Chemical control of 3T stacking order in a Li-poor biotite mica

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ABSTRACT

The microstructural features of a biotite (Mg-rich annite) crystal from dacite rocks of Džep, Serbia, were studied by X-ray diffraction topography (XRDT) and high-resolution and analytical transmission electron microscopy (HRTEM and ATEM, respectively). The average chemical composition, obtained by electron microprobe analysis (EMPA) and secondary-ion mass spectrometry (SIMS) data, is

 $(K_{0.87}Na_{0.05}Ca_{0.01})_{\Sigma=0.93}(Fe_{1.36}^{2+}Mg_{1.25}Ti_{0.22}Al_{0.14}Mn_{0.03}Li_{0.01})_{\Sigma=3.01}(Si_{2.84}Al_{1.16})_{\Sigma=4.00}O_{10}[(OH)_{1.53}O_{0.35}F_{0.10}Cl_{0.02}]_{\Sigma=2.00}.$

Inhomogeneous regions from either different polytypes or twins were mapped by XRDT, and these images were used to guide sampling for TEM analysis. Three stacking arrangements, each belonging to subfamily-A of mica polytypes, were identified by selected area electron diffraction (SAED) patterns and HRTEM images: (1) dominant semi-random $1M_r$ - $n(120^\circ)$, including an occasional repetition of long-period inhomogeneous stacking sequences belonging to the 3T structural series; (2) highly faulted $2M_1$, sometimes with short-range-ordered long-period inhomogeneous sequences based on the $2M_1$ structural series; and (3) perfectly ordered 3T stacking repeating over long distances (several micrometers). ATEM data revealed that the microchemical composition of 3T differs from that of the host matrix. The 3T is enriched in interlayer cations (K and Na), and depleted in Si and octahedral cations. No evidence of Li was detected. Compositional control on the stability of 3T stacking is suggested.

Keywords: Polytypism, biotite, electron microscopy, chemical analysis

INTRODUCTION

Micas are major rock-forming minerals of the Earth's crust and have been the subject of many investigations. Special attention has been paid to their propensity to form polytypic structures (Baronnet 1992 and references therein).

One concern about mica polytypism (and polytypism in general) relates to whether polytypes are genuine equilibrium phases or phases controlled by kinetic growth factors. The understanding of the factors responsible for various polytypes in micas is important for field and experimental studies insofar as polytypism is an indicator of the conditions prevailing during petrogenesis. For example, phengitic muscovite favors 3T stacking over $2M_1$ stacking at high pressure (Sassi et al. 1994; Amisano-Canesi et al. 1994; Pavese et al. 1997, 1999, 2000).

Unlike stoichiometric compounds (e.g., SiC), micas are compositionally complex and the probability that many factors are involved in mica polytype formation is high. The most likely factors (Amouric and Baronnet 1983) are (1) composition of the crystallizing melt/fluid; (2) temperature and (H₂O) pressure of formation; (3) crystal-chemistry-induced distortions; (4) stacking-scheme-induced distortions; and (5) growth mechanisms. Whereas the first four are primarily related to equilibrium thermodynamics, the last factor is not and may be able to operate independently. These two general factors account for the mica literature on polytypism in the past 70 years.

Pandey et al. (1982) demonstrated how all inhomogeneous and long-period stacking sequences could be explained by a spiral growth mechanism, owing to screw dislocations created in a faulted matrix of the basic 1M, $2M_1$, and 3T structures. In this case, no structural control is required because the spiral growth has its own memory. However, the faulted matrix model may not satisfactorily account for the common simple polytypes, for which structural control should prevail (Smith and Yoder 1956).

On the other hand, Güven (1971) and others used the derivative crystal structure theory of Buerger (1947) to study variations in the crystal structure of micas as a function of compositional substitutions, cation ordering, and polyhedra distortions to explain mica polytypism. Similarly, structural control for the formation of regular stacking of the simple polytypes 1M and $2M_1$ was proposed for volcanic (hydrogenated) oxybiotites from Ruiz Peak, New Mexico (Takeda and Ross 1975), and extended also to plutonic biotites (Bigi and Brigatti 1994). Takeda and Ross (1975) found dissimilarities in the unit-layer structure of the two polytypes, owing to different atomic and geometric constraints that each unit-layer exerts over adjacent layers, as a function of their relative orientation (stacking angle). The authors designated these constraints as the cause, once a platelet with 1M or $2M_1$ stacking is formed, for subsequent structural control for an ordered sequence.

