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Article in *European Journal of Mineralogy* · November 2001

DOI: 10.1127/0935-1221/2001/0013-1013

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# First structure determination of an MDO-2O mica polytype associated with a 1M polytype<sup>1</sup>

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**Abstract:** The structure refinement of associated phlogopite-2O and phlogopite-1M from the Khibiny massif (Kola Peninsula, Russia) is reported. Crystal data are:  $a = 5.2781(5)$ ,  $b = 9.141(1)$ ,  $c = 20.124(4)$  Å,  $Ccmm$  (2O);  $a = 5.305(2)$ ,  $b = 9.199(2)$ ,  $c = 10.232(4)$  Å,  $\beta = 100.03(2)^\circ$ ,  $C2/m$  (1M). Least-squares refinement of single-crystal X-ray diffraction data converged to  $R1 = 0.034$  (2O, 926 independent reflections) and 0.037 (1M, 677 independent reflections). This is the first structure refinement of an MDO (standard) mica-2O: two previous structure reports concerned anandite-2O, which was not a true polytype, having an  $oP$  (primitive orthorhombic) lattice not compatible with the  $C$ -centred cell common to all mica polytypes. The two phlogopite polytypes show practically the same chemical composition ( $K_{0.95}Na_{0.01})(Mg_{2.16}Fe_{0.34}Ti_{0.04}Mn_{0.04}Li_{0.40})[Si_{3.40}Al_{0.60}O_{10}][OH]_{1.35}F_{0.65}$ ) and no cation ordering. Both polytypes are affected by stacking disorder, which broadens the non-family reflections ( $k \neq 3n$ ). As a consequence, the diffracted intensities of the two types are measured at different scales and large residues in the difference Fourier maps were observed at  $\pm b/3$  along [010], [310] and  $[3\bar{1}0]$ . These residues (*Durovic effect*) disappear by carrying out the refinement with separate scale factors for the two types of reflections. On the basis of structural, morphology and zoning considerations the formation of the two associated polytypes is attributed to chemical oscillation in the crystallization mean.

**Key-words:** phlogopite-2O, phlogopite-1M, crystal structure, polytypism, stacking disorder.

## Introduction

Mica polytypes are built by stacking an M unit layer (also known as *TOT* or 2:1 layer) through local symmetry operations, *i.e.* space-groupoid operations. Successive layers are differently oriented, and the relative rotations about  $c^*$  are  $n \times 60^\circ$  ( $0 \leq n \leq 5$ ). The unit M layer consists of a pair

of packets of opposite polarity (each packet corresponding to half an M layer plus half the plane of the interlayer cations: Durovic, 1974; Dornberger-Schiff *et al.*, 1982) and is usually described as built by an octahedral (*O*) sheet sandwiched between a pair of tetrahedral (*T*) sheets with opposite polarity, stacked along  $c$  and ideally staggered by  $|a|/3$  in the (001) projection. Two translationally indepen-

<sup>1</sup> Dedicated to Professor Boris B. Zvyagin, in occasion of his 80th birthday, for his pioneering contributions to the polytypism of layer silicates.

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dent cation sites (*T* sites) are present in each *T* sheet, and three (*M* sites) in the *O* sheet. Of the latter, one (*M1*) has two OH groups in *trans*, whereas the other two sites (*M2* and *M3*) have two OH groups in *cis*. Besides the common classification in tri- and dioctahedral micas, on the basis of the occupancy of the three octahedral sites, micas are classified into three families: *homo-octahedral* (all the three *M* sites have the same cation content), *meso-octahedral* (one *M* site is differently occupied from the other two), and *hetero-octahedral* (all the three *M* sites are differently occupied). In these three families the idealised layer symmetry ( $\lambda$ -symmetry) of the *O* sheet is  $H\bar{3}1m$ ,  $P\bar{3}1m$ , and  $P312$  respectively (Dornberger-Schiff *et al.*, 1982; the layer-group notation is given according to Dornberger-Schiff, 1959).

The ideal  $\lambda$ -symmetry of the *T* sheet is  $P(6)mm$  (Pauling model), but in real cases the so-called ditrigonal rotation  $\alpha$  of the tetrahedra about  $c^*$  reduces the  $\lambda$ -symmetry to  $P(3)1m$  (Trigonal model). Within the Trigonal model, each family of mica polytypes is subdivided into three groups: *subfamily A polytypes* [only  $2n \times 60^\circ$  rotations], *subfamily B polytypes* [only  $(2n+1) \times 60^\circ$  rotations], and *mixed-rotation polytypes* [both  $2n \times 60^\circ$  and  $(2n+1) \times 60^\circ$  rotations] (Backhaus & Đurovic, 1984; Đurovic *et al.*, 1984; Nespolo, 1999). Polytypes in which pairs, triples, quadruples *etc.* of packets are geometrically equivalent (or, when this is not possible, they contain the smallest number of *n*-ples) are termed *Maximum Degree of Order* (MDO). The ideal space-group types of the six homo-octahedral MDO polytypes are:  $C2/m$  (*1M*);  $C2/c$  ( $2M_1$  and  $2M_2$ );  $P3_1212$  (*3T*);  $Ccmm$  (*2O*);  $P6_1,522$  (*6H*). In the meso- and hetero-octahedral families, the symmetry of a mica polytype can be lowered to a subgroup of the ideal homo-octahedral space-group type because of cation ordering and the number of MDO polytypes increases (Backhaus & Đurovic, 1984).

