

REFINEMENT OF THE CRYSTAL STRUCTURE OF PHENGITE- $2M_1$

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Abstract—The crystal structure of phengite- $2M_1$ from Rio de Oro, Spanish Sahara, was refined in space group $C2/c$ to a residual of 3.3% with 1267 independent X-ray diffraction reflections. The composition of the mica determined by electron microprobe analysis is $(K_{0.948}Na_{0.051}Ba_{0.027})(Al_{1.510}Mg_{0.273}Fe_{0.144}Cr_{0.095}Ti_{0.010}Mn_{0.003})_{2.035}(Si_{3.253}Al_{0.747})O_{10}(OH)_2$. The cell dimensions are $a = 5.2153(5)$, $b = 9.043(2)$, $c = 19.974(9)$ Å, $\beta = 95.789(9)^\circ$, and $V = 937.2(3)$ Å³. The substitution of Si for Al in the tetrahedral sheet and larger divalent cations for Al in the octahedra allows the amount of distortions that are generally required to alleviate tetrahedral-octahedral sheet lateral misfit in muscovite, such as tetrahedral rotation and octahedral flattening, to be reduced. The O...H vector is nearly horizontal and points slightly into the octahedral sheet where it may be involved in hydrogen bond contacts inside M(1). In contrast to previously reported refinements of all but one other phengite, no ordering of tetrahedral cations was found in the study specimen. This disorder is considered to be due to the low-pressure, high-temperature amphibolite facies environment of crystallization.

Key Words—Cation ordering, Crystal structure, Mica, Phengite.

INTRODUCTION

Previous refinements of the crystal structures of phengite- $2M_1$ (Güven, 1971), phengite- $2M_2$ (Zhoukhlistov *et al.*, 1973), phengite- $1M$ (Sidorenko *et al.*, 1975), Li,Fe-phengite- $1M$ (Zhoukhlistov *et al.*, 1983), and phengitic muscovite- $3T$ (Güven and Burnham, 1967) have indicated some degree of ordering of tetrahedral Si and Al, although the accuracy of some of the studies is less than optimum. Only one refinement of a phengite reported in the literature, that of phengite- $1M$ by Tshipursky and Drits (1977), has found tetrahedral cation disorder. Because tetrahedral ordering is rare in micas (Bailey, 1984), the present study was undertaken to provide a high-accuracy refinement of an additional phengite.

EXPERIMENTAL

A bright green chromium-bearing phengite crystal (mariposite), about $0.54 \times 0.32 \times 0.14$ mm in size, from Rio de Oro, Spanish Sahara, was chosen for study because of its sharp extinction under the polarizing microscope and unstreaked X-ray diffraction spots. True X and Y directions determined from precession photographs were parallel to the optical extinction directions on (001). The chemical composition, $(K_{0.948}Na_{0.051}Ba_{0.027})(Al_{1.510}Mg_{0.273}Fe_{0.144}Cr_{0.095}Ti_{0.010}Mn_{0.003})_{2.035}(Si_{3.253}Al_{0.747})O_{10}(OH)_2$, was determined by electron microprobe analysis assuming 11 oxygens (Table 1).

Intensities of 5546 reflections were collected over all octants out to $2\theta = 60^\circ$ with a Nicolet P2₁ automated single-crystal diffractometer in the $2\theta:\theta$ variable scan rate mode using graphite monochromated MoK α radiation. These reflections were merged into 1267 independent non-zero reflections. Crystal and electronic

stability were checked after every 50 reflections by monitoring one standard reflection. The integrated intensity, I , was calculated from $I = [S - (B1 + B2)/Br]Tr$, where S is the scan count, $B1$ and $B2$ the background counts, Br the ratio of background time to scan time, and Tr the 2θ scan rate in degrees per minute. Reflections were considered to be observed if $I > 2\sigma(I)$. Values of $\sigma(I)$ were calculated from standard counting statistics. Integrated intensities were corrected for Lp factors and for absorption by using the semi-empirical ψ -scan technique of North *et al.* (1968). Cell parameters (Table 2) were determined by least squares refinement of 15 independent low- to medium-angle reflections.

REFINEMENT

The atomic coordinates of muscovite as refined by Rothbauer (1971) were the starting point for refinement in ideal space group $C2/c$ using a modified least-squares program ORFLS (Busing *et al.*, 1962). Scattering factors from Cromer and Mann (1968) corresponding to 50% ionization were used in the refinement. The scale factor and non-fixed atomic positions were varied first, followed by isotropic temperature factors. A few cycles of refinement indicated that unit weights were more appropriate to the data than sigma weights, and these were used for the balance of the refinement. Anisotropic temperature factors were then added to the variables to reduce the residual to $R = 3.6\%$. At this point the hydrogen proton was successfully located near its predicted position as a spherical volume of excess electron density (about 0.5 electrons) by the use of difference electron-density maps. The O...H vector is nearly horizontal and points slightly into the octahedral sheet. An unexpected concentration

Table 1. Microprobe¹ analysis of phengite-2M₁ (this study).