Although some authors maintained that chemical composi-

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tion is not a likely factor controlling mica polytypism (Takeda and Ross 1975; Bigi et al. 1993; Bigi and Brigatti 1994), others considered compositional variation itself a structural factor, thus playing a dominant role in controlling the formation of different mica polytypes (Smith and Yoder 1956; Güven 1971). In addition, there are high-resolution and analytical transmission electron microscopy (HRTEM and ATEM, respectively) studies showing chemical differences among different coexisting stacking sequences (Baronnet and Kang 1989; Baronnet et al. 1993; Xu and Veblen 1995). For example, Baronnet et al. (1993) combined a HRTEM and ATEM study of a biotite crystal from the Zhong Tia Mountain molybdenum ore deposit (Henan Province, China) with a syntactic texture of 1M, $2M_1$, faulted 3T, and semirandom $1M_r$ - $n(120^\circ)$ polytypes. They found a significant correlation between the local microstructure and the local chemical composition, and suggested that both of them may be fingerprints of the environmental growth conditions. Furthermore, they found oscillatory stacking modes in the transition zones between any two of the large ordered 1M and $2M_1$, and faulted 3T domains. Similarly, in a study on biotite from the Bingham Canyon porphyry copper deposit (Utah), Xu and Veblen (1995) found that disordered $1M_r$ -n(120°) stacking was interlayer K-deficient relative to coexisting ordered 1M and $5M_1$ polytypes. They suggested that stacking disorder could be more easily induced in the low K regions by fluctuations of the fluid composition during crystallization. Moreover, they assumed that all 1M, $2M_1$, and 3Tpolytypes have different unit-layer structures. They suggested a dynamical model of periodic and/or non-periodic oscillations among 1M, $2M_1$, and 3T structural states, occurring during farfrom-equilibrium crystal growth of biotite and being related to compositional fluctuations of the growth fluid.

The review article on refined crystal structures of micas by Brigatti and Guggenheim (2002), which updates Bailey (1984), noted that most of the structures described were trioctahedral true micas, with many 1M forms, a few $2M_1$, three $2M_2$, and two 3T. The latter, however, are Li-rich compositions, being polylithionite (Brown 1978) and lithian siderophyllite (Weiss et al. 1993). Also, Brigatti et al. (2003) reported on lithian siderophyllite-3T. Thus, compositional control over long-range-ordered 3T stacking in trioctahedral micas appears to emerge at least for Li-rich compositions, but this stacking trend is not common in rock-forming, Li-poor biotite. In addition to the study by Baronnet et al. (1993), 3T sequences with limited stacking order have been reported by TEM investigations in a H-poor, Fe-rich phlogopite from the Valle del Cervo (Italy) plutonic body (Bigi et al. 1993; Bigi and Brigatti 1994), and in the H-poor and Fe3+rich oxybiotites from the volcanic Ruiz Peak rhyodacites, New Mexico (Kogure and Nespolo 2001).

The present study reports on a H-poor and Fe-rich biotite from volcanic dacite rocks of Džep, Serbia, showing a syntactic texture of disordered $1M_r$ - $n(120^\circ)$, highly faulted $2M_1$, and ordered 3T sequences. This is the first report of 3T long-range-ordered stacking with a unique interlayer composition in a Li-poor trioc-tahedral mica. We used X-ray diffraction topography (XRDT) to map the areas of the coherent scattering domains, and HRTEM techniques (Kogure 2002) to characterize these domains. We suggest that fluctuations of the fluid composition controlled the formation of the 3T stacking sequence.

EXPERIMENTAL METHODS

A reddish-dark brown platy crystal of biotite ($7.5 \times 7.5 \times 3$ mm) labeled Bt9568a was used. The sample is from dacite rocks of Džep, Serbia, and belongs to the Earth Sciences Museum, University of Bari. The crystal was cut in several slices parallel to (010) and was first investigated by XRDT. These slices were mechanically thinned and polished on both sides using standard methods. Some of them were selected for electron microprobe analyses (EMPA), secondary-ion mass spectrometry (SIMS), HRTEM, and ATEM. The specimens for TEM observations (labeled γ lb and γ 2) were thinned to electron transparency by argon ion milling at low angle with a Gatan precision ion-polishing system (PIPS), and carbon coated to avoid electrostatic charging.

XRDT experiments were performed at the Dipartimento Geomineralogico, University of Bari, Italy, using a RIGAKU Lang diffractometer, operating at 50 kV and 12 mA, with MoK α_1 radiation. The thickness (t) of the (010) slices varied between about 0.3 and 1 mm, corresponding to operating conditions μ t ranging between 1.0 and 3.7 (where μ is 36.91 cm⁻¹, the linear absorption coefficient, calculated from the composition of Bt9568a). Topographs were recorded on ILFORD L4 nuclear plates, with emulsion thickness of 50 μ m. The spatial resolution of diffraction contrasts imaged on the topographs is about 2–3 μ m. Exposure time was about 60 h for each Bragg reflection.

EMPA data were acquired at the Earth Sciences Department, University of Milan, Italy, using a JEOL JXA 8200 Superprobe operating at 15 kV, 15 nA, and with a 5 µm beam size. All analyses were performed in wavelength-dispersive (WDS) mode. The analyzed elements on 16 spots were K, Na, Ca, Fe, Mg, Ti, Al, Mn, and Si. Natural and synthetic standards were used: omphacite USNM10607 and albite for Na; olivine USNM2566 for Mg; anorthite USNM137041 for Al; wollastonite for Ca and Si; K-rich feldspar PSU-Or1A for K; ilmenite USNM6189 for Ti; rhodonite for Mn; fayalite USNM85276 for Fe. All standards are calibrated within 0.5% relative at one standard deviation (1σ %). The counting times were 20 s at the peak and 10 s at each background. Raw data were corrected using a Phi-Rho-Z quantitative analysis program.