Subfamily A polytypes are by far more common and among them *1M* and  $2M_1$  are the most abundant in trioctahedral and dioctahedral micas, respectively. The *3T* polytype occurs particularly for phengitic compositions, ideally  $KAl_{1.5}(Mg,Fe)_{0.5}[Si_{3.5}Al_{0.5}O_{10}](OH)_2$  (see Ivaldi *et al.*, 2001); its occurrence in trioctahedral micas is also known (*e.g.* Ross *et al.*, 1966), but the small number of structural reports might be due to difficulty of distinguishing it from a three-individual twin of *1M* ("apparent polytypism": Takano & Takano, 1958). Subfamily B polytypes are rarer and *6H* is so far unknown;  $2M_2$  occurs mainly in lepidolites (*e.g.* Guggenheim, 1981). A 'non-ortho-

dox' *2O* polytype has been reported in anandite,  $BaFe^{2+}_3[Si_3Fe^{3+}O_{10}](OH)_S$ , from Sri Lanka and structurally refined (Giuseppetti & Tadini, 1972; Filut *et al.*, 1985) in the space-group type  $Pn\bar{m}n$ . Because of ordering between S and OH, neither the structure nor its building layers can be described on the basis of the *C*-centred cell common to all mica polytypes: this anandite does not represent a true mica polytype. The presence of S seems essential to stabilise the structure, which shows coordination 13 for Ba in the interlayer (12 O plus S). A *2O* polytype has been reported in a synthetic fluor-phlogopite (Sunagawa *et al.*, 1968), on the basis of surface observation only (the space-group type was not investigated), and a short *2O* sequence has been observed by High Resolution Transmission Electron Microscopy (HRTEM) in a matrix of a magnesian annite (Kogure & Nespolo, 1999a). Lazarenko *et al.* (1978) observed by electron diffraction associated *2O* and *1M* polytypes of lepidolite,  $(K_{1.03}Na_{0.01}Rb_{0.02}Ca_{0.02})(Li_{1.49}Al_{0.89}Fe^{3+}_{0.05}Fe^{2+}_{0.39}Mg_{0.03}Ti_{0.02})(Si_{3.58}Al_{0.42}O_{10})F_{1.59}(OH)_{0.41}$ , within fine-lamellar aggregates; no crystal data were reported.

## Experimental

In pegmatitic samples from the Khibiny massif (Mt. Koashva, Kola Peninsula, Russia) rare crystals of *2O* associated with more abundant *1M* polytype have been discovered. The two polytypes occur, with nacaphite, as dispersed millimetric crystals in masses of natrite and thermonatrite from which were recovered by water dissolution. The shown morphology is unusual, being the crystals quite equidimensional with respect to the usual {001} tabular shape of mica crystals; the most developed forms are {110} in *2O* and {100} plus {010} in *1M*. The well developed morphology of the phlogopite crystals indicates a primary genesis. The Khibiny pluton already gave another rare polytype, the non-MDO biotite-3A<sub>1</sub> (Borutskiy *et al.*, 1987). The macroscopic association in nature of mica polytypes is not common (see Ivaldi *et al.*, 2001) and can have petrologic meaning (Sassi *et al.*, 1994); even larger is the interest if one of the associated polytypes corresponds to the already unknown 'orthodox' *2O*.

The microprobe chemical analysis (Modena University; wavelength-dispersive ARL-SEM-Q electron microprobe; 15 kV accelerating voltage, 20 nA sample current) given in Table 1 refers to the *1M* crystal used for X-ray data collection.

Table 1. Average (5 point analyses) and range of the microprobe chemical analysis (wt %) of phlogopite with the standards.

Oxide	wt %	range of wt %	standard
SiO <sub>2</sub>	48.49	46.16-50.55	Clinopyroxene
TiO <sub>2</sub>	0.88	0.81-0.96	Ilmenite
Al <sub>2</sub> O <sub>3</sub>	7.18	5.84-8.45	Spessartite
FeO	5.71	4.44-7.15	Ilmenite
MgO	20.61	20.44-20.76	Olivine
MnO	0.62	0.47-0.76	Spessartite
CaO	0.00	0.00-0.01	Clinopyroxene
BaO	0.01	0.00-0.04	Paracelsian
Na <sub>2</sub> O	0.05	0.03-0.07	Albite
K <sub>2</sub> O	10.70	10.25-10.85	Microcline
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.00-0.03	Chromite
S	0.03	0.00-0.05	FeS <sub>2</sub>
Li <sub>2</sub> O*	1.40	-	-
F	2.91	1.5-3.60	Fluorite
Fl <sub>2</sub> O*	2.88	-	-
Total	101.49		
	- F = O = 1.22		
Total	100.27		

\*calculated

Table 2. Miscellaneous data collection and structure refinement information for the 2O and 1M-polytype of phlogopite.

