} , Cr, Ti, and Al (Virgo and Popp 2000; Richter et al. 2002). These findings indicate that Fe- and Ti-oxy substitutions indeed play a major role in magmatic phlogopites, as also confirmed by crystal-structure analysis (Cruciani and Zanazzi 1994).

Concerning metamorphic biotites, Dyar et al. (1991, 1993) provided clear evidence of the non-stoichiometry of H, of its negative correlation with metamorphic grade, and of the absence of Fe-oxy components. Their data, obtained from lower-greenschist to upper-amphibolite facies, graphite-ilmenite-bearing metapelites from NW Maine (Guidotti 1984), did not consider Ti-rich biotite from granulite-facies rocks. Analysis of H in Ti-rich (5.4 wt% TiO_2) metamorphic biotite coexisting with ilmenite and magnetite is provided by Bohlen et al. (1980) and again indicates a strong H deficiency that can be modeled primarily by a Ti-oxy substitution.

Although these are probably the most recent works on metamorphic biotite, and are based on complete analytical data sets, their results are almost forgotten, and the H (or H_2O) content of biotite is still considered stoichiometric for most purposes, even those in which non-stoichiometry would determine significant consequences: experimental studies of melt production (e.g., Pickering and Johnston 1998), mass-balance calculations (e.g., Kriegsman 2001a), fluid-rock interactions

(Harlov and Förster 2002) and thermodynamic simulations (e.g., White et al. 2000). One exception is the recent work of Waters and Charnley (2002), where the deprotonation and Ti-oxy substitution have been constrained by statistical treatment of EMP data.

With the present work we have studied some well-characterized, Ti-rich metamorphic biotites close to their melting conditions. Complete chemical analyses of the biotites from three samples have been obtained by combining EMP and Mössbauer spectroscopy, and by measuring hydrogen by both SIMS and C-H-N elemental analyzer. In addition, single-crystal XRD refinements were obtained. We extend the observations of Guidotti (1984), made on a suite of samples with <2.5 wt% TiO_2 , with new data on partially melted rocks in which biotite has TiO_2 in the range 4.5–5.0 wt%. The rationale behind this research is straightforward: to verify whether the H deficiency and its correlation with Ti are also present in high-grade rocks and, if so, to discuss its petrologic consequences. In fact, if the Ti-oxy exchange is active in metamorphic biotites, its role will be maximized at the highest Ti concentrations, i.e., at high-temperature, granulite-facies conditions. With this research, we also add detailed constraints on the crystal chemistry of biotite from high-grade metapelites.

SAMPLE PETROGRAPHY

In order to study the behavior of natural Ti-rich biotites at high-grade metamorphic conditions, the problems related to post-peak thermal and mechanical evolution should be minimized. It is well known, in fact, that the high-grade chemistry of minerals can be easily changed by retrograde inter- and intracrystalline diffusion (e.g., Ganguly 1991), that the peak assemblage can be modified by retrograde or back-reactions (Kriegsman 2001b), and that at the same time the crystal lattice can be modified by strain and/or recrystallization occurring after growth or equilibration at the metamorphic climax (e.g., Noe and Veblen 1999).

Unfortunately, owing to the slow speed of geologic processes, most granulite and migmatite complexes have suffered to a variable extent the above reequilibration processes, and rocks from these areas are not ideal for the aim of the present research. Thus, we have chosen the Bt-Grt-Sil-bearing restitic xenoliths of El Joyazo (SE Spain). Due to fast cooling and decompression through magma uprise and volcanic eruption, these rocks have maintained the mineralogical and chemical conditions at which they formed. The petrography of these rocks was described by Cesare et al. (1997): they are restites from extensive partial melting and syndeformational extraction of leucogranitic melt, which took place at 850 ± 50 °C and ca. 7 kbar, corresponding to the depth of the Lower Miocene paleo-Moho (Cesare and Gomez-Pugnaire 2001). The xenoliths show no signs of post-peak retrograde effects, and contain abundant biotite that equilibrated close to its upper thermal stability in equilibrium with a melt phase. These biotites represent the ideal extension, at very high metamorphic grades and Ti contents, of the sample suite analyzed by Guidotti et al. (1977, 1988) and Dyar (1990).

Three xenoliths (HO20, HO30, and HO50), sharing similar microstructures, phase assemblages, and chemistries, were chosen as representative of biotite at thermal conditions just be-

low its breakdown. The xenoliths contain plagioclase (An_{30-35}), biotite, garnet ($X_{Mg} = 0.15$), fibrolite, graphite, and fresh rhyolitic glass, with accessory cordierite ($X_{Mg} = 0.5$) only in HO50. They have a compositional layering characterized by alternating Bt-Sil-rich and Pl-rich layers, and a fine to medium grain size (0.5–2 mm), with garnet porphyroblasts up to 5 mm in diameter. Biotite forms mica-rich layers or elongate aggregates with decussate texture, where it occurs as undeformed crystals up to 2 mm (averaging 0.5) in length, with straight grain boundaries. Unlike other xenoliths in the same volcanic edifice (Cesare 2000), the selected samples do not show evidence of the incongruent melting of biotite to hercynitic spinel.

Biotite crystals often contain inclusions (Figs. 1 and 2¹), whose amount and distribution vary among the microstructural sites. In order of abundance they are graphite, fibrolite, and melt. Inclusions need to be taken into account in the interpretation and discussion of analytical data, as they may affect the results of bulk analyses, in particular the C (contamination by graphite) and H (contamination by melt) concentrations. In this regard it is worth noting that inclusions are scarce ($<<1\%$) in HO20 and HO30, but are larger and more abundant in HO50.

Graphite is present in all the xenoliths, but only HO50 contains ilmenite. Thus the Ti concentration of HO20 and HO30 biotites should not be considered a maximum for the P - T conditions of equilibration (Guidotti 1984). Although the xenoliths are devoid of quartz, we assume that the SiO_2 -rich melt exerts the same effect on Si-saturation of biotite.

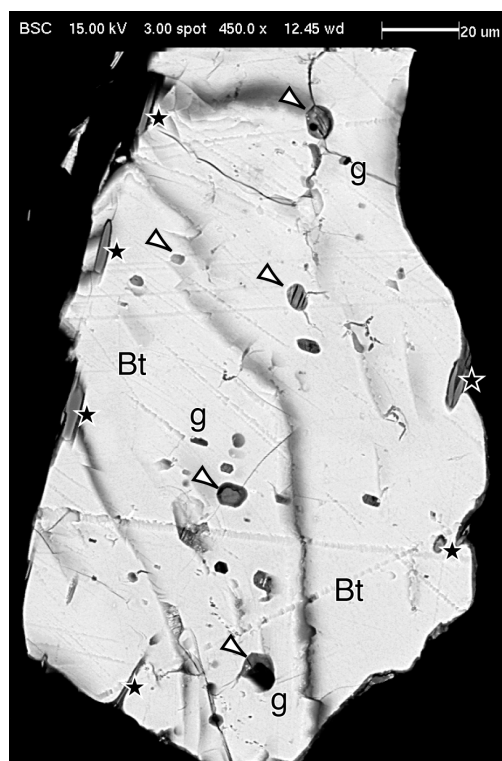


FIGURE 1. Back-scattered electron image of HO30 biotite from separates used in this study. Biotite contains small ($<10\ \mu m$) inclusions of glass (arrows), acicular sillimanite (stars) and graphite (g).

ANALYTICAL TECHNIQUES

Biotite concentrates were obtained by initial crushing of the rocks followed by alternating passes through the Frantz isodynamic separator and an agate mortar mill, to reach a final grain size of 100–160 μm . The purity of the concentrates was estimated as $>99\%$ by optical microscopy. Overall, the grinding and milling time did not exceed 5 minutes, so that possible oxidation induced by sample preparation can be considered negligible (Dyar and Burns 1986). Aliquots of the concentrates were then used for the various chemical determinations.

Major-element compositions were obtained on biotite grains from the concentrates, mounted in araldite, with a JEOL JXA-8600 electron microprobe (EMP) at CNR-IGG, Florence. Analytical conditions were 15 kV accelerating voltage and 10 nA beam current, with 15 s peak counting times for all elements, except F and Cl (40 s) and Na, analyzed for 10 s as the first element. The standards used were olivine (Mg), plagioclase (Al), albite (Si, Na), sanidine (K), diopside (Ca), ilmenite (Ti, Fe), chromite (Cr), fluorite (F), and apatite (Cl), and data correction was performed using a Bence-Albee routine. The beam was generally expanded to a size of 5–10 μm .