SIMS measurements were performed with a CAMECA IMS 4f ion microprobe installed at CNR-IGG, Pavia, Italy. A 12.5 kV accelerated 16O- primary-ion beam was used with a current intensity of 2 nA and about 3 um beam diameter. The sample-mount together with that of the standards was left to degas overnight in the ion-microprobe sample chamber. Secondary-ion signals of the following isotopes were monitored at the electron multiplier: 1H+, 7Li+, 9Be+, 19F+, 30Si+, and both the isotopes 35Cl+ and 37Cl+ for Cl. 30Si+ were used as the inner reference for the matrix. Acquisition times were 6 s (H and Li, each), 8 s (Be), 16 s (F), 30 s (35Cl+), 40 s (37Cl+), and 6 s (Si) over 2 analytical cycles. Detection of positive secondary ions in the range of 75-125 eV emission kinetic energies was obtained under steady-state sputtering conditions after 15 min of pre-sputtering. In accord with SIMS work on light elements in silicates, the analysis of "filtered" secondary ions is useful to reduce most chemical matrix effects and to improve the overall measurement reproducibility (Ottolini et al. 1993, 2002). Several medium-silica silicate standards were employed for the quantification of the ion signals for H, Li, (Be), and F: Finero phlogopite (40.04 wt% SiO₂, 4.20 wt% H₂O, 712 ppm F), schorl no.16, dravite no.18, and elbaite no.19 (Ottolini et al. 2002). Beryllium was mainly calibrated with a danalite sample and Cl with an international standard of scapolite, meionite, Brazil USNM R6600-1 (Scambelluri et al. 2004; Ottolini and Le Fèvre 2008). Residual bi-atomic interferences on Cl isotopes (if any) can be thus monitored by detecting both $^{35}\mathrm{Cl^{+}}$ and $^{37}\mathrm{Cl^{+}}$ signals and comparing the experimental ³⁵Cl^{+/37}Cl⁺ signal ratio with the theoretical abundance ratio. Additional inner CNR-IGG standards, represented by amphiboles, were also used to check for the accuracy of F and Cl.

The 16 SIMS spots were obtained close to the micro-areas investigated by EMPA; thus the SiO₂ (wt%) data were used in the final SIMS quantification procedures. Precision of the SIMS analysis, tested on the standards, is typically on the order of 1–2% relative (as 1 σ %), and accuracy is about 5% relative for Li, and 10% relative for H, F, Cl, and Be.

TEM investigations were performed at the Dipartimento Geomineralogico, University of Bari with a JEOL-JEM 2010 operating at 200 kV, with LaB₆ source, nominal point resolution of 2.0 Å, spherical aberration of 0.5 mm. A double-tilt specimen holder ($\pm 20^{\circ}$) was used. ATEM microanalyses were performed using an Oxford LINK energy dispersive X-ray spectrometer (EDS) with a Si(Li) detector and ultra-thin window. The elements O, Na, Mg, Al, Si, Cl, K, Ca, Ti, Mn, and Fe were measured and then quantified in the INCA spectrum analyzer software by using k-factors derived from EMPA and SIMS data. Care was taken to minimze elemental diffusion and to make results internally consistent. The electron nanoprobe was defocused on the analyzed areas (actual spot size area at the sample surface 0.07 μ m²) and the electron dose was maintained constant between locations by always using the same spot size, acquisition time (60 s), and mean counting rate (800 cps). Because the thickness involved is unknown and may vary between locations, chemical raw concentrations were corrected for thickness effects using the "electron neutrality criterion" (Van Cappellen and Doukhan 1994) to avoid any differential absorption among different analyses. Through a trial-and-error routine, we determined the unique thickness where the positive charge given by the cationic concentration equals the negative charge given by the anionic concentration. The absorption correction was applied consequently.

Images were recorded with a Gatan MSC794 CCD camera. To remove noise contrast from amorphous materials, HRTEM images were rotationally filtered (Kilaas 1998) with the HRTEM filter (Mitchell 2007), as implemented in the Gatan Digital Micrograph version 3.9.

In keeping with Kogure and Nespolo (1999) and Kogure (2002), to determine the polytypic stacking sequences, we recorded selected area electron diffraction (SAED) patterns and HRTEM images along [010] and [$\overline{1}10$], which are rotated 30° apart about **c***.