Parameters	2O	1M
<i>a</i> (Å)	5.2781(5)	5.305(2)
<i>b</i> (Å)	9.141(1)	9.199(2)
<i>c</i> (Å)	20.124(4)	10.232(3)
$\beta$ (°)	90	100.03(2)
<i>V</i> (Å <sup>3</sup> )	970.9(4)	491.7(4)
Space-group type	<i>Ccmm</i>	<i>C2/m</i>
<i>Z</i>	4	2
Abs. Coef. (mm <sup>-1</sup> )	1.79	1.78
F(000)	838.8	419.4
D <sub>calc</sub> (g/cm <sup>3</sup> )	2.827	2.815
Crystal size (mm)	0.24x0.16x0.06	0.20x0.16x0.07
Radiation/monochrom.	MoK $\alpha$ / graphite	MoK $\alpha$ / graphite
Scan mode	$\omega$	$\omega$
2 $\theta$ -range (°)	69.90	59.98
R(int)	0.039	0.047
Reflections collected	4313	1568
Independ. Reflections	1157	757
[F <sub>o</sub> ] > 4 $\sigma$ ([F <sub>o</sub> ])	926	677
Refinement method	Full-matrix LS on F <sup>2</sup>	Full-matrix LS on F <sup>2</sup>
Weight <sup>§</sup>	a = 0.0415 b = 1.47	a = 0.0736 b = 0.28
Goodness of fit on F <sup>2</sup>	1.108	0.999
R1 [[F <sub>o</sub> ] > 4 $\sigma$ ([F <sub>o</sub> ])]	0.034	0.037
R1 (all data)	0.047	0.041
WR2	0.092	0.100

$$^{\S}\text{weight} = 1/[\sigma(F_0^2) + (aP)^2 + bP], \text{ where } P = [\max(F_0^2) + 2(F_c^2)]/3$$

We preferred to keep entire the “rare” 2O crystal used for X-ray data collection; a semiquantitative test on another poorly crystalline 2O grain showed values close to those reported for 1M. In all analyses, an apparent large deficiency of octahedral

cations is observed. A qualitative test by Atomic Absorption Spectrophotometry (FMD4 “Opton”) clearly showed the presence of abundant Li. Supposing that Li represents the missing octahedral cations (see the structural refinement below),

the following crystal-chemical formula is obtained for the data of Table 1, on the basis of (11.35O + 0.65F), *i.e.* 22.35 negative charges:

$(K_{0.95}Na_{0.01})_{\Sigma 0.96}(Mg_{2.16}Fe_{0.34}Ti_{0.04}Mn_{0.04}Li_{0.40})_{\Sigma 2.98}[Si_{3.40}Al_{0.60}O_{10}][OH]_{1.35}F_{0.65}]_{\Sigma 2.00}$ . The range of composition shows (Table 1) chemical zoning for most elements (except Mg and K). That for sure has negative consequences in estimating the Li content, whose uncertain value is further discussed in the structural section. The present Khibiny mica is the first litian phlogopite reported from the Khibiny-Lovozero complex; it can be classified (Rieder *et al.*, 1998) as a solid solution of phlogopite,  $KMg_3[Si_3AlO_{10}](OH)_2$ , with minor annite,  $KFe^{2+}_3[Si_3AlO_{10}](OH)_2$ , and tainiolite,  $KLiMg_2[Si_4O_{10}]F_2$ .

Four (2O) and two (1M) sets of equivalent X-ray single-crystal diffraction intensities have been collected (Siemens P4 diffractometer) on a crystal for each polytype and cell parameters have been obtained by least-squares refinement of 26 reflections (Table 2, together with experimental and refinement data). In both polytypes, the non-family ( $k \neq 3n$ ) are broader than the family ( $k = 3n$ ) reflections, an indication of some degree of disorder as discussed below.

In general, for 1M (non-orthogonal) and 2O (orthogonal) twins by reticular pseudo-merohedry

and by pseudo-merohedry respectively can be expected, where the obliquity  $\omega$  is a function of the deviation from the orthohexagonal relation  $b/a = 3^{1/2}$  (Nespolo *et al.*, 2000). In our samples the orthohexagonal relation is obeyed by the cell parameters (Table 2) within the experimental error, and thus an almost perfect hexagonal lattice (2O) or sublattice (1M) is present. It follows that the twin obliquity is zero and twins by reticular merohedry and metric merohedry would be possible for 1M and 2O respectively (Nespolo & Ferraris, 2000); however, such twins have not been found in the limited number of crystals we have tested.