Analysis of H by SIMS was performed on polished thin sections using a Cameca ims-4f ion microprobe at the Department of Geology and Geophysics, University of Edinburgh. The sections and a standard (NBS30 biotite) were cleaned, coated with Au, and then stored in the ion microprobe for 3 days at a vacuum of $\sim 5 \times 10^{-8}$ Torr prior to analysis. ^1H and ^{30}Si were analyzed using a 10 kV, 20 nA, primary O 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 error in the H content is within ca. 10%. Possible contamination by biotite inclusions was minimized by careful selection of analysis sites using back-scattered electron imaging.

Bulk C, H, and N analysis of biotite concentrates was performed with the EA 1108 elemental analyzer of CE Instruments at CNR-IGG, Padova. Sample size was ca. 20 mg, and the instrument was calibrated with standard Acetanilide (C_8H_9NO).

Mössbauer spectra were acquired at room temperature using a constant acceleration spectrometer with symmetrical waveform and a ^{57}Co source (nominal strength 1.4 MBq) in a Rh matrix. The finely ground powder was suspended in vaseline, wrapped in thin plastic foil, and inserted in the γ -ray beam. In order to improve the absorption line resolution, the thickness of the Mössbauer absorbers was optimized at about 2.5 mg/cm² Fe, so that thickness corrections were not necessary. As expected for sheet silicates, the spectra contained clearly asymmetrical doublets. After recollection with the nor-

¹For a copy of Figures 2, 3, 7, 9, and 12 and Tables 2, 6, 7, 9, 10, 11, 12, and 13, document item AM-03-026, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

mal to the sample at an angle of 54.7° with the γ -ray direction, the so-called “magic angle,” the asymmetry decreased approaching the value of 1. Only the results of these last spectra are reported and discussed. Spectra were fitted either with pure Lorentzian line-shapes or by using a quadrupole splitting distribution according to Voigt-based methods (QSD), utilizing in both cases the Recoil program of Rancourt and Ping (1991). The former procedure considered two or three asymmetric doublets due to Fe^{2+} and two symmetric due to Fe^{3+} ; this last constraint was introduced because of the strong overlap of the low-velocity components of all the four doublets. The latter approach used a QSD to take into account all the absorption area attributable to Fe^{2+} and one or two for that due to Fe^{3+} . In both cases, the distributions were fitted to gaussian lines with different areas and widths. Values of δ at the maxima of the distribution curves were calculated according to the equation: $\delta = \delta_0 + \delta_1 \Delta E_Q$.

X-ray diffraction data were collected from single crystals, directly hand-picked from crushed rocks, using a Nonius Kappa four-circle diffractometer equipped with a CCD area detector and graphite-monochromatized $\text{MoK}\alpha$ radiation (55 kV and 30 mA operating conditions) at the University of Ferrara. Several sets of frames (621×576 pixels, binned mode) were recorded with a crystal-to-detector distance of 25 mm and a strategy optimized by the Nonius COLLECT program suite (Nonius 1998). A set of 10 frames was used for the initial cell determination, each frame with 1° phi rotation and 120 s exposure time. The complete data collection was accomplished by several ϕ - and ω -scans, each frame measured with 2° rotation width and 140 to 160 s exposure time. The whole Ewald sphere ($\pm h, \pm k, \pm l$) was recorded in the 2θ ranges 4 – 55° , 4 – 60° , 4 – 64° for HO20, HO30 and HO50, respectively. Reflection intensities were extracted and corrected for Lorentz-polarization using the DENZO-SMN program (Nonius 1998). During the frame-to-frame scaling and outlier rejection procedure, the high redundancy of data provides a kind of semi-empirical absorption correction. Least-squares refinements were carried out using the SHELXL-97 program (Sheldrick 1998). Starting atomic coordinates in the $C2/m$ space group were taken from sample no. 1 in Cruciani and Zanazzi (1994). Neutral atomic scattering factors were taken from the *International Tables for Crystallography*, vol. C (Wilson 1992). The electron density of the octahedral sites was fitted with the Fe vs. Mg scattering curves; a combination of 75% Si and 25% Al was used for tetrahedral sites. The refined parameters were scale factors, atomic positions, cation occupancy factors, and atomic displacement factors. The latter factors were initially assigned as isotropic, then were allowed to vary anisotropically. Occupancy factors and displacement parameters were refined in alternate cycles to avoid correlation.

RESULTS

Hydrogen content

Bulk H, N, and C contents of the biotite concentrates are reported in Table 1. Concerning the possible effects of inclusions on the H contents of biotite, it should be noted that the

inclusions consist of both anhydrous (graphite and sillimanite) and hydrous phases (glass with ca. 5–6 wt% H_2O ; Cesare et al. 1997). Owing to their counteracting contributions on H contents, and to their low modal abundance ($<1\%$), we conclude that their effect is negligible ($<1\%$ relative). Hydrogen values have been recalculated into H_2O in two ways: directly and by subtracting the H fraction that would combine with N to form NH_4^+ . The second option, noted as H_2O^* , assumes that all N is stored in the lattice of biotite as NH_4^+ groups substituting for K^+ in the A-site (e.g., Sadofsky and Bebout 2000). As N contents of HO20 and HO50 are significant (0.5–0.7 wt%), the effect of NH_4^+ subtraction results in a ca. 5% relative decrease of the calculated H_2O . Bulk H_2O contents are 2.51 wt% for HO20 (2.37 after NH_4^+ correction), 2.45 wt% HO30 (2.44 after NH_4^+ correction), and 2.88 wt% for HO50 (2.71 after NH_4^+ correction). The appreciable C contents (0.17–0.29 wt%) are due to the fine-grained dispersions of graphite. In addition to the H_2O values, Table 1 also lists calculated NH_4 contents of the micas. The sum of calculated H_2O^* and NH_4 ranges from 2.4 to 2.8 wt%, and gives a measure of the structurally bound volatiles not analyzed by EMP.

Hydrogen contents obtained by SIMS analysis have been converted to H_2O values and are reported in Tables 2¹ and 3. Data from HO20 and HO30 cluster in a narrow range (averages 2.56 and 2.52 wt% H_2O , respectively) with the exception of a single data point (3.64 wt%), assumed to reflect contamination by a glass inclusion and omitted from the average calculation. The H_2O contents of HO50 are spread over a wider range, from 2.24 to 3.34 wt% (average 2.72), and display a marked bimodal distribution (partial averages 2.50 and 3.09) that appears to record H_2O intracrystalline inhomogeneities. The H_2O^* values, corrected for H in NH_4^+ , are 2.49 wt% in HO20, 2.51 wt% in HO30 and 2.63 wt% (lower average 2.41 wt% and higher average 3.00 wt%) in HO50.

The average results of bulk elemental analysis and point

TABLE 1. Bulk hydrogen, nitrogen, and carbon contents (in wt%) of the three biotite concentrates, as determined by C-H-N elemental analysis

Sample	Elemental Analysis			Recalculation			
	H	N	C	H_2O	NH_4	H_2O^*	Sum†
HO 20	0.28	0.05	0.17	2.51	0.07	2.37	2.44
HO 30	0.27	0.01	0.20	2.45	0.01	2.44	2.44
HO 50	0.32	0.07	0.29	2.88	0.09	2.71	2.79

Notes: Recalculation includes direct conversion of H into H_2O and N into NH_4 .

* H_2O content after subtraction of H in NH_4 .

† Sum of H_2O^* and NH_4 .

TABLE 3. Minimum, maximum, average and standard deviation of H_2O concentrations recalculated from SIMS measurement of hydrogen

Sample	n. analyses	H converted to H_2O				H_2O^*
		Min	Max	Average	Std. Dev.	
HO20	15	2.28	2.86	2.56	0.15	2.49
HO30	11	2.34	2.70	2.52	0.10	2.51
HO50	19	2.24	3.34	2.72	0.34	2.63

Note: Also calculated is the H_2O^* value, obtained by subtracting the H contribution to NH_4 as from C-H-N analyses.

SIMS analysis show a remarkable agreement, overlapping within less than 5% relative uncertainty (Fig. 3¹).