RESULTS

X-ray topography

X-ray diffraction topography showed similar results for each (010) slice. Consequently, XRDT results for one (010) slice are shown here as representative of the entire specimen. XRDT produces a map of the diffracted intensity variation for each Bragg reflection, which is shown as diffraction contrasts on the topographic image. Two topographs, each corresponding to a Bragg reflection, are shown in Figure 1. Variably spaced thinband diffraction contrasts indicate inhomogeneous features in the specimen that may relate to coexisting polytypes and/or to twins in contact through the (001) plane. In fact, the same diffraction vector (g) of each topograph in Figures 1a and 1b may correspond to different reflections in the axial settings of the homogeneous polytypes 1M, $2M_1$, and 3T, as shown by Table 1. Therefore, XRDT indicates inhomogeneities in the sample, but fails to discriminate among all possible solutions. Consequently, X-ray topographs were used as a guide to identify areas for TEM examination (γ 1b and γ 2 in Fig. 1a).

EMPA and SIMS analyses

The chemical composition of Bt9568a was analyzed by EMPA and SIMS techniques, the latter for H, Li, F, Cl, and Be, both using 16 spot determinations along a traverse crossing the entire (010) slice nearly parallel to **c***. No significant variation in concentration of the analyzed elements was observed for TEM specimens γ 1b and γ 2, with the exception of one spot with a closure percentage that is too low. The chemical composition was averaged for all but one spot, and the average formula, calculated on the basis of 12 (O,OH,F,Cl) atoms per formula unit (apfu) and assuming all Fe as Fe²⁺ and all Ti as Ti⁴⁺, is as follows: (K_{0.867}Na_{0.047}Ca_{0.008})_{D=0.922}(Fe²⁺_{1.358}Mg_{1.247}Ti_{0.220}Al_{0.140}Mn_{0.033} Li_{0.009})_{D=3.007}(Si_{2.836}Al_{1.164})_{D=4.000}O₁₀[(OH)_{1.535}O_{0.349}F_{0.095}Cl_{0.021}]_{D=2.000}. Trace amounts of Be (0.54 ppm, on average) were detected by SIMS analyses.

[010] SAED patterns and HRTEM images

Each SAED pattern along [010] from TEM specimens γ 1b and γ 2 was identical. No streaking along *h*0*l* rows was observed (Fig. 2a). The *h*0*l* rows, $h \neq 0 \pmod{3}$, show one reflection in the c_{1M}^* repeat, and the projections of the *h*0*l* and \overline{h} 0*l* reflections on the **c*** axis divide c_{1M}^* in thirds (Fig. 2a). Hence, the *h*0*l* reflections





FIGURE 1. X-ray diffraction topographs taken from a (010) slice of Bt9568a under two different (**a**) and (**b**) Bragg conditions. The indices of diffraction vectors **g** are listed in Table 1 for the different axial settings of 1M, $2M_1$, and 3T polytypes. (**a**) The sampling locus of TEM specimens γ 1b and γ 2 is within the white rectangles; the approximate location of the stacking arrangements $1M_r$ - $n(120^\circ)$, $2M_1$ highly faulted (h.f.), and 3T, as observed by HRTEM, is shown.

 TABLE 1.
 Indices of the diffraction vector g in the topographs of

 Figure 1 for the different axial settings of 1*M*, 2*M*₁, and 3*T*

 polytypes

	Fig. 1a	Fig. 1b
1 <i>M</i>	201	200
2 <i>M</i> ₁	204	202
3T	115	112

tions are subfamily-*A* reflections, and all the polytypic stacking sequences observed belong to subfamily-*A*.

Each HRTEM image viewed down [010] was identical also, conditions being equal, with the projections of the stacking vectors pointing to the right in Figure 2b. Each vector is indistinguishable from a stacking vector labeled "1," "3," or "5" in Figure 2c. The projection of their shifts viewed down [010] equals -a/6 for either stacking vectors 3 and 5, with the vectors pointing to the right (Fig. 2c), while the shift is +a/3 for stacking vector 1, pointing to the left. However, a shift of +a/3 to the left is equivalent to a shift of -a/6 to the right. Consequently, the [010] HRTEM images confirmed that all stacking sequences in the specimens belonged to the subfamily-A of mica polytypes, but we could not discriminate between stacking vectors 1, 3, and 5.

[110] SAED patterns and HRTEM images

To characterize the stacking sequences, stacking vectors must be viewed along a direction 30° from [010] around c^* , i.e.,



FIGURE 2. Each [010] SAED pattern (a) and HRTEM image (b) from γ 1b and γ 2 is identical, showing that all the stacking sequences observed belong to subfamily-*A* and are composed of various combinations of the stacking vectors 1, 3, and 5 (c). The latter are indistinguishable if viewed only down the (010) projection.

along [$\overline{1}10$] for the present case (Banfield and Murakami 1998; Kogure and Banfield 1998; Kogure 2002). Stacking vectors 1, 3, and 5 are discriminated on the [$\overline{1}10$] HRTEM images, where their projections point to the left (1), straight (s), and to the right (r), respectively, as shown by Figure 3 and Table 2.

SAED patterns and HRTEM images taken along [$\overline{1}10$] showed three stacking arrangements: (1) $1M_r$ - $n(120^\circ)$ rotational disorder; (2) highly faulted $2M_1$; and (3) perfectly ordered 3T. They are described separately in the following sections.