Oxide	Wt. %
SiO ₂	48.15
Al ₂ O ₃	28.34
MgO	2.71
FeO	2.54
MnO	0.06
Cr ₂ O ₃	1.77
TiO ₂	0.19
K ₂ O	11.00
Na ₂ O	0.39
CaO	0.00
BaO	1.02
Sum	96.17

¹ The microprobe analysis was performed by Charles A. Geiger on an Applied Research Laboratories EMX microprobe at the University of Wisconsin, Madison, Wisconsin. Each measurement was the average of six points measured on two different grains of phengite. The 15 kV beam was defocused at 10 μm to avoid damage to the specimen and counts were collected for about 30 sec on each point. The following were used as standards: microcline, Si, Al, K; omphacite, Na, Ca, Mg; synthetic TiO₂, Ti; rhodonite, Mn; chromite, Cr; hematite (Okahandja), Fe; and barite, Ba.

of electron density equal to 1.5 electrons occurred at the usually vacant M(1) octahedral site on the center of symmetry, indicating that it was partially occupied. Small volumes of excess electron density (each about 0.25 electrons) were also discovered halfway between the tetrahedral cations and their bonded oxygens. This excess electron density is evidence of the partial covalent nature of these bonds. All other atom locations on the difference electron density map appeared flat. Further least-squares refinement with the hydrogen and partially occupied M(1) site added (but not varied) produced a final unweighted residual of 3.3%. Fortran programs SHELLS (W. A. Dollase, Department of Geology, University of California, Los Angeles, California, unpublished) and ORFFE (Busing *et al.*, 1964) were used to determine structural bond lengths and errors. Final atomic parameters are listed in Table 2; thermal parameters and shape and orientation of thermal ellipsoids are presented in Tables 3 and 4. Tables of F_o and F_c can be obtained from the authors upon request.

To investigate ordering within the M(2) octahedra, refinement in one of the subgroup symmetries is required, such as Cc or C $\bar{1}$. Because ten reflections plus Friedel equivalents were observed to violate extinctions required by the c-glide and six reflections and Friedel equivalents to violate monoclinic symmetry, additional refinement was attempted in triclinic subgroup C $\bar{1}$. Only the octahedral anions were varied in an attempt to determine if the two M(2) octahedra were of different sizes, but no satisfactory refinement could be achieved.

Table 2. Phengite-2M₁ unit-cell parameters and final atomic positions.

$a_0 = 5.2153(5)$ Å, $b_0 = 9.043(2)$ Å, $c_0 = 19.974(9)$ Å, $\beta = 95.789(9)^\circ$, $V = 937.2(3)$ Å³

Atom	x/a	y/b	z/c
T(1)	0.4643(2)	0.92930(9)	0.13565(4)
T(2)	0.4522(2)	0.25864(9)	0.13565(4)
M(1)	0.25	0.75	0.0
M(2)	0.2486(2)	0.08292(9)	0.00003(5)
K	0.0	0.0971(1)	0.25
O(1)	0.4582(4)	0.9402(3)	0.0541(1)
O(2)	0.3916(4)	0.2516(3)	0.0541(1)
O(3)	0.4335(5)	0.0933(3)	0.1689(1)
O(4)	0.2410(5)	0.8206(3)	0.1598(1)
O(5)	0.2410(5)	0.3621(3)	0.1691(1)
O(6)	0.4556(5)	0.5643(3)	0.0519(1)
H	0.3443	0.6435	0.0488

DISCUSSION

One of the fundamental problems in putting a mica 2:1 layer together is fitting a laterally large tetrahedral sheet to a smaller octahedral sheet. Sometimes the presence of different size cations substituting for those generally present reduces the initial amount of tetrahedral-octahedral sheet misfit, but distortions such as tetrahedral rotation or flattening of octahedra generally must occur to help the sheets fit together. The amount of distortion necessary to achieve a good fit varies with composition in the muscovite-phengite solid solution. As the micas become more phengitic, the lateral misfit decreases and the tetrahedral rotation and octahedral flattening become smaller. Throughout the rest of this paper, the phengite-2M₁ of this study will be compared to the muscovite-2M₁ studied by Rothbauer (1971) and the phengite-2M₁ studied by Güven (1971) so that these and other differences can be related to a single structural type.