Mössbauer spectroscopy

As the Mössbauer parameters of the three samples are very similar (Tables 4, 5, 6¹, and 7¹), only the representative spectra of HO20 are reported (Figs. 4 and 5). All spectra are characterized by two main, asymmetric absorptions centered at about -0.2 and 2.3 mm/s, due to two different sites containing Fe^{2+} . A small residual absorption is centered around 1.0 mm/s, and corresponds to the high-energy lines of two doublets due to Fe^{3+} species, the low-energy lines hidden inside the Fe^{2+} absorption. No shoulder is evident around 0.4 mm/s, suggesting the absence of tetrahedral Fe^{3+} (Rancourt et al. 1992). Introducing such a component did not improve results, thus confirming this conclusion. The fit of the spectra allowing the areas of the high- and low-velocity absorptions of Fe^{2+} components to vary independently slightly improved the χ^2 values, which is evidence of some residual preferred orientation in spite of the “magic angle” arrangement. The same procedure for the two Fe^{3+} doublets did not give good results, probably because of the strong overlap of the low-velocity lines.

The fitting procedure that utilizes Lorentzian line shapes gives well-defined components with parameters that are quite independent of the starting values for all samples. The introduction of constraints on the linewidths, such as forcing those of Fe^{2+} and Fe^{3+} to be equal to each other, or on the A/A_+ ratio, results in a substantial increase in χ^2 . Spectra were first fitted to two Lorentzian doublets for both Fe^{2+} and Fe^{3+} , and the calculated parameters are in agreement with those reported in the literature for similar biotites (Dyar 1990). The stability of the results, even in the presence of different input values, lends credibility to both the values and the attributions (model c).

The most serious objections to this procedure are the residual errors, unacceptable in HO30, mainly due to the misfit of the high-velocity component of the Fe^{2+} absorption. To minimize this problem, a third Fe^{2+} component was introduced, im-

proving the fitting of this absorption line and the χ^2 value (model b). It is obvious that, due to the total overlap of the Fe^{2+} components, not much physical meaning can be attributed to each of the sites (Rancourt 1998; Redhammer 1998). In fact, the hyperfine parameters, particularly the quadrupole splitting, are the consequence of the reciprocal positions of the OH^- groups in the first coordination sphere and of the type of cations in the

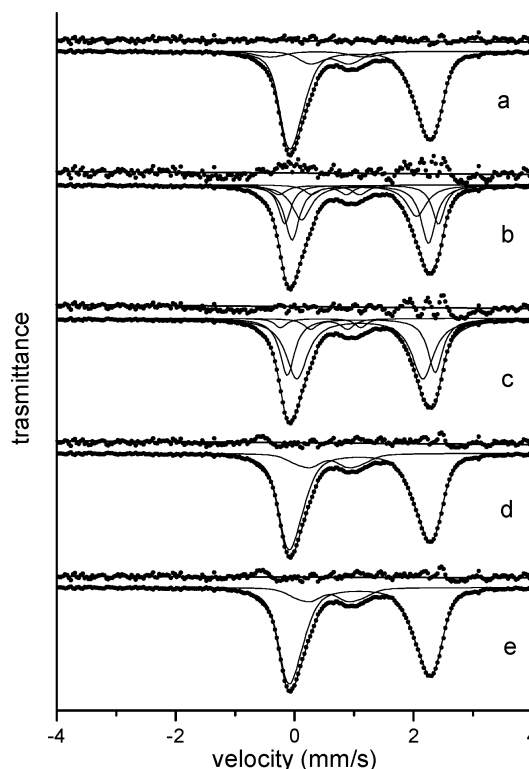


FIGURE 4. Mössbauer spectra at room temperature and residuals multiplied by 3 for sample HO20 according to the fitting models a to e from top to bottom.

TABLE 4. Mössbauer parameters for sample HO20 obtained by Lorentzian line profiles according to models b and c

χ^2		Fe^{2+}					Fe^{3+}				
		δ (mm/s)	ΔE_0 (mm/s)	Γ (mm/s)	A (%)	A/A _*	δ (mm/s)	ΔE_0 (mm/s)	Γ (mm/s)	A (%)	A/A _*
HO20 b	1.155	1.128(5)	2.59(2)	0.24(2)	22(5)	0.99(9)	0.58(1)	0.58(5)	0.28(4)	6(2)	1*
		1.106(8)	2.29(2)	0.30(4)	36(8)	0.94(8)	0.41(2)	1.36(6)	0.32(6)	7(2)	1*
		1.10(1)	1.93(4)	0.40(2)	29(7)	1.05(9)					
HO20 c	2.644	1.123(3)	2.49(1)	0.30(9)	34(5)	1.05(9)	0.58(1)	0.62(3)	0.28(4)	6(1)	1*
		1.099(6)	2.12(2)	0.43(9)	55(5)	1.00(6)	0.44(1)	1.35(3)	0.24(4)	4(1)	1*

* Value constrained during the fitting procedure.

TABLE 5. Mössbauer parameters for sample HO20 obtained by quadrupole splitting distribution method according to models a, d, and e

	χ^2	Γ	Fe^{2+}										Fe^{3+}									
			δ_0	δ_1	A/A_+	ΔE_0	σ	P	ΔE_0	σ	P	ΔE_0	σ	P	δ_0	δ_1	ΔE_0	σ	P	ΔE_0	σ	P
		(mm/s)	(mm/s)	(mm/s)	(mm/s)		(%)	(mm/s)		(%)	(mm/s)		(%)	(mm/s)	(mm/s)	(mm/s)		(%)	(mm/s)		(%)	
HO20 a	0.702	0.097	0.993	0.0472	0.97	2.463	0.225	44	2.07	0.33	40			0.598	0*	0.645	0.31	10				
														0.386	0*	1.60	0.41	6				
HO20 d	1.081	0.125	1.003	0.0403	0.97	2.467	0.196	47	2.08	0.30	39			0.583	0*	0.60	0.22	8	1.12	0.24	7	
HO20 e	0.583	0.107	0.980	0.0523	0.98	2.641	0.11	12	2.33	0.22	56	1.82	0.23	16	0.595	0*	0.644	0.29	11			
														0.389	0*	1.62	0.29					

* Value constrained during the fitting procedure.

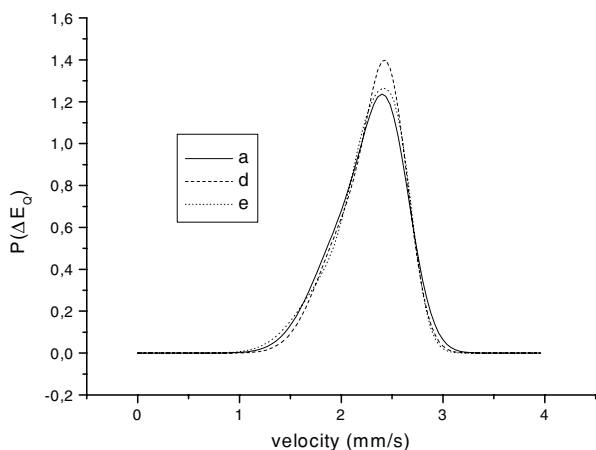


FIGURE 5. Quadrupole splitting distributions for the Fe^{2+} site in sample HO20, according to models a, d, and e.

second one. As the two contributions cannot be separated, the result is an algebraic addition of two parameters that in turn influence each other. It follows that the situation seen by the γ -rays is continuously varying from one extreme to the other, concentrating around two or three most probable structures stabilized by an energy minimum. Because it seemed impossible to hypothesize the existence of well-defined Fe^{2+} sites with the same crystallographic parameters and chemical environment in the first and the second coordination sphere, the logical approach was to fit the spectra with QSDs (Rancourt and Ping 1991; Rancourt 1994). Mathematically acceptable results have been obtained only in cases that strictly follow those obtained with the Lorentzian site analyses reported above. Both the Fe^{2+} and Fe^{3+} contributions have been fitted as QSDs, but in the case of Fe^{3+} , only the fits with δ_1 constrained to 0, i.e., keeping the isomer shift constant, were acceptable. The approach considered two (models a and d) or three components (model e) for the Fe^{2+} site and either one site with two components (model d) or two sites with one component for Fe^{3+} (models a and e). The results are consistently dependent on the input parameters, especially the relative areas and the linewidths, obviously due to the fitting procedure, because in the Lorentzian doublet approach, the linewidths are fit independently for each doublet, whereas in the QSD approach, a single value is used for all the sites (Rancourt 1998).