Disordered $1M_r$ - $n(120^\circ)$ **sequences.** The non-family reflections (Nespolo 1999) distinctive of each mica polytype are visible along the 11*l* and 22*l* rows of the SAED patterns taken along [$\overline{110}$]. For rotational disorder, with successive random rotations, such rows are semi-continuously streaked (Fig. 3a). Figures 3b and 4a enabled a reconstruction of disorder disorder disorder sequences $1M_r$ - $n(120^\circ)$. This type of disorder is dominant in both TEM specimens γ 1b and γ 2, although with some variations. Random unit cells of 3T, $2M_1$, and 1M (Fig. 3c), as well as partly random multiple repeats of 3T and $2M_1$ sequences, with 3T dominant, were observed (Fig. 4b). The Ross-Takeda-Wones (RTW) symbols (Ross et al. 1966) for the stacking sequences of Figures 3c and 4b are given in Table 3. A few repetitions of long-period stacking sequences were found within these $1M_r$ - $n(120^\circ)$ areas. For example, repetitions of a 9-layer [$(222)\overline{22}(2\overline{2})\overline{22}$] (Fig. 3c),

a 5-layer [(222)2 $\overline{2}$], and an 8-layer [(222)₂2 $\overline{2}$] sequence (Fig. 4b) are recognized. The stacking sequence of Figure 4b (see Table 3) is composed of two repetitions of a 21-layer sequence (2 $\overline{2}$)0[(222)₂2 $\overline{2}$][(222)2 $\overline{2}$]₂ with intercalation of one unit cell of $3T[\overline{2}\overline{2}\overline{2}]$. Thus, the disordered $1M_r$ - $n(120^\circ)$ areas are composed of a few repetitions of long-period stacking sequences, mainly based on the 3T structural series, with the intercalation of single unit cells of 1M and, mostly, $2M_1$.

Highly faulted $2M_1$ sequences. In one area of TEM specimen y1b, HRTEM images (Figs. 5a and 5b) show highly faulted stacking sequences (Figs. 6a and 6b), with corresponding RTW symbols in Table 3. These sequences are composed of variably long segments of the $[2\overline{2}]$ stacking sequence identified as the $2M_1$ polytype, broken-up by faults of ($\overline{2}2$). Figures 5 and 6 show the $[2\overline{2}]$ stacking sequence projected down [100]. The faults $(\overline{2}2)$ correspond to single layers of the $[2\overline{2}]$ stacking sequence in the [110] projection (Xu and Veblen 1995). Thus, this area is interpreted as a $2M_1$ highly faulted area twinned through [310] with respect to the host disordered matrix. The $(\overline{2}2)$ stacking faults are frequent and sometimes periodic. Locally, they occur in a few repetitions of long-period inhomogeneous polytypic sequences, based on the $2M_1$ structural series, as is the case of a 14-layer sequence that repeats twice in Figure 6a. Apparently, very long-period polytypic sequences were observed by bright



FIGURE 3. Semi-continuously streaked [$\overline{110}$] SAED pattern (**a**) and HRTEM image (**b**) of a rotationally disordered $1M_r$ - $n(120^\circ)$ area. Graphical representation of the sequence of 31 stacking vectors of the type 1, 3, and 5 (**c**), whose shift are drawn in **b**, from the bottom to the top (l = left; r = right; s = straight). The RTW symbol of this sequence is shown in Table 3.

field (BF) images (Fig. 7a), with a period so long (about 230 nm repeat) that a HRTEM investigation is difficult. The corresponding [$\overline{110}$] SAED pattern (Fig. 7b) shows reflections along the 11*l* and 22*l* rows simulating the non-family reflections of a 2-layer polytype, possibly $2M_1$, with the c_{1M}^* unit divided in two, and with an intensity modulation with maxima at the $2M_1$ diffraction positions. Higher magnifications (Fig. 7c) show that those rows are composed by many partially resolved spots.

Long-range ordered 3*T* **sequences.** TEM specimen $\gamma 2$ shows the 11*l* and 22*l* rows of a [110] SAED pattern of non-family reflections characteristic of the homogeneous polytype 3*T*, with perfectly resolved, periodically repeating and equally

spaced spots, with three reflections within the c_{1M}^* repeat (Fig. 8a). These non-family reflections of the polytype 3T have equal intensity also (Fig. 8a), at least under non-kinematical conditions

 TABLE 2.
 Magnitude and directions of the six stacking vectors, as viewed down [010] and [110] (r = right; l = left; s = trained)

S	traight)										
Observation		Stacking vectors									
direction	1		2		3		4	5		6	;
[010]	-a/6 (+a/3)	r (I)	+a/6	Ι	<i>-a</i> /6	r	+a/6 (-a/3) (r)	<i>-a</i> /6	r	+a/6	i I
[110]	+b/6	ï	+ <i>b</i> /6	Ι	0	s	<i>-b</i> /6 r	- <i>b</i> /6	r	0	s
Notes: Equiva	alent trai n bold.	nslat	tions witl	hin	paren	the	eses. Stacki	ing rela	te	d to t	he



(i.e., for thick crystal areas). This observation is important to distinguish 3T from the common $<3\overline{10}>$ triple twinning of the 1M polytype. However, all doubts are eliminated by the corresponding HRTEM image (Fig. 8b) showing the ordered [222] stacking sequence of the 3T polytype, which repeats with no faults over large distances of several micrometers.