Octahedra

The only type of octahedral ordering present is ordering of vacancies into the *trans* M(1) site. Octahedral bond lengths and distances for the study specimen are listed in Table 5. The octahedra of the phengite in the present study are intermediate in composition, size, and amount of distortion between Rothbauer's muscovite and Güven's phengite (Table 6, octahedral parameters). As the composition of the mica becomes more phengitic (larger divalent cations replace some Al), the generally vacant M(1) site shrinks as the M(2) site expands. This change permits the distortion of both octahedra to decrease because they are becoming more similar in size. The amount of octahedral rotation also decreases as the charge on the M(2) cation is lowered and the shortening of shared edges becomes less. The increased size of the octahedral cations causes the octahedral sheet to be thicker and the flattening of oc-

Table 3. B equivalent and anisotropic thermal parameters for phengite-2M₁.

Atom	B (equiv) ¹	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
T(1)	0.524	0.0053(3)	0.00113(8)	0.00040(2)	-0.0001(1)	0.00016(5)	0.00005(3)
T(2)	0.518	0.0048(2)	0.00134(8)	0.00038(2)	0.0001(1)	0.00005(5)	0.00003(3)
M(2)	0.814	0.0075(3)	0.00205(8)	0.00061(2)	0.0000(1)	0.00012(5)	0.00007(3)
K	1.946	0.0184(4)	0.0058(1)	0.00124(3)	0	0.00030(8)	0
O(1)	0.952	0.0104(7)	0.0028(2)	0.00052(5)	-0.0002(3)	0.0001(1)	0.00013(9)
O(2)	0.965	0.0097(7)	0.0031(2)	0.00053(5)	0.0001(3)	0.0001(1)	0.00015(9)
O(3)	1.294	0.0170(9)	0.0026(2)	0.00076(5)	0.0004(4)	0.0005(2)	0.0000(1)
O(4)	1.374	0.0124(8)	0.0049(3)	0.00075(5)	-0.0021(4)	0.0000(2)	0.0003(1)
O(5)	1.264	0.0119(8)	0.0041(3)	0.00074(5)	0.0022(4)	0.0002(2)	0.0000(1)
O(6)	1.161	0.0125(8)	0.0031(3)	0.00071(5)	0.0008(4)	0.0005(2)	-0.00030(9)
M(1)	1.0						
H	2.0						

$$^1 B(\text{equiv}) = 4/3[\beta(1,1)/(a^*)^2 + \beta(2,2)/(b^*)^2 + \beta(3,3)/(c^*)^2].$$

tahedra (which extends the sheet laterally) to be reduced.

A semi-quantitative comparison can be made as to the degree of intermediate nature of the octahedral parameters for the phengite of this study. Assuming a linear series between the composition and structural features of the Rothbauer moscovite and the Güven phengite, the phengite of this study is 79% toward the

phengite end of the series based on its octahedral Al content. In accord with this intermediate position, eight of the ten octahedral parameters listed for the Spanish Sahara phengite in Table 6 occupy positions in the series ranging between 69% and 86%. The two excep-

Table 4. Shape and orientation of thermal ellipsoids for phengite-2M₁.

Atom	Axis	RMS displacement	Angle (°) with respect to		
			X	Y	Z
T(1)	r1	0.068(3)	94(6)	172(5)	82(5)
	r2	0.085(2)	4(8)	94(6)	94(19)
	r3	0.090(2)	89(19)	97(5)	171(10)
T(2)	r1	0.074(2)	74(14)	160(14)	80(7)
	r2	0.081(2)	27(12)	70(15)	77(11)
	r3	0.089(2)	69(10)	95(7)	164(9)
M(2)	r1	0.092(2)	92(9)	171(4)	81(4)
	r2	0.101(2)	16(7)	89(9)	80(7)
	r3	0.112(2)	74(7)	99(4)	166(6)
K	r1	0.155(4)	90(0)	180(0)	90(0)
	r2	0.155(3)	52(32)	90(0)	43(32)
	r3	0.161(2)	38(11)	90(0)	133(11)
O(1)	r1	0.098(5)	94(10)	62(18)	150(15)
	r2	0.110(5)	70(19)	33(18)	67(18)
	r3	0.121(4)	20(18)	105(17)	107(11)
O(2)	r1	0.100(5)	95(13)	65(12)	152(12)
	r2	0.115(4)	22(20)	69(20)	91(56)
	r3	0.117(4)	69(20)	146(76)	117(12)
O(3)	r1	0.103(5)	95(4)	174(7)	93(11)
	r2	0.123(4)	96(6)	93(11)	3(11)
	r3	0.152(4)	172(5)	95(4)	90(6)
O(4)	r1	0.113(5)	51(20)	51(5)	121(27)
	r2	0.121(5)	58(22)	86(18)	38(24)
	r3	0.160(4)	56(4)	141(4)	110(5)
O(5)	r1	0.107(5)	43(5)	133(5)	94(15)
	r2	0.121(4)	87(12)	87(11)	9(10)
	r3	0.148(4)	133(5)	137(5)	82(7)
O(6)	r1	0.100(5)	72(6)	140(7)	127(7)
	r2	0.127(4)	71(27)	118(15)	39(11)
	r3	0.134(4)	153(21)	116(16)	79(23)

Table 5. Octahedral bond lengths and distances.