Although the ratio among the different components is affected by the input data, the $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ depends neither on the input data nor on the model used in the fitting procedure. The ratio of the Mössbauer recoilless fraction has been considered equal to 1 on the basis of literature results (Lalonde et al. 1998). Values of $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ vary from 86% in HO20, to 84% in HO30, and to 90% in HO50. These values, used below for the recasting of biotite formulae, are similar to the results of other studies on biotites from graphite-ilmenite-bearing metapelites (Dyar 1987; Guidotti and Dyar 1991; Dyar et al. 2002).

EMP analyses

Biotite chemical compositions are reported in Table 8 as the average and standard deviation of n EMP spots on different

grains. The EMP totals are notably “high,” averaging at ca. 97 wt% in all samples. Low values of the standard deviations for all oxides >1 wt% indicate that the biotites are chemically homogeneous. The samples overlap in composition for their contents of SiO_2 (34.4 wt%), Al_2O_3 (18.8 wt%), FeO_{tot} (23.6 wt%), MgO (6.3 wt%), and Na_2O (0.45 wt%). They exhibit subtle variations of K_2O (8.5 to 8.8 wt%) and TiO_2 , with the ilmenite-bearing sample (HO50) showing a greater amount (4.86 wt%) than HO20 (4.50 wt%) and HO30 (4.66 wt%). This finding is in agreement with the variable degrees of Ti saturation. TiO_2 variations are not accompanied by changes of X_{Fe} [$\text{Fe}_{\text{tot}}/(\text{Fe}_{\text{tot}} + \text{Mg})$], which is 0.675–0.679, and probably reflect differences in the Ti content of the bulk xenoliths.

In all samples, the contents of F are below the detection limit (ca. 0.2 wt%). Chlorine concentrations are also negligible. This implies that these biotites do not show evidence of substitution of OH by either F or Cl. Table 8 also reports H_2O^* and NH_4 concentrations determined by SIMS and elemental analysis, as well as FeO and Fe_2O_3 values recalculated on the basis of Mössbauer results. As the recalculated sums deviate by less than ± 0.3 wt% from a perfect total, we infer that these analyses are a good approximation to the full chemical composition of the studied biotites.

X-ray diffraction

Analysis of the $0kl$ and $1kl$ synthetic precession images obtained from the collected images allowed to identify the polytype as $1M$ in all the samples; in addition, a $2M_1$ crystal was found in HO30. The precession images also showed diffuse streaks parallel to c^* along the $k \neq 3n$ reflections, in amounts larger in HO20 and HO30 than in HO50 crystals.

TABLE 8. Full biotite analyses (in wt%) based on EMP, C-H-N, SIMS, and Maussbauer data

Sample	HO20		HO30		HO50	
n	14		15		13	
SiO_2	34.38	0.30	34.37	0.24	34.43	0.24
TiO_2	4.50	0.08	4.66	0.12	4.86	0.11
Al_2O_3	18.90	0.14	18.84	0.18	18.84	0.19
Cr_2O_3	0.05	0.06	0.05	0.04	0.06	0.03
FeO_{tot}	23.61	0.44	23.74	0.45	23.44	0.34
MnO	0.04	0.02	0.06	0.03	0.04	0.02
MgO	6.36	0.12	6.29	0.11	6.35	0.11
CaO	0.01	0.01	0.02	0.03	0.01	0.02
Na_2O	0.48	0.10	0.44	0.06	0.41	0.10
K_2O	8.56	0.18	8.82	0.17	8.55	0.16
F	b.d.		b.d.		b.d.	
Cl	b.d.		0.06	0.07	0.02	0.01
EMP Total	96.91	0.74	97.32	0.49	97.04	0.66
FeO^*	20.30		19.94		21.09	
Fe_2O_3^*	3.67		4.22		2.60	
$\text{NH}_4^{\dagger}$	0.07		0.01		0.09	
$\text{H}_2\text{O}^{\ddagger}$	2.49		2.51		2.41	
Total	99.92		100.29		99.86	
X_{Fe}	0.675	0.005	0.675	0.005	0.679	0.005

Notes: EMP compositions of the three biotites are reported as mean and standard deviations of n point analyses for each sample. b.d. = below detection limit.

* Recalculated from Mössbauer results.

† From elemental analysis.

‡ SIMS H_2O^* value from Table 3. H_2O^* of HO50 corresponds to the lower partial average (see text for details). Also reported are the X_{Fe} values ($\text{Fe}_{\text{tot}} / (\text{Fe}_{\text{tot}} + \text{Mg})$).

Streaks are responsible for the rather large mosaicity parameter refined by DENZO-SMN for the former samples (1.41° and 1.83°) compared to the latter (0.49°). Diffuse $k \neq 3n$ reflections coexisting with sharp $k = 3n$ reflections are a well-known feature in micas, and usually hamper accurate measurement by point counter detector. The three-dimensional description of peaks provided by the area-detector allows a better integration of diffuse reflections. Nevertheless, as discussed later, the first trial refinements suggested that $k \neq 3n$ intensities were systematically underestimated, so that different scale factors were adopted.

Difference-Fourier maps of HO20 and HO30 revealed five residual peaks corresponding to the K-, T-, O1-, and O2- sites shifted with respect to the basic structure by $\pm b/3$ along [010], [310] and $[3\bar{1}0]$. Only a very small fraction of shifted K- and T-positions was found in HO50. These residuals are reported by several authors (e.g., Oberti et al. 1993) and interpreted as due to [310] (micro)twinning and/or $2M_1$ polytype domains in the $1M$ dominant crystal. Oberti et al. (1993) showed that by introducing a separate scale factor for $k \neq 3n$ reflections, the spurious peaks were eliminated and the substantial correctness of the refined model was not invalidated. At the end of the second trial of anisotropic refinements, the highest peak in the difference-Fourier map for all samples was in the expected position for the H site, which was added to the model and refined keeping the isotropic displacement factor fixed.

EMP analyses also were performed on the crystals used for XRD, with results similar to those reported in Table 8 within experimental error. Further calculations including chemical parameters are based on these EMP data, with the only exceptions being the H_2O^* , NH_4 , and the Fe^{3+}/Fe_{tot} values determined by SIMS, CHN, and Mössbauer analysis, respectively. The H_2O^* content of HO50 was that corresponding to the lower partial average.

Unit-cell parameters and further details on data collection and structure refinements are given in Table 9¹. Final atomic coordinates and temperature parameters are listed in Table 10¹. Interatomic bond distances are reported in Table 11¹, and selected parameters describing the mica polyhedral geometry are reported in Table 12¹. The population of the octahedral sites was determined by the least-square minimization procedure developed by Cruciani and Zanazzi (1994), in which the tri- and tetravalent cations are partitioned into the M2 site, with the only exception being Fe^{3+} , which also was allowed in M1 according to Mössbauer results. Mean atomic numbers (m.a.n.) and mean bond lengths for cation sites, as obtained from struc-

ture refinements and as calculated from chemical analyses, are compared in Table 13¹. The discrepancies found between the observed and calculated $\langle M1-O \rangle$ distances can be explained by allowing an uncertainty of about 10% on the estimation of the vacancy component owing to its large (fictive) ionic radius (0.75 Å).

Chemical features of biotite

Table 14 reports the structural formulae of the analyzed biotites, calculated on the basis of $[O_{12-(x+y)}(OH)_xCl_y]$. As a whole, the studied samples can be considered a homogeneous group, representative of biotites from reduced metapelites, close to their melting conditions. In this context, their first-order chemical features (e.g., the relationships between Ti and H contents) can help define the possible substitutions describing deviations from the ideal biotite plane (Guidotti 1984). This is equivalent to determining the major exchange components to be combined, along with $FeMg_{-1}$ and $(MgSiAl)_2$, to the ideal additive component Phlogopite $[KMg_3AlSi_3O_{10}(OH)_2]$. This approach, used among others by Virgo and Popp (2000) and Waters and Charnley (2002), investigates the large-scale, average variations that best describe the overall compositional trends, but cannot model the fluctuations of compositional variation as a function of metamorphic grade, as described by Guidotti (1984).