FIGURE 4. [$\overline{1}10$] HRTEM image (**a**) and graphical representation (**b**) of an other $1M_r$ - $n(120^\circ)$ sequence of 46 stacking vectors of the type 1, 3, and 5. The RTW symbol of this sequence is shown in Table 3.



TEM-EDS analyses (ATEM)

The results of TEM-EDS analyses on $\gamma 2$ for an ordered 3Tand an adjoining disordered $1M_r$ - $n(120^\circ)$ sequence are plotted in Figure 9 for comparison of the analyzed elements. The unique chemical composition of the ordered 3T stacking was also compared to the $2M_1$ highly faulted (h.f.) area from the γ lb TEM specimen (right portion in Fig. 9). Care was taken to minimize elemental diffusion and to make results comparable, as described above.

Chemical differences among the three areas were observed. The long-range-ordered 3T stacking is markedly enriched in interlayer cations (K and Na) compared to disordered $1M_r$ - $n(120^\circ)$ and $2M_1$ highly faulted regions. The 3T area is depleted in Si compared to the $2M_1$ highly faulted area. The consistent enrichment in total interlayer cations (Fig. 9), and consequently in the interlayer mean charge, of the 3T ordered area is compensated by a depletion in Si and octahedral cations, and thus by a lower mean charge in the tetrahedral and octahedral sites, resulting in a balanced formula. This observation is limited by the sensitivity of the EDS technique and the inability to analyze H, F, and Li, known to be present from the SIMS analyses. Also, differences in oxidation state of iron may affect the different studied areas.

DISCUSSION

Ideally, polytypism should be a one-dimensional polymorphism, where the only structural difference between two modifications is the stacking sequence. However, the chemical composition is not necessarily fixed for polytypic minerals with complex compositions, such as micas. Polytypism arises from the structural features of micas (see Ferraris and Ivaldi 2002 for a review), i.e., from the ideally hexagonal symmetry of the tetrahedral ring, leading to six possible stacking vectors rotated by 60° from one another about c^* . The different sequences of these stacking vectors produce different polytypes. Biotite

TEM sample	Polytype	Figure	RTW symbol of the stacking sequence
γ1b and γ2	1 <i>M_i-n</i> (120°): random unit cells of 3 <i>T,</i> 2 <i>M</i> ₁ , and 1 <i>M</i>	3c	[(222)22(22)22] ₂ (222)20(22)2 (22)020
	1 <i>M</i> r- <i>n</i> (120°): partly random repeats of 2 <i>M</i> ₁ , 1 <i>M</i> , 8 <i>M</i> ₈ , 5 <i>M</i> and 3 <i>T</i>	4b	$(2\overline{2})0[(222)_22\overline{2}][(222)2\overline{2}]_2(\overline{2}\overline{2}\overline{2})$ (2\overline{2})0[(222)_22\overline{2}][(222)2\overline{2}]_2
γ1b	2 <i>M</i> ₁ highly faulted	ба	$[(2\overline{2})\overline{2}2(2\overline{2})_4\overline{2}2]_2\overline{2}2(2\overline{2})\overline{2}2(2\overline{2})$
		6b	$(2\overline{2})_{3}\overline{2}2(2\overline{2})_{2}\overline{2}2(2\overline{2})\overline{2}2(2\overline{2})_{6}\overline{2}2$ (2\overline{2})_{4}\overline{2}2
γ2	3T ordered	8	[222]

TABLE 3. RTW symbols of the stacking sequences

samples from both igneous and metamorphic regimes often consist of several coexisting polytypes. Most common is 1Mfollowed by $2M_1$, and inhomogeneous (complex) forms. Disordered $1M_t$ - $n(120^\circ)$ layer stacking sequences are also common. On diffraction patterns, this rotational disorder is identified by continuous to semi-continuous streaking along the $k \neq 3n$ rows parallel to c^* . This streaking, especially when accompanied by sharp sub-cell spots, is frequently unresolved periodic stacking faults possibly related to long-period inhomogeneous polytypes (Ross et al. 1966).

For Bt9568a, the absence of streaking along h0l rows of [010]

32 - s

31 - I 30 - r 29 - I

28 - r 27 - l 26 - r 25 - l

23 - I 22 - r

21 - 1

20 - r

19 - I 18 - s

17 - 1

16 - r 15 - I 14 - s 13 - I

12 - 1

11 - 1

10 - r

9-1

8 - s

7 - 1

6 - r

5-1

b

4







FIGURE 6. Graphical representation of the $2M_1$ highly faulted sequences of 38 (a) and 42 (b) stacking vectors derived from the HRTEM images of Figures 5a and 5b, respectively. The RTW symbol of these sequences are shown in Table 3.