M(1)-O bond lengths (Å)		M(2)-O bond lengths (Å)	
M(1)-O(1)	2.251(2) × 2	M(2)-O(1)	1.946(2)
M(1)-O(2)	2.252(2) × 2	M(2)-O(1)	1.970(2)
M(1)-O(6)	2.196(2) × 2	M(2)-O(2)	1.972(3)
Mean	2.233(1)	M(2)-O(2)	1.945(2)
		M(2)-O(6)	1.938(3)
		M(2)-O(6)	1.939(3)
		Mean	1.952(1)
Shared diagonal edges (Å)		M(2) unshared diagonal edges (Å)	
O(6)-O(6)	2.462(5)	O(1)-O(2)	2.939(3)
O(2)-O(2)	2.493(4)	O(1)-O(6)	2.867(3)
O(1)-O(1)	2.493(4)	O(2)-O(6)	2.869(3)
Mean	2.483(3)	Mean	2.891(2)
M(1) unshared lateral edges (Å)		M(2) unshared lateral edges (Å)	
O(1)-O(2)	3.412(3)	O(1)-O(2)	2.838(3)
O(1)-O(6)	3.400(3)	O(1)-O(2)	2.831(3)
O(2)-O(6)	3.399(3)	O(1)-O(6)	2.848(3)
Mean	3.404(2)	O(2)-O(6)	2.831(3)
		O(2)-O(6)	2.833(3)
		O(2)-O(6)	2.848(1)
		Mean	2.838(1)
Hydrogen bond length (Å)			
H-O(6)	0.920(2)		
ρ_{obs}	3.91 degrees		
Interlayer cation bond lengths			
Inner bonds (Å)		Outer bonds (Å)	
K-O(3)	2.912(3) × 2	K-O(3)	3.223(3) × 2
K-O(4)	2.944(3) × 2	K-O(4)	3.397(3) × 2
K-O(5)	2.918(3) × 2	K-O(5)	3.216(3) × 2
Mean	2.925(1)	Mean	3.279(1)

Table 6. Octahedral parameters.

	Muscovite-2M ₁ (Rothbauer, 1971)	Phengite-2M ₁ (this study)	Position ¹ in series	Phengite-2M ₁ (Güven, 1971)
Octahedral composition	(Al _{1.81} Fe _{0.14} Mg _{0.12})	(Al _{1.51} Mg _{0.27} Fe _{0.14} Cr _{0.09} Ti _{0.01})	0.79 ²	(Al _{1.43} Fe ³⁺ _{0.05} Mg _{0.50} Fe ²⁺ _{0.09} Ti _{0.01})
Mean M–O bond length (Å)	M1 2.241 M2 1.930	2.233 1.952	0.42 0.85	2.222 1.956
ψ _{oct} (°)	M1 62.22 M2 57.23	61.65 57.09	0.71 0.93	61.42 57.08
Octahedral rotation (°)	M1 0.00 M2 15.35	0.00 13.69	— 0.68	0.00 12.92
RMS deviation 15 internal bond angles from ideal (°)	M1 9.00 M2 8.77	8.34 7.85	0.71 0.72	8.07 7.50
RMS deviation 36 external angles from ideal (°)	M1 6.70 M2 5.66	6.12 5.02	0.73 0.74	5.91 4.79
Octahedral sheet thickness (Å)	2.089	2.121	0.86	2.126

¹ The position of compositional or structural parameters for the phengite of this study in a linear series from the Rothbauer (1971) muscovite at 0.00 to the Güven (1971) phengite at 1.00.

² Al content only was considered for this calculation.

tions are mean M–O bond length for M(1) and the flattening parameter for M(2). These exceptions will be addressed in a later section.

Tetrahedra

The tetrahedral sheet of the study specimen is intermediate in composition between ideal muscovite and Güven's phengite. Tetrahedral angles and distances for the phengite in this study are listed in Table 7, and a comparison of tetrahedral and interlayer parameters for all three is given in Table 8. No tetrahedral ordering was found in the study specimen; bond lengths for T(1) and T(2) are the same within experimental error, the tetrahedral angles of both tetrahedra are identical, and both cation sites are flat on difference electron density maps.

The coupled substitution in phengite of smaller Si for Al in the