Under the assumption that excess Al enters in tetrahedral coordination primarily by a Tschermak substitution, the major deviations from the ideal biotite plane are, in decreasing order of magnitude: H deficiency (0.70–0.74 atoms per formula unit, or apfu), Ti (0.26–0.29 apfu), Fe^{3+} (0.15–0.25 apfu), ^{VI}Al in excess of Tschermak (0.07–0.12 apfu), and Na (0.06–0.07 apfu).

The studied biotites have an average OH content of ca. 1.3 apfu, more than one third less than the stoichiometric value. Such H deficiency is not compensated by F or Cl, implying that one third of OH positions are occupied by O (in excess), as can occur in response to oxy-type substitutions.

Figure 6 shows no apparent correlation between OH and Fe^{3+} , suggesting that OH variations are independent of Fe^{3+} contents. This finding also reinforces the conclusions of Guidotti and Dyar (1991) and Dyar et al. (2002) that biotite from graphite- and ilmenite-bearing metapelites has a roughly constant Fe^{3+}/Fe_{tot} value of ca. 12%, regardless of the metamorphic grade, and that Fe-oxy exchange is not the primary cause of H deficiency.

Octahedral vacancies (0.01–0.05 p.f.u.) are a very minor feature of the samples, much less than commonly reported from metamorphic biotite (Guidotti 1984). Based on these data, it is

TABLE 14. Structural formulae of the studied biotites

Sample	Based on O _(12-x-y) (OH) _x Cl _y									
HO20	^[XII] [K _{0.852} Na _{0.073} (NH ₄) _{0.018} Ca _{0.001}] _{Σ=0.944} ^[VI] (Mg _{0.741} Fe _{1.324} ²⁺ Fe _{0.215} ³⁺ Mn _{0.003} Al _{0.417} Ti _{0.264} Cr _{0.003}) _{Σ=2.967} ^[IV] (Si _{2.680} Al _{1.320} O _{10.705} (OH) _{1.296})									
HO30	^[XIII] [K _{0.874} Na _{0.066} (NH ₄) _{0.002} Ca _{0.002}] _{Σ=0.944} ^[VI] (Mg _{0.728} Fe _{1.296} ²⁺ Fe _{0.247} ³⁺ Mn _{0.004} Al _{0.395} Ti _{0.272} Cr _{0.003}) _{Σ=2.945} ^[IV] (Si _{2.670} Al _{1.330} O _{10.689} (OH) _{1.303})									
HO50	^[XII] [K _{0.852} Na _{0.063} (NH ₄) _{0.023} Ca _{0.001}] _{Σ=0.939} ^[VI] (Mg _{0.740} Fe _{1.378} ²⁺ Fe _{0.153} ³⁺ Mn _{0.003} Al _{0.426} Ti _{0.286} Cr _{0.004}) _{Σ=2.990} ^[IV] (Si _{2.691} Al _{1.309} O _{10.739} (OH) _{1.256})									
	Based on O ₍₁₀₎ (OH, Cl) ₂									
HO20	^[XIII] [K _{0.826} Na _{0.071} (NH ₄) _{0.017} Ca _{0.001}] _{Σ=0.915} ^[VI] (Mg _{0.718} Fe _{1.283} ²⁺ Fe _{0.209} ³⁺ Mn _{0.003} Al _{0.280} Ti _{0.256} Cr _{0.003}) _{Σ=2.752} ^[IV] (Si _{2.597} Al _{1.403} O _{10.0} (OH) _{2.0})									
HO30	^[XIII] [K _{0.848} Na _{0.064} (NH ₄) _{0.002} Ca _{0.002}] _{Σ=0.916} ^[VI] (Mg _{0.706} Fe _{1.256} ²⁺ Fe _{0.239} ³⁺ Mn _{0.004} Al _{0.260} Ti _{0.264} Cr _{0.003}) _{Σ=2.732} ^[IV] (Si _{2.588} Al _{1.412} O _{10.0} (OH) _{2.0})									
HO50	^[XIII] [K _{0.824} Na _{0.061} (NH ₄) _{0.022} Ca _{0.001}] _{Σ=0.908} ^[VI] (Mg _{0.716} Fe _{1.334} ²⁺ Fe _{0.148} ³⁺ Mn _{0.003} Al _{0.281} Ti _{0.276} Cr _{0.004}) _{Σ=2.762} ^[IV] (Si _{2.609} Al _{1.397} O _{10.0} (OH) _{2.0})									
Notes: First three rows display formulae calculated on the basis of [O _{(12-(x+y))} (OH) _x Cl _y]. Second three rows report normalization on the basis of [O ₁₀ (OH, Cl) ₂].										

Notes: First three rows display formulae calculated on the basis of $[O_{12-(x+y)}(OH)_xCl_y]$. Second three rows report normalization on the basis of $[O_{10}(OH)_2Cl_2]$.

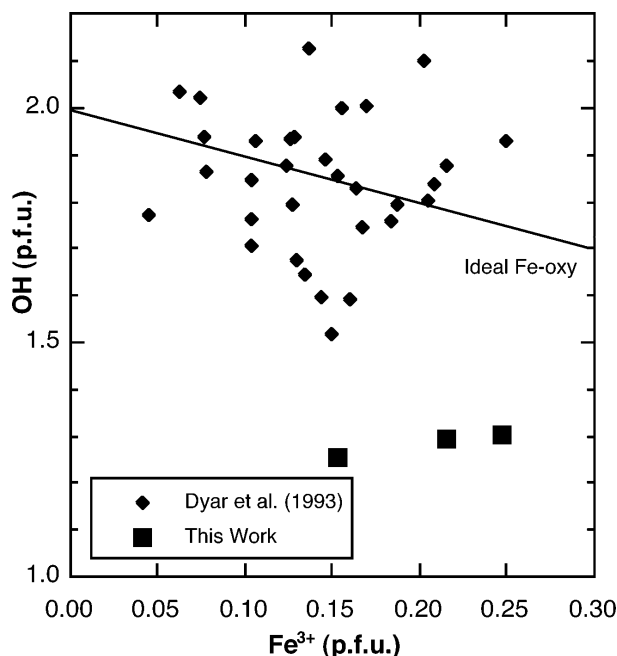


FIGURE 6. OH vs. Fe³⁺ diagram. Squares = this work; diamonds = data from graphitic metapelites of Dyar et al. (1993). Dashed line = model Fe³⁺(OH)₋₁ exchange as in the Fe-oxy substitution.

apparent that octahedral vacancy-producing exchanges (e.g., Ti-vacancy or di-trioctahedral Al³⁺□R²⁺) are unimportant. Similarly, the occurrence of the Ti-Tschermak exchange (1) can be ruled out confidently, as all the excess tetrahedral Al (0.31–0.33 apfu) is accommodated by entrance of ^vAl through the Tschermak substitution. In contrast, because the H deficiency is very pronounced, oxy-type exchanges are very likely involved in the octahedral site. It can be observed that H defects are in all samples >2Ti, but also <(2Ti + Fe³⁺ + Al³⁺). Thus, oxy-type substitutions can account for the entrance of all Ti in the studied biotites, but not for the whole non-divalent octahedral occupancy, which requires accommodation of further (ca. 15% relative) positive charges. We propose that the possible additional exchange involves vacancies in the A site (ca. 0.06 p.f.u.). Within the oxy-type exchanges, Ti-oxy accounts for roughly 2/3 of the H deficiency, and is by far the most important, in agreement with the observations of Richter et al. (2002) on magmatic phlogopites.

The importance of the Ti-oxy substitution is highlighted when results are integrated with data on lower-grade metamorphic biotites, which allow a more-comprehensive view of compositional deviations from the ideal biotite plane. The nice negative correlation observed in the Ti vs. OH diagram of Figure 7¹ is clear evidence of the Ti-oxy substitution. The TiO₂ vs. H₂O diagram of Figure 8 reports the same analyses as in Figure 7, and data points plot in a very similar manner. The advantage of this visualization is that it allows a better discrimination of the main exchanges involving Ti. In addition, it shows the difference of absolute quantities of H₂O as a function of the FeMg₋₁ substitution in biotite. As the trends exceed the ideal Ti-oxy correlations these plots also show that, as discussed

above, additional H deficiency is probably introduced through substitutions involving other non-divalent octahedral cations. Interpretation of diagrams such as Figures 7 and 8 must take into consideration the possible complexities added by F and Cl substituting for OH. Because F and Cl are virtually absent in the samples of the present study, the Ti-OH (or TiO₂-H₂O) relationships are straightforward.