SAED patterns (Fig. 2a) indicates the absence of mixed-rotation subfamily polytypes (Kogure and Nespolo 1999). Therefore, reflections along *h0l* rows are family reflections (Nespolo 1999) of either subfamily-*A* or subfamily-*B* polytypes (Backhaus and Ďurovič 1984; Ďurovič et al. 1984). The *h0l* rows, $h \neq 0$ (mod 3), show one reflection in the c_{M}^* repeat (Fig. 2a). This is characteristic of subfamily-*A* polytypes (Kogure and Nespolo 1999). Hence, the *h0l* reflections are subfamily-*A* reflections, and all the polytypic stacking sequences observed belong to subfamily-*A*: $1M_t$ - $n(120^\circ)$, $2M_1$ highly faulted, and 3T stacking arrangements were found.

The $1M_r$ - $n(120^\circ)$ stacking sequences of Figures 3c and 4b are not completely disordered, as shown by the [$\overline{1}10$] SAED pattern (Fig. 3a), where the $k \neq 3n$ rows parallel to c^* are not highly streaked. This result indicates that the stacking faults are neither so frequent nor completely random, and semi-periodic. A few repetitions of long-period stacking sequences were found, e.g., a 5-layer [$(222)2\overline{2}$] and an 8-layer [$(222)_22\overline{2}$] sequence (Fig. 4b). The latter two sequences are identified as inhomogeneous polytypes (Zvyagin 1988) 5*M* and 8*M*₈, respectively, both belonging to the 3*T* structural series (see Rieder 1970; Ross et al. 1966). Thus, the disordered 1*M*_r- $n(120^\circ)$ areas are composed of a few repetitions of long-period stacking sequences, mainly based on the 3*T* structural series, with the intercalation of single unit cells of 1*M* and, mostly, 2*M*₁.

BF images from the $2M_1$ highly faulted area of Bt9568a (Fig. 7a) show a few (2 or 3) repetitions of an apparent very long-period polytypic sequence, based on the $2M_1$ structural series. The corresponding [$\overline{1}10$] SAED pattern (Fig. 7b) show an intensity modulation with maxima at the $2M_1$ diffraction posi-



FIGURE 7. Apparent very long period inhomogeneous stacking sequences, based on the $2M_1$ structural series, near the $2M_1$ highly faulted region. (a) BF image showing the partly periodic stacking faults: the white angles outline two, maybe three, repetitions of the same long-period stacking sequence; (b) [$\overline{110}$] SAED pattern with camera length L = 30 cm, showing a modulation of intensity distribution, with maxima at the $2M_1$ diffraction positions; (c) the same [$\overline{110}$] SAED pattern as in **b**, but with L = 200 cm, showing many partially resolved reflections.



FIGURE 8. [$\overline{110}$] SAED pattern (a) and perfectly aligned atomic-structure HRTEM image (b) of a long-range-ordered 3T region with about 3 nm periodicity along the c axis. The RTW symbol of its stacking sequence is shown in Table 3.

tions. However, we cannot assess that this sequence identifies a long-period polytype because there is no clear evidence that it repeats at least three times (see Fig. 7a). Overall evidence of really periodic long-range sequences is lacking, at least at the present time. Consequently, the validity of long-period polytypes vs. non-periodic highly faulted $2M_1$ sequences is questionable.

The bulk composition of Bt9568a has been determined by EMPA and SIMS data. Based on Rieder et al. (1998), Bt9568a is a magnesian annite, slightly interlayer-deficient, with a low Li content and a relatively high Ti content, and (OH),F,Cl deficient ($\Sigma = 1.65$ apfu) and oxygen enriched ($\Sigma = 10.35$ apfu). This result is likely related to incorporation of Ti either by means of Ti-oxy substitution ^{VI}M²⁺ + 2(OH)⁻ \rightarrow ^{VI}Ti⁴⁺ + 2O²⁻ + H₂↑, or by Ti-Tschermak substitution ^{VI}M²⁺ + 2^{IV}Si⁴⁺ \rightarrow ^{VI}Ti⁴⁺ + 2^{IV}Al³⁺. High Ti concentrations are common in Fe-rich reddish brown biotites and may be indicative of high temperature, low pressure, and/or high-oxygen fugacities (Henry and Guidotti 2002).

The local composition associated with the different stacking arrangements of Bt9568a has been determined by ATEM. Following Baronnet et al. (1993) and Xu and Veblen (1995), we suggest that the compositions relating to the stacking sequences observed here reflect a structural response to fluctuations of the fluid composition at the crystallization front. We suggest here that the long-range-ordered 3T stacking is favored over disordered sequences by increased concentration of K and Na interlayer cations in the fluid. The stacking sequences and compositions may be related to the geometric constraints the 3T unit-layer places on adjacent unit-layers of the 3T ordered sequence with respect to those of disordered sequences (i.e., Güven 1971; Weiss et al. 1992; Amisano-Canesi et al. 1994). For the specimen studied here, the nature of the stacking induced distortions is not precisely known because a detailed crystal structure analysis is lacking. However, the varying ratio of (Na + K) to interlayer-vacancies would presumably play a crucial role in the occurrence of the