### Data treatment

The crystal structures of both polytypes have been anisotropically refined by using the SHELX-97 package (Sheldrick, 1997). The main indicators of the refinements are reported in Table 2; the positional and displacement atomic parameters are shown in Table 3. The symmetry of the space-group types implies only one independent tetrahedral site and two independent octahedral sites in both polytypes. While the electron contents of the T site has been kept (after testing) at the Si/Al ratio required by the chemical analysis (0.85Si + 0.15Al), those of the M and I sites have been

Table 3. Number of electrons per site (*el*, when refined), atomic content, atom positions (*xyz*) and isotropic equivalent displacement factors ( $U_{eq}$ ) ( $\times 10^4$ ) for the 2O-(1<sup>st</sup> line) and the 1M-polytype (2<sup>nd</sup> line) of phlogopite; *esd*'s in parentheses.

<i>el</i>	<i>Atomic content</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>	
<i>T</i>	0.85Si + 0.15Al	0.16620(9)	0.16668(4)	0.13564(2)	86(1)	
	0.85Si + 0.15Al	0.0762(1)	0.16676(6)	0.22871(6)	85(3)	
<i>M1</i>	11.7(1)	0.68Mg + 0.11Fe + 0.21Li	0	0	105(3)	
	12.2(1)	0.72Mg + 0.12Fe + 0.16Li	0	1/2	106(5)	
<i>M2</i>	11.5(1)	0.66Mg + 0.11Fe + 0.23Li	0	0.66627(9)	106(3)	
	12.0(1)	0.71Mg + 0.11Fe + 0.18Li	0	0.3337(1)	123(5)	
<i>K</i>	18.8(1)	0.97K + 0.03Na	0.6662(2)	0	326(3)	
	18.8(1)	0.97K + 0.03Na	0	1/2	366(5)	
<i>O1</i>		0.1550(4)	0	0.16637(9)	181(4)	
		0.0419(5)	0	0.1676(8)	198(5)	
<i>O2</i>		0.4215(2)	0.2448(2)	0.16636(6)	182(3)	
		0.3127(3)	0.2432(2)	0.1675(1)	196(4)	
<i>O3</i>		0.1660(2)	0.1667(1)	0.05551(6)	115(2)	
		0.1298(3)	0.1670(1)	0.3895(1)	109(4)	
<i>OH/F</i>	8.4(1)	0.6(OH) + 0.4F	0.6681(4)	0	0.05185(8)	131(4)
	8.6(1)	0.4(OH) + 0.6F	0.1330(4)	1/2	0.3968(2)	137(7)
<i>H</i>		0.655(9)	0	0.088(3)	300	
		0.112(9)	1/2	0.301(5)	300	

refined (Table 3). For the *M* sites a mixed 0.86Mg + 0.14Fe (Mg/Fe ~ 6 as in the chemical analysis) scattering curve against the Li scattering curve has been used. The higher values of *R* and estimated standard deviations (*esd*'s) observed for the 1*M* polytypes are related to a higher degree of disorder present in this polytype (see below) and to a smaller limiting  $\sin\theta/\lambda$  value used in the data collection.

In both polytypes, the most striking feature of the refinement is the presence of large residues in the Fourier difference maps. The highest electron (*el*) residue is on the *m* mirror plane with the same *z* coordinate of the *T* cations (5.0 *el* for 1*M* and 2.9 *el* for 2*O*) and occurs at the centre of the pseudo-hexagonal rings in the tetrahedral sheet, with shifts  $\pm b/3$  from the *T* position along the directions [010], [310] and  $[\bar{3}\bar{1}0]$ . The next-highest residues occupy (i) one independent position on the two fold axis in the plane of the interlayer cations (2.4 *el* for 1*M* and 1.3 *el* for 2*O*) and (ii) three general independent positions (2.6 *el* in total for 1*M* and 1.5 *el* in total for 2*O*) in the plane of the basal oxygen atoms, again with the same  $\pm b/3$  shifts given above. Similar electron residues have been reported for plutonic 1*M* biotites and have been interpreted as the consequence of [310] or  $[\bar{3}\bar{1}0]$  microtwins (Brigatti & Davoli, 1990), but this interpretation should be reconsidered (see Nespolo & Ferraris, 2001).

In the refinement procedures, the observed residues have been taken into account in two ways.

(i) Assuming they quantitatively represent the images of coherent structural disorder due to the occurrence of stacking faults corresponding to *M* layers rotated by  $\pm 120^\circ$  rotations with respect to the orientation expected in the unfaulted matrix. In case of homo-octahedral micas like ours, these rotations cannot be distinguished from  $\pm b/3$  slips in the octahedral sheet (*crystallographic slips*: Takéuchi & Haga, 1971), which modify the orientation of one of the OD packets of the *M* layer. If these slips occur in pairs on the two sides of the interlayer, the latter preserves its coordination polyhedra. Instead, single un-recovered slips destroy the coordination of the interlayer and produce vacancies in the interlayer, giving rise to talc-like layers (for details see Nespolo, 2001; Nespolo & Ferraris, 2001).