Two samples do not contain a Ti-saturating phase. Thus, their Ti contents are not the saturation values, and are lower than in ilmenite-bearing assemblages at the same P-T conditions. In Ti-saturated rocks, and in biotites close to dehydration melting conditions, the observed H deficiency is probably higher than the values measured in this study (box in Figure 8), enhancing the petrologic consequences outlined below.

For comparison, Table 14 also lists structural formulae calculated on the basis of [O₁₀(OH, Cl)₂]. This scheme is commonly used in the absence of direct H analyses, but is clearly not applicable to dehydrogenated biotites. Note how such wrong normalization would create octahedral vacancies in amounts almost equal to Ti atoms, thereby suggesting a totally fictive Ti-vacancy substitution.

Concerning substitutions in the interlayer, C-H-N analyses indicate NH₄ contents ranging from 0.01 to 0.09 wt%, consistent with those reported in other studies (e.g., Sadofsky and Bebout 2000). Guidotti and Sassi (1998) pointed out that NH₄ replacing K⁺ in the interlayer is an important component in

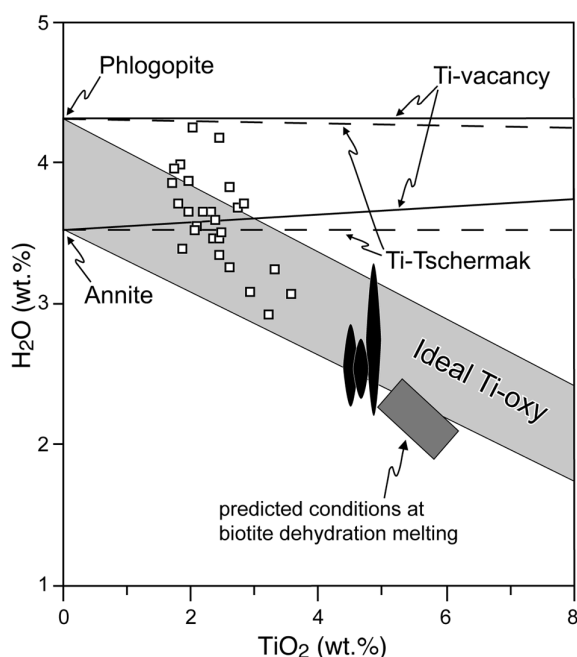


FIGURE 8. H₂O vs. TiO₂ diagram. Filled ellipses represent the H₂O ranges obtained by SIMS in this study. Empty squares are data points for biotite from graphitic metapelites of Dyar et al. (1993). Starting from stoichiometric annite and phlogopite (TiO₂=0), figure reports ideal H₂O-TiO₂ relationships for the main Ti-involving exchanges. Shaded band represents the Ti-oxy exchange; solid lines contour the Ti-vacancy exchange; dashed lines contour the Ti-Tschermak exchange. Shaded box = visual extrapolation of natural trend to contents of 5–6 wt% TiO₂, as common at dehydration melting conditions.

metamorphic micas, but has received little attention mainly due to analytical difficulties. Our samples show a clear 1:1 inverse relationship between NH_4 and $(\text{K} + \text{Na})$ contents (Fig. 9¹) supporting the occurrence of the $(\text{NH}_4)(\text{K},\text{Na})_{-1}$ exchange.

Structural features of biotite

The a and b cell dimensions (Table 9¹) of the biotites, consistent with the Mg-fraction relationships found by Cruciani and Zanazzi (1994), indicate that the major control is from the octahedral layer and also support the absence of $^{\text{IV}}\text{Fe}^{3+}$ as indicated by Mössbauer spectroscopy. Figure 10 shows that the c cell parameter vs. the $^{\text{VI}}\text{Ti}$ and OH contents of all samples, taken as a group, agree with those estimated by the linear inverse relationships observed by Cruciani and Zanazzi (1994). These authors interpreted the shortening of the c -edge, mostly due to shortening of the K-O4 distance, as one of the structural indications for Ti-oxy substitution. However, this inverse relationship is no longer evident considering the three single entries, owing to the variable amount of $2M_1$ -like stacking faults observed in the three samples.

The tetrahedral sites are very similar in all samples (Table 11¹): the tetrahedral volumes and mean distances decrease slightly from HO20 and HO30 to HO50 whereas the bond-length distortion (BLD) increases; the tetrahedral thickness is similar in the former samples and slightly less in HO50. There is agreement (within 1σ) between the observed mean tetrahedral distances and those calculated from the chemical analyses by assuming that only Si and Al are in tetrahedral coordination (Table 12¹).

The in-(001)-plane rotation angle of adjacent tetrahedra (α), averaged on the three samples, is 7.9° . Benisek et al. (1999) observed that most metamorphic biotites have α values between 7 and 9° , and concluded that biotite with α of about 8° appears to be more stable than others. The decrease of tetrahedral rotation and the associated decrease of dimensional misfit between the tetrahedral and octahedral sheets (D.M., see Table 11¹) are correlated to the increase of Ti content, indicating a role for Ti substitution to produce a better fit. The variation of α is geometrically associated with the difference between outer and inner mean interlayer bond distances ($\Delta_{\text{K-O}} = \langle \text{K-O}_{\text{outer}} \rangle - \langle \text{K-O}_{\text{inner}} \rangle$); the studied samples are consistent with the linear regression $\Delta_{\text{K-O}} = 0.009(3) + \alpha \cdot 4.5(5) \times 10^{-2}$, and show a linear decrease of the $\langle \text{K-O} \rangle_{\text{outer}}$ with the decreasing OH content (Fig. 11), in agreement with Cruciani and Zanazzi (1994).

Concerning the octahedral layer of the studied micas, the $\langle \text{M2-O} \rangle$ distances are very similar in all three samples whereas the $\langle \text{M1-O} \rangle$ distance in HO50 is remarkably larger than in HO20 and HO30 (Table 11¹). As a consequence, the ratio $\langle \text{M1-O} \rangle / \langle \text{M2-O} \rangle$ is similar in HO20 and HO30 (~ 1.004), and greater in HO50 (1.013). Similarly, the ratio of the refined mean atomic numbers of the M1 and M2 sites ($m.a.n._{\text{M1}}/m.a.n._{\text{M2}}$) is very close to 1 for HO20 (0.999) and HO30 (1.007), but larger in HO50 (1.043). An explanation of these differences on the basis of chemical composition is not straightforward: possible correlations with increasing $^{\text{VI}}\text{Fe}^{2+}$ and $^{\text{VI}}\text{Ti}$ and decreasing $^{\text{VI}}\text{Fe}^{3+}$ content can be invoked (see Table 8). Despite the 2:1 ratio of M2 vs. M1 sites in the unit cell, the lengthening of the $\langle \text{M1-O} \rangle$ appears to be the major factor responsible for the increase

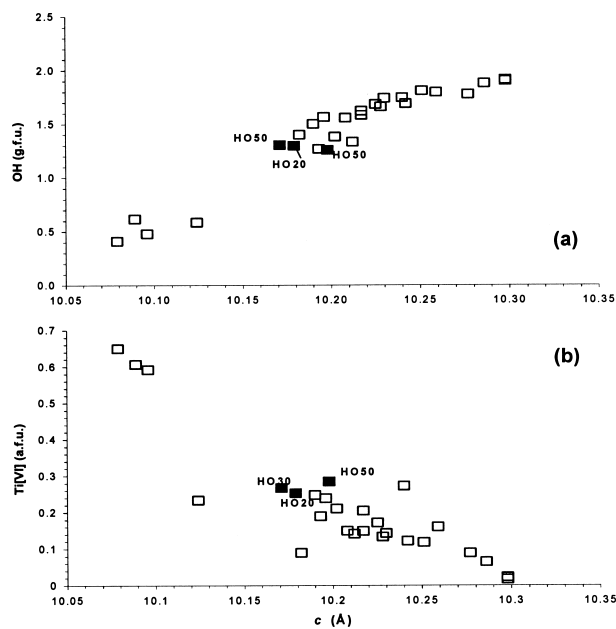


FIGURE 10. Plot of c lattice parameter vs. (a) OH content, and (b) $^{\text{VI}}\text{Ti}$ content. Solid symbols are for micas in this study; open symbols refer to data from Cruciani and Zanazzi (1994).