anfu	Na										anfu	Ся									
0.30		3 <i>T</i>		1 <i>M</i>	r-n (120°)		2 <i>M</i> ₁	h.f.		0.15		3 <i>T</i>		1 <i>M</i>	r -n (1	120°)		2 <i>M</i>	_l h.f.	
0.20	0.09 호	0.10 호	0.11 조	0.03 호	0.03 ହ	0.02 •	0.02 호	0.02 호	0.00 조		0.05	0.01	0.01 호	0.01 호	0.02 호	0.00 &	0.01 호	0.02 호	0.00 호	0.00 호	
-0.10	0 1	2	3	4	5	6	7	8	9	10	-0.05 ‡	1	2	3	4	5	6	7	8	9	10
apfu	К										apfu	ı (Na+ŀ	K+Ca)							
1.40	-	1.08	1.03	1 <i>M</i>	_r -n (1	20°)		2 <i>M</i> ₁	h.f.		1.40	- 1.08	1.19 §	1.15 조	1 <i>M</i>	r-n (120°)		2 <i>M</i> ₁	h.f.	
1.00	- \$	∑3T	₹	0.89 T	0.79 호	0.83	0.72 호	0.76 호	0.75 •		1.00	-	3 <i>T</i>	1	0.94 &	0.82	0.86 호	0.76 호	0.78 호	0.75 •	
0.00 4	1	2	3	4	5	6	7	8	9	10	0.00 4) 1	2	3	4	5	6	7	8	9	10
apfu	Si										apfu l	Mg									
4.00	-	3 <i>T</i>		1 <i>M</i>	_r -n (1	20°)		2 <i>M</i> ₁	h.f.		2.20 1.80		3 <i>T</i>		1 <i>M</i>	r-n (120°)	2	2 <i>M</i> ₁ ł	ı.f.	
3.00 2.50	2.62	2.69 5	2.74 ହ	2.74 호	2.79 •	2.75 •	2.95 X	2.97 호	2.88		1.40 1.00	1.17 호	1.17 호	1.21 호	1.31 호	1.23 호	1.22 T	1.14 호	1.10 ক	1.17 호	
2.00 4) 1	2	3	4	5	6	7	8	9	10	0.60	0 1	2	3	4	5	6	7	8	9	
apfu	Al										apfu l	Fe									_
2.40 2.00	-	3 <i>T</i>		1 <i>M</i>	_r -n (1	20°)		2 <i>M</i> ₁	h.f.		2.10 1.90		3 <i>T</i>		1 <i>M</i>	[_r -n (120°)		2 <i>M</i> ₁	h.f.	
1.60 1.20	1.39	1.31 호	1.25 •	1.16 호	1.28 호	1.30 호	1.23 호	1.21 호	1.25 호		1.70 1.50 1.30	1.42 호	1.37 호	1.34 호	1.45 T	1.37 호	1.40 \\$	1.29 호	1.34 T	1.34 \S	
0.80 4	1	2	3	4	5	6	7	8	9	10	1.10 -	0 1	2	3	4	5	6	7	8	9	
apfu	Ti										apfu l	Mn									
0.60	-	3 <i>T</i>		1 <i>M</i>	_r -n (1	20°)		2 <i>M</i> ₁	h.f.		0.15		3 <i>T</i>		1 <i>M</i>	[_r -n (120°)		2 <i>M</i> 1	h.f.	
0.40 0.30 0.20	0.24	0.23 •	0.22 •	0.25 호	0.22 §	0.22 §	0.21 호	0.19 •	0.22 •		0.05	0.05 &	0.03 •	0.05 •	0.04 호	0.05	0.04 호	0.01 호	0.02 호	0.01 호	
0.10	1	2	3	4	5	6	7	8	9	10	-0.05	0 1	2	3	4	5	6	7	8	9	10
apfu	0										apfu	Cl									
15	-	3 <i>T</i>		1 <i>M</i>	_r -n (1	20°)		2 <i>M</i> ₁	h.f.		0.15		37		1 <i>M</i>	_r -n (120°)		2 <i>M</i> ₁	h.f.	
13	- 10.97 - 호	10.97 &	10.97 •	11.00 호	10.98 &	10.99 ক	10.99 조	0 10.97 호	10.97 •		0.05	0.03	0.03	0.03	0.00 •	0.02	0.01 •	0.01 호	0.03	0.03	
9+) 1	2	3	4	5	6	7	8	9	10	-0.05 -	0 1	2	3	4	5	6	7	8	9	10

FIGURE 9. Diagrams comparing the ATEM microchemical compositions of the three distinct types of stacking arrangements observed: 3T on the left, $1M_r$ - $n(120^\circ)$ in the middle, and $2M_1$ highly faulted (h.f.) on the right, respectively. Concentrations of all the analyzed elements are expressed by atoms per formula unit (apfu). Accuracy of measurements is at $\pm 1\sigma$ apfu.

stacking arrangements. These observations suggest that 1M, $2M_1$, and 3T structures are not ideally polytypic in biotite.

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