(ii) Assuming they are essentially an artefact deriving from a broadening (including streaks) of the non-family reflections, as a consequence of random stacking disorder. This effect, as shown by Đurović and co-workers (Đurović, private

communication; Smrcok *et al.*, 1994; Hybler *et al.*, 2000), may cause loss of intensity in the measure of the non-family reflections and essentially put them on a scale different from that of the family reflections. This drawback can be overcome by applying separate scale factors to family and non-family reflections. The occurrence of spurious peaks in the Fourier map as a result of constraining all the reflections to a single scale factor is the so-called *Đurović effect* and is discussed in a companion paper by Nespolo & Ferraris (2001).

In both cases and for both polytypes the structural parameters and the refinement indicators converged to the same values within  $3\sigma$  (3 times the *esd*'s); in Table 3 the average values obtained from the two refinements are reported for the structural parameters. The scale factor to be applied to the experimental intensities of the non-family reflections ( $k \neq 3n$ ) turned out to be about 18 and 36 % higher than for the family reflections ( $k = 3n$ ) for the 2*O* and 1*M* polytype, respectively. A sound discrimination between the two cases (i) and (ii) described above could presumably come from High Resolution Transmission Electron Microscopy (HRTEM) images. However, values of the electron residues given above would require an amount of stacking disorder of about 3 % and 7 % in 2*O* and 1*M* polytypes, respectively. These values are physically not realistic, if they arose from unrecovered slips [case (i)] and consequent presence of widespread talc-like layer, or would require large regions corresponding to the 1*M*<sub>d-A</sub> disordered polytype coherently diffracting. Stacking faults normally occur within a still coherently diffracting ordered matrix much more dispersed and usually their presence does not appear at an X-ray investigation, being instead revealed only by HRTEM observations (Baronnet, 1997; Ferraris *et al.*, 2001). Consequently, the attribution of the observed residues to the presence of octahedral slips provisionally given by Ferraris *et al.* (2000) is abandoned in favour of the *Đurović effect* (Nespolo & Ferraris, 2001).

Residues of electron density are also present in the expected H positions in both polytypes; they have been assigned to the hydrogen atoms and their coordinates refined, keeping instead constant the atomic displacement factor (Table 3). The lengths of the O-H bonds are given in Table 4 and must be evaluated on the basis of the very large *esd*'s which, in this case, are influenced also by the partial F → OH substitution. As expected for trioctahedral micas, the O-H bond is almost perpendicular to (001) with the angle  $\angle(\text{O-H}^{\wedge}c^*) = 5^\circ$  and  $3^\circ$  in 2*O* and 1*M* respectively.

Table 4. Selected interatomic distances (Å) and deformation indicators (*di*) for 2O and 1M-polytype of phlogopite; *esd*'s in parentheses.

Bonds/ <i>di</i>	2O	1M	Bonds/ <i>di</i>	2O	1M	Bonds/ <i>di</i>	2O	1M
<i>T-O1</i>	1.645(1)	1.655(1)	<i>M1-O3</i> ×4	2.082(1)	2.092(2)	<i>M2-O3</i> ×2	2.085(1)	2.088(2)
<i>T-O2</i>	1.645(1)	1.652(2)	<i>M1-OH</i> ×2	2.039(1)	2.047(2)	<i>M2-O3'</i> ×2	2.085(1)	2.094(2)
<i>T-O2'</i>	1.645(1)	1.653(2)				<i>M2-OH</i> ×2	2.046(1)	2.055(2)
<i>T-O3</i>	1.613(1)	1.620(2)						
<i>&lt;T-O&gt;</i>	1.637(1)	1.645(1)	<i>&lt;M1-O&gt;</i>	2.068(1)	2.077(1)	<i>&lt;M2-O&gt;</i>	2.072	2.078(1)
<i>K-O1</i> ×2	3.080(2)	3.081(3)	<i>K-O1'</i> ×2	3.180(2)	3.209(3)	<i>O-H</i>	0.73(5)	0.97(5)
<i>K-O2</i> ×4	3.083(2)	3.086(2)	<i>K-O2'</i> ×4	3.177(2)	3.207(2)			
<i>&lt;K-O&gt;</i> <sub>in</sub>	3.082(1)	3.084(1)	<i>&lt;K-O&gt;</i> <sub>out</sub>	3.178(1)	3.208(1)			
<i>Thick<sub>T</sub></i> (Å)	2.231	2.236	$\alpha$ (°)	2.13	2.73	$\psi(M1)$ (°)	58.50	58.77
<i>Thick<sub>O</sub></i> (Å)	2.161	2.153	$\Delta z$ (Å)	0.0	0.0	$\psi(M2)$ (°)	58.58	58.79
<i>Thick<sub>I</sub></i> (Å)	3.366	3.376	$\Delta TM$ (Å)	0.365	0.390	<i>BLD(M1)</i>	0.92	0.96
			$\tau$ (°)	112.07	111.88	<i>BLD(M2)</i>	0.84	0.83

Symbols: *thick* = thickness of *T* and *O* sheets and of interlayer (*I*);  $\alpha$  ditrigonal rotation;  $\Delta z$  tetrahedral tilting,  $\tau$  tetrahedral elongation,  $\psi$  octahedral flattening,  $\Delta TM$  misfit between *T* and *O* sheets, *BLD* bond length distortion.