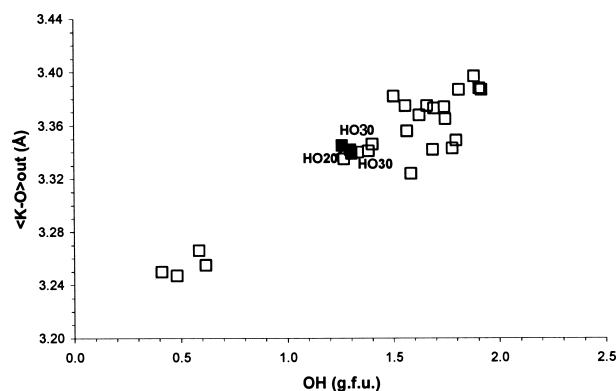


FIGURE 11. Variation of longer $\langle \text{K-O} \rangle$ distance vs. OH content. Symbols as in Figure 10.

in the octahedral sheet thickness, particularly evident in the HO50 sample (see Table 12¹).

Among the geometric distortions of the M1 and M2 sites (Table 12¹), the most interesting is the clear positive relationship between the $^{\text{VI}}\text{Ti}$ content and the BLD of the M2 octahedron (Fig. 12¹), caused by the out-of-center shift of the M2 cation from the geometric center of the octahedron toward the O4 oxygen. This can be regarded as an indication for the preferential partitioning of $^{\text{VI}}\text{Ti}$ into the M2 site and the occurrence of Ti-oxy substitution: in fact, the concomitant displacement of the $^{\text{VI}}\text{Ti}$ toward O4, the hydroxyl site, and the loss of a proton attached to this oxygen are both consistent with local charge-balance requirements. The average observed M2-BLD value of our micas (1.39) is consistent with that calculated (1.45)

from their average ^{51}Ti content (0.269) using a linear regression from the data in Cruciani and Zanazzi (1994).

It is noteworthy that the observed off-center shift of ^{51}Ti leads to a shortened metal-to-metal distance across the O4-O4 edge shared by two adjacent M2 sites. This shortening is obviously unfavored by the increased electrostatic mutual repulsion between cations and would decrease the stability of micas. However, the mutual repulsion is relieved, at least partially, by the improved charge screening of the O4-O4 edge itself, whose length is shortened due to shrinkage of the M2-O4 bond distances. The mutual repulsion is also avoided if it is assumed that the actual ^{51}Ti distribution does not comply with the mirror plane that makes two adjacent M2 sites equivalent in the $C2/m$ layer symmetry. In other words, it is likely that Ti actually occupies only one out of two M2 sites. Such an ordering possibly occurs at the short range, so that the average $C2/m$ symmetry is maintained. A long-range ordering is also conceivable, but evidence for it is very weak; for this reason, no attempts were made to perform subgroup refinements. The most striking consequence of Ti ordering into an M2 split site would be the existence of a third non-equivalent octahedral site characterized by a different distortion of the ligand environment. Although not visible from XRD data, a third octahedral environment around Fe^{2+} and Fe^{3+} was indeed detected by Mössbauer investigation of the biotites. As a further remark, we might argue that this conclusion would apply, to various extents, to Mössbauer spectra of all Ti-bearing biotites. For example, the Mössbauer spectral features assigned to tetrahedral Fe^{3+} in biotites from NW Maine by Dyar (1990, 1993) could, instead, be due to $^{51}\text{Fe}^{3+}$ in an additional, highly distorted octahedral site (M. D. Dyar, personal communication).

Ti-oxy substitution

Our data help explore the cause-and-effect relationships between ^{51}Ti uptake in biotite and dehydrogenation. As a first issue, the proton loss can be regarded as a response to the overbonding induced by ^{51}Ti approaching to O4. In this case, the triggering cause would be the tendency for Ti^{4+} to shift out-of-center within an octahedral environment (Kunz and Brown 1995). According to the distortion theorem (Brown 1992), the Ti^{4+} off-center shift is expected in order to achieve a more-satisfactory sum of Pauling bond strengths. Thus, the average bond valence can be increased by lengthening of some of the Ti-O bonds and shortening of others, the average bond length remaining constant. This interpretation predicts that Ti^{4+} will intrinsically be incorporated via a Ti-oxy mechanism, the uptake being favored in hydroxylated minerals where the overbonding can be compensated by the loss of a proton. This feature would explain the relatively high Ti levels commonly found in the octahedral sites of micas and amphiboles, compared to pyroxenes. The presence of a large oxy-component in biotite would not necessarily require formation under oxidized conditions because the H deficiency would be governed primarily by the amount of Ti (or other highly charged cations). A similar conclusion was reached by Richter et al. (2002) who noted that oxy-components can also be stable at reducing conditions. They argued that the mica H contents could respond to crystal-chemical constraints rather than to oxygen fugacity

constraints.

As an alternative view, dehydrogenation might be regarded as a response to environmental conditions, mainly temperature. In this case the loss of a proton itself would trigger the incorporation of tri- and tetravalent cations into the M2 site in order to maintain charge balance. The presently available crystal-chemical data on oxy-substitutions in micas do not allow us to favor one or the other interpretation. Kunz and Brown (1995) showed that, unlike other octahedrally coordinated d^0 transition metals (e.g., V^{5+}) always found in a distorted configuration simply due to electronic effects, distortions involving Ti^{4+} only occur if structural distortions are also present. Accordingly, we suggest that both the above-discussed mechanisms are probably coexisting to promote the Ti-oxy substitution.

Other substitutions

The results on distribution of Fe^{2+} , Mg, and Fe^{3+} over the octahedral sites obtained from the least-squares minimization might be questioned as they largely depend upon the initial assumptions. If taken as reliable, further insights on the substitution mechanisms can be derived. The Fe^{3+} content determined by Mössbauer spectroscopy appears to be completely (HO20 and HO30) or preferentially (HO50) partitioned in M1 site. The inverse linear correlation of $\text{Fe}_{\text{M1}}^{3+}$ vs. $\text{Fe}_{\text{M1}}^{2+}$ suggests that the Fe oxidation primarily occurs within the M1 site. However, the Fe^{3+} partitioning in M1 can be regarded as an indication of little (or no) involvement of Fe^{3+} in the dehydrogenation process. A linear inverse relationship is also observed for $\text{Fe}_{\text{M2}}^{2+}$ vs. Ti_{M2} (Fig. 13); in this case, a slope of 1:1 (as in Ti-oxy) gives a much better description than a 2:1 slope (as in Ti-vacancy) suggesting a principal $\text{TiFe}_{\text{M2}}^{2+}$ exchange vector in M2. It follows that Fe oxidation (retrograde or post-metamorphic?) would primarily occur at the M1 site whereas the Ti (vs. Fe^{2+}) incorporation, which is a function of metamorphic grade (Guidotti et al. 1977), mainly affects the M2 site in metapelitic biotites.

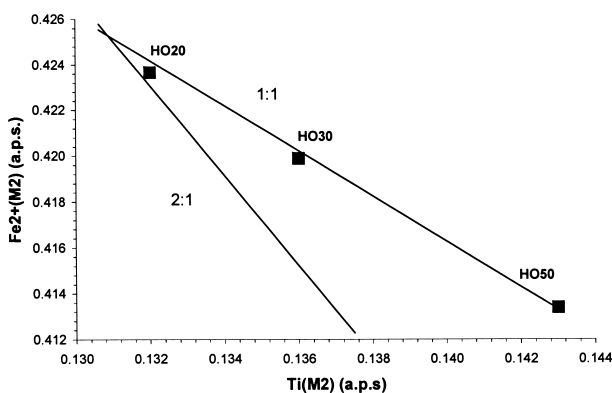


FIGURE 13. Variation of the Fe^{2+} vs. ^{51}Ti in the M2 octahedral site given as atom per site (a.p.s.). The $\text{Fe}_{\text{M2}}^{2+}$ content as determined by the minimization procedure.

PETROLOGIC CONSEQUENCES

Melt productivity by biotite fluid-absent melting

Biotite fluid-absent ("dehydration") melting is considered the most-important mechanism of granite genesis and granulite formation at low and medium crustal pressures, where biotite is the principal reservoir of H₂O. It follows that for a given *P-T* condition, the amount of H₂O-undersaturated melt (melt productivity or rock fertility) depends on the modal proportion of biotite (e.g., Vielzeuf and Holloway 1988). This relationship is often used to estimate or model the productivity of a melting reaction, but in most cases, the OH content of biotite is assumed to be stoichiometric. Although this conclusion is valid when modeling synthetic, Ti-free systems (e.g., Carrington and Harley 1995), it has also been applied to experiments where biotite contained >5 wt% TiO₂ (e.g., Le Breton and Thompson 1988) or to mass balances in natural migmatites (e.g., Kriegsman 2001a).

Because our results and other published full analyses (Bohlen et al. 1980) indicate that biotite approaching melting conditions is highly H-deficient, melt productivities must be considered a function not only of biotite mode, but also of its actual H₂O content.

As an example, consider the model calculations of melt productivity made by Kriegsman (2001a), who considered the common melting reaction: Bt + Sil + Qtz ± Kfs = Grt + melt.

If the H₂O content of biotite is changed from 1 mole (per 11 oxygen atoms) to 0.6, as inferred from Figure 7, large variations in reaction stoichiometries are produced (Table 15). The primary effects are the consumption of much higher amounts of reactants per melt produced, and the lower ratio of melt vs. the sum of minerals involved. In addition, the model melt/Grt ratio, a parameter for estimating melt production in the field, decreases by ca. 30–40%. Finally, the change of reaction stoichiometry leads to the possibility of achieving a refractory behavior for K-feldspar. This shows that model melt productivities calculated assuming OH stoichiometry may be overestimated by 30–40 % relative. This overestimation adds to the lower melt fractions that are predicted by recent data on the water contents of anatectic melts (Holtz et al. 2001). Such differences may help understand some reported discrepancies between model and calculated melt fractions (e.g., Le Breton and Thompson 1988; Montel and Vielzeuf 1997).

Mass balance

Melt productivity calculations are only one type of mass balance that can be performed in biotite-bearing high-grade rocks. Other applications include estimate of mineral modes, balancing of reaction stoichiometry, modeling of fluid-rock interactions, and fluid behavior during metamorphism and partial melting.

Also in these cases, if H₂O is taken into account in mass-balance calculations, then results are strongly affected by the OH content used for biotite. In the most common case of lack of direct H₂O determination, care should be taken to assume full OH occupancy in biotite. We suggest that H₂O should not be included in the calculations or, alternatively, that a safer assumption is to diminish OH in the amount of twice the atomic Ti content. Based on the data reported in Figures 7 and 8, this is likely to be a minimum estimate of the actual H deficiency. Similar considerations probably apply also to mass balance involving Ti-rich amphiboles, in which the Ti-oxy exchange has also been proposed (e.g., Popp et al. 1995).

The thermal stabilization of biotite

Titanium has a major effect on the thermal stability of biotite, raising its final melting temperature of up to 80 °C (Stevens et al. 1997). This effect can be explained by the relatively small thermal expansion of Ti⁴⁺-containing octahedra (Hazen and Prewitt 1977) and by the hypothesis that the thermal breakdown takes place along the chains of M2 sites (Toraya 1981), which have a greater expansion rate (Takeda and Morosin 1975). On this basis, Cruciani and Zanazzi (1994) suggested that even low contents of ^vTi, partitioned into M2 sites, can increase remarkably the thermal stability of biotite. However, our data and earlier studies show that Ti entry into biotite is coupled to dehydrogenation via the Ti-oxy exchange. Thus it may be questioned, as discussed above, whether octahedral Ti is the cause of the thermal stabilization of biotite or, by contrast, whether the actual cause is the loss of H, in a way similar to the progressive thermal dehydration of cordierite (e.g., Harley and Carrington 2001).

In the absence of precise data to discriminate the energetic effects of each exchange, we suggest the possibility that progressive dehydrogenation of biotite may be the actual mechanism for stabilizing biotite at high temperatures (see also Valley et al. 1990), and that its extent is maximized in the presence of Ti, which allows for Ti-oxy exchange.

TABLE 15. Stoichiometries, total reactants involved, liquid/garnet and liquid/reactants ratios for the reaction Bt + Sil + Qtz ± Kfs = Grt + Liq, using mineral and liquid compositions as in Kriegsman (2001a)

Example	Bt (mol)	Sil (mol)	Qtz (mol)	Kfs (mol)	Grt (mol)	Liq ₁ (mol)	Liq ₂ (mol)	reactants (mol)	Liq/Grt	Liq/reactants
A (Kriegsman)	0.23	0.17	1.12	-0.03	-0.20	-1.00		1.52	5.05	0.66
A (This work)	0.38	0.27	1.47	-0.18	-0.34	-1.00		2.13	2.97	0.47
B (Kriegsman)	0.11	0.10	0.85	0.08	-0.09		-1.00	1.14	10.90	0.88
B (This work)	0.19	0.15	1.02	0.01	-0.16		-1.00	1.36	6.27	0.73

Notes: Two examples with different liquid compositions are modeled: example A with Liq₁ (4 wt% H₂O) and example B with Liq₂ (2 wt% H₂O). For each example the first rows report Kriegsman (2001a) calculations assuming biotite stoichiometry (H₂O = 1 mol p.f.u.); the second rows, labeled "This work" report results obtained assuming H₂O = 0.6 mol p.f.u.

Thermodynamic modeling

Because the H content of high-grade metamorphic biotite from “reducing” conditions (graphite-ilmenite) can be described, as a first-order approximation, by the Ti-oxy substitution, it follows that the modeling and interpretation of H₂O/melt/mineral relationships in pelitic compositions require: (1) proper incorporation of Ti into the model (CN)KFMASH(-O) system, and (2) adequate description of OH non-stoichiometry in biotite by means of the Ti-oxy exchange.

Titanium recently has been introduced in thermodynamic data sets and has been used for the modeling of medium- and high-grade processes in the KFMASHTO system (e.g., White et al. 2000, 2002). However, the thermodynamic model used for biotite considers a stoichiometric OH content, and the Ti-vacancy model (TiFe₂) for Ti substitution (White et al. 2000). As outlined by Patiño Douce (1993), such simplification can lead to significant errors, especially in the case of Ti-oxy substitutions.

In view of the present research, which supports the Ti-oxy component as the principal mechanism for the incorporation of Ti in biotites, we recommend that thermodynamic models for biotite should consider the Ti-oxy exchange instead of, or along with, the Ti-vacancy exchange. In addition, the cation distribution scheme adopted in these models should be consistent with the so-called “normal ordering scheme” obtained from crystal structure analysis (Toraya 1981; Bailey 1984), which predicts the partitioning of octahedral high-charge cations (e.g., Ti⁴⁺) and vacancies into M2 and M1, respectively.

Reliability of EMP analyses

The EMP data reported in Table 8 indicate that biotites from high-grade metasediments, granulites, or melting experiments, all of which may contain significant Ti and be H-deficient, are likely to provide EMP oxide totals ≥ 97 wt%. This value, notably higher than commonly assumed (96 wt%; e.g., Montel and Vielzeuf 1997), should provide a refined criterion for selecting reliable chemical analyses, especially if these are used for mass-balance calculations. A test of this hypothesis, based of careful evaluation of wavelength- and energy-dispersive analyses, is given by Waters and Charnley (2002), who note the systematic increase of biotite EMP totals with increasing TiO₂. Because biotite approaching melting conditions commonly contains 5–6 wt% TiO₂, the TiO₂-H₂O trend defined in Figure 8 indicates that it is not surprising if reliable totals of ca. 98 wt% are obtained by EMP analysis.

The marked dehydrogenation of Ti-rich metamorphic biotite confirms that hydrogen non-stoichiometry in biotite cannot be neglected, particularly at high and very high metamorphic temperatures. In most cases, the assumption of a Ti-vacancy (TiFe₂) exchange is arbitrary, or is a necessary consequence of assuming (OH + F + Cl = 2) as a normalizing constraint (see Table 14). The Ti-oxy exchange must be considered in the re-assessment of crystal-chemical and thermodynamic properties of natural biotites, and in the modeling of petrologic processes of high-temperature metamorphism, crustal anatexis and granite production.

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