## Discussion and conclusions

### The crystal-chemical formula

The electron content of the octahedral sites is the same within  $3\sigma$  (Table 3) both in the independent *M* sites and in the two polytypes. Under the double constrain of (*i*) the refined electron contents and (*ii*) a Mg/Fe ratio as closer as possible to that of the chemical analysis ( $\sim 6$ ) (but *a fortiori* ignoring the Al and Ti content in order to simplify the problem), an average octahedral content (Mg<sub>2.07</sub>Fe<sub>0.34</sub>Li<sub>0.59</sub>) is obtained [(Mg<sub>2.14</sub>Fe<sub>0.34</sub>Li<sub>0.52</sub>) for 1M and (Mg<sub>2.00</sub>Fe<sub>0.33</sub>Li<sub>0.67</sub>) for 2O]. This composition corresponds to an average octahedral electron content of 11.8 *el* (12.1 *el* for 1M and 11.85 *el* for 2O) per site to be compared with 12.6 *el* of the chemical analysis performed on a 1M sample. However, it must be kept in mind that the errors generated by the ignored cations have a high weight on the derived structural Li content since this atom, with its 3 electrons, contributes by only about 3% to the total octahedral electron content. The structural Li content is significantly higher (0.52 apfu in 1M) than that (0.40 apfu) obtained from the chemical analysis (1M sample), where severe uncertainty came from zoning and normalisation basis. Presumably, a realistic Li content for 1M is represented by an average between the analytical and structural values, *i.e.* about 0.46 apfu. Both polytypes do not show octahedral ordering of cations,

within the experimental error, and ignoring slight differences in the octahedral dimensions, they belong to the homo-octahedral family and the M (*TOT*) layer preserves its ideal symmetry *C12/m(1)*.

### The structures

A part the different stacking sequence and some dimensional features discussed below, the two studied polytypes of phlogopite are reasonably similar in crystal chemical terms. The coordination polyhedra centred on the cations are very close to regular polyhedra, as shown by their ECoN (Effective Coordination Number; Hoppe, 1979; Hoppe *et al.*, 1989), which is practically identical to the ideal integer value for the corresponding regular polyhedra (Table 5). The average of the two independent  $\langle M-O \rangle$  values for the octahedral distances are 2.070(1) and 2.077(1) Å for 2O and 1M; the average tetrahedral  $\langle T-O \rangle$  is 1.637(1) and 1.645(1) Å in the same order. Thus, both  $\langle M-O \rangle$  and  $\langle T-O \rangle$  (and  $\langle K-O_{out} \rangle$  below) are slightly, but significantly, different in the two polytypes. The ditrigonal rotation is very small ( $\alpha = 2.1^\circ$  for 2O and  $2.7^\circ$  for 1M) and the coordination for the interlayer cation K is close to a hexagonal prism [1M:  $\langle K-O_{in} \rangle = 3.082(1)$  Å,  $\langle K-O_{out} \rangle = 3.178(1)$  Å; 2O:  $\langle K-O_{in} \rangle = 3.084(1)$  Å,  $\langle K-O_{out} \rangle = 3.208(1)$  Å]. According to Fig. 12 in Weiss *et al.* (1992), most of the micas show a ditrigonal rotation angle between 5 and  $14^\circ$ ; a

Table 5. Effective Coordination Number (ECoN), Charge Distribution ( $Q$ ) and Bond-Valence ( $s$ ) for the phlogopite-1M (the values for the phlogopite-2O are not significantly different).

Site	ECoN	$q$	$Q$	$q/Q$	$s_1$	$s_2$	$s_3$
K	11.99	1.00	0.98	1.02	0.92	0.66	0.78
T	3.99	3.85	3.84 <sub>5</sub>	1.00	3.85	3.77	3.83
M1	5.97 <sub>5</sub>	1.84	1.89	0.97	1.99	1.97	2.00
M2	5.98	1.82	1.87	0.97	1.97	1.95	1.98
$\sigma$			0.04		0.13	0.23	0.18
O1		-2.00	-2.02	0.99	-2.02	-1.94	-1.99
O2		-2.00	-2.04	0.98	-2.03	-1.95	-2.00
O3		-2.00	-1.93	1.04	-1.99	-1.95	-1.98
OH		-1.00	-0.99	1.01	-1.08	-1.04	-1.07
$\sigma$			0.05		0.05	0.06	0.04

$\sigma$  measures the deviation of the calculated charge  $Q$  with respect to input charge  $q$  and is defined as  $\sigma = [\sum_i (q_i - Q_i)^2 / (N-1)]^{1/2}$ . For comparison the values of BV calculation obtained from the curves of Brown & Shannon (1973),  $s_1$ , Brown & Wu (1976),  $s_2$ , and Brown & Altermatt (1985),  $s_3$ , are reported.

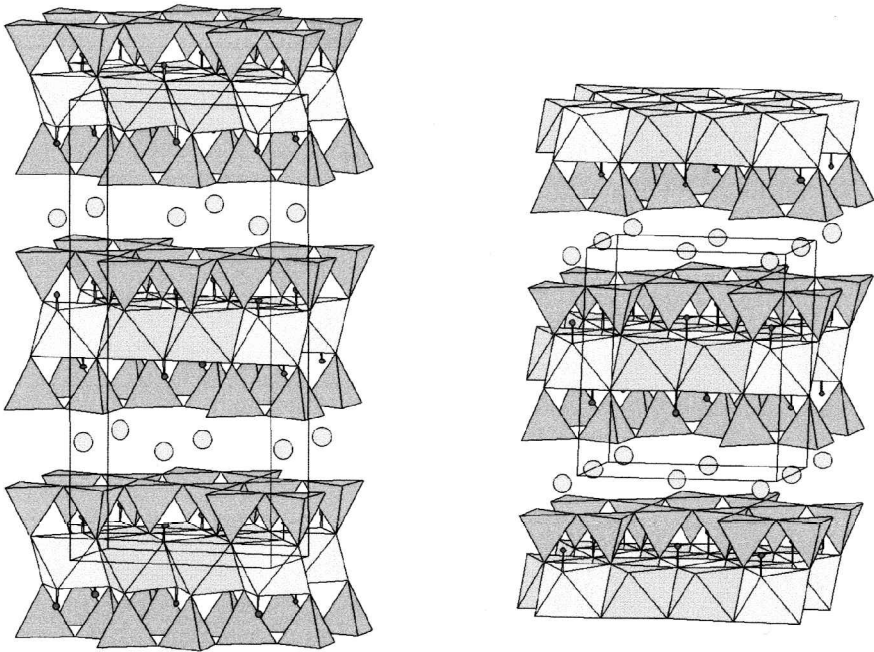


Fig. 1. Perspective view of the crystal structure of 2O (left side) and 1M (right side) polytypes. Crystallographically independent polyhedra are differently shadowed. Interlayer cations and hydrogen atoms are shown as large and small filled circles respectively.

remarkable, and rare, case of almost absent ditrigonal rotation ( $\alpha = 0.24^\circ$ ) is represented by the synthetic Cs-tetra-ferri-annite (Mellini *et al.*, 1996).

All the dimensions (Tables 2, 3 and 4), except the octahedral thickness, are larger in 1M than in

2O polytype. In particular, significant differences in average bond lengths,  $a$  and  $b$  cell parameters and unit-layer volume ( $491.7 \text{ \AA}^3$  in 1M and  $485.5 \text{ \AA}^3$  in 2O) occur. Due to the uncertainty in the Li content and the lacking quantitative chemical analysis of 2O, the octahedral dimensions cannot be



soundly discussed in terms of cation ionic radii. [Actually, on this basis, the higher Li (0.76 Å ionic radius) content associated with the lower Mg (0.72 Å ionic radius) content observed in *2O* is even at variance with the dimensional differences between the two polytypes]. However, the following consideration seems supporting the observed dimensional differences even in presence of close chemical composition in the two polytypes.

Even if the small values of the ditrigonal rotation makes very similar the environment of the interlayer cation in the two phlogopite polytypes, it must be kept in mind that the interlayer coordination polyhedra are conceptually different being in principle ditrigonal prismatic and ditrigonal antiprismatic in *2O* and *1M*-polytype respectively. In particular, the ditrigonal prismatic coordination is considered (Radoslovich, 1961) to be a reason for the lower occurrence of subfamily B polytypes. The ditrigonal antiprismatic coordination occurring in subfamily A polytypes stabilises the coordination environment of the interlayer cation, which has the six nearest-neighbours in trigonal prismatic (distorted octahedral) configuration. In presence of equal  $\langle K-O_{out} \rangle$  values in the two polytypes, the larger difference between  $\langle K-O_{in} \rangle$  and  $\langle K-O_{out} \rangle$  observed in the *1M* (subfamily A) polytype can be interpreted as a requirement to approach the stabilising configuration. A priority given to this requirement undoubtedly leads to larger dimensions in *1M*. Opposite considerations can be applied to *2O* which instead needs to avoid the destabilising trigonal prismatic configuration for the inner oxygen atoms. Such a reduction of the destabilisation can be reached by keeping as small as possible the ditrigonal rotation  $\alpha$  at the expenses of some readjustment within the *TOT* layer in a direction which is opposite to that observed in *1M*.

The Charge Distribution (CD) (Hoppe *et al.*, 1989) analysis for the phlogopite-*1M* is given in Table 5. As shown by Nespolo *et al.* (1999), the ratio  $q/Q$  of the formal and computed oxidation numbers indicate the correctness of the structure refinement [ $(q/Q)_{cations}$ ] and the degree of over- or under-balance [ $(q/Q)_{anions}$ ]. Both these ratios are very close to 1 for all the atoms thus indicating that the structure is correctly refined and it is well balanced from the bond strength viewpoint (notice that H was not considered, because of the uncertainty of its position; instead, taking into account that O-H does not form a hydrogen bond, a value of  $q = -1$  was assigned to O4). Since the structure of the layer in the *2O* polytype is only

slightly different, the same results hold also for the latter. For comparison, the bond-valence (BV) calculation has been done for three (Brown & Altermatt, 1985; Brown & Shannon, 1973; Brown & Wu, 1976) of the curves available in literature by taking into account the composition of the cation sites (Table 5). All BV calculations show some unbalance, which is likely an artefact due to the limitations of the method in accounting for composite cation sites and the weak K-O bonds.

### The polytype association

Likely the formation of few crystals of *2O* together with more abundant crystals of *1M* was favoured by the average chemical composition and the very small differences in the interlayer coordination of the two polytypes, which has been discussed above. Note that Li and F occur both in our phlogopite and in the Lazarenko *et al.* (1978) lepidolite. Also the *2O* polytype reported by Sunagawa *et al.* (1968) is a synthetic fluor-phlogopite. Both Li and F could be crucial in stabilising the rare *2O* polytype. In particular, the F substitution for OH reduces the repulsion between the interlayer cation and OH, whose O-H bond is nearly perpendicular to (001), and inverts the stability range of  $2M_1$  (subfamily A) and  $2M_2$  (subfamily B) polytypes (Takeda *et al.*, 1971). The same role of stabilisation is evidently played by F also in the subfamily B *2O* polytype. The complete substitution of OH by S in the anandite pseudo-*2O*-polytype mentioned in the Introduction plays a similar role.

Strictly speaking, the polytypes of a same compound differ only for the stacking sequence of one (or more) basic modules and, in principle, show the same total energy; because of that, they are considered a category separated from the polymorph category (Verma & Krishna, 1966). In practice, particularly for complex compounds as micas, (i) chemical differences and consequent deformation of the M unit layer, and (ii) possible order/disorder phenomena influencing the configurational contribution to the total energy, can produce energetically different 'polytypes' (*i.e.*, polymorphs) which, in principle, are stable under different thermodynamic conditions. Even if in literature often only one mica polytype is reported in a given geological ambient, the association of different mica polytypes is well documented (particularly for micas from igneous rocks) both at optical and TEM scale in natural (*e.g.*, Abbona & Aquilano, 1970; Černý *et al.*, 1970; Bocchio,

1977; Borutskiy *et al.*, 1987; Chattergie, 1971; Ivaldi *et al.*, 2001; Kogure & Nespolo, 1999b; Koval *et al.*, 1988; Lazarenko *et al.*, 1978; Ohta *et al.*, 1982; Rieder, 1970; Zhukhlistov *et al.*, 1993) as well as synthetic samples (Amouric & Baronnet, 1983). Examples of associated mica polytypes which clearly differ in their chemical composition are reported [*e.g.*, the  $2M_1$  and  $3T$  phengites described by Ivaldi *et al.* (2001)]; in these cases we are not in presence of *stricto sensu* polytypes and their association is likely due to the preservation of non re-equilibrated polytypes formed in metamorphic rocks under changing P/T conditions (*e.g.*, Sassi *et al.*, 1994).

Most of the examples of association given above deal with polytypes formed in a fluid ambient, as it is the case of our phlogopite formed under pegmatitic conditions and grown dispersed in natrite and thermonatrite. A fluid phase plays in fact a fundamental role in the growth and differentiation of crystals (Sunagawa, 1977). Keeping in mind that and the structural features discussed above, the following scenario reasonably explains the associated occurrence of the two polytypes reported in this paper.

1. The different (and unusual) morphology between the two polytypes excludes a transition from a parent to a daughter polytype under changed geological (thermodynamic) conditions.

2. The chemical zoning witnesses oscillations in the chemical environment during the crystallisation process. That likely favoured the nucleation of two different polytypes under (slightly) different chemical conditions.

**Acknowledgement:** The authors wish to express their gratitude to Slavomil Āurovic (Slovak Academy of Sciences, Bratislava) for profitable discussions and to Leonid A. Pautov (Fersman Mineralogical Museum, RAS Moscow) for the Atomic Absorption test. The constructive criticism of Marcello Mellini (referee) well improved the logical flow of the paper. Research financially supported by MURST ('Layer silicates: crystal chemical, structural and petrologic aspects' project) and CNR ('Igneous and metamorphic micas' project). The microprobe instrument used at the University of Modena has been installed and is maintained through CNR financial support.

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*Received 12 January 2001*

*Modified version received 5 March 2001*

*Accepted 4 April 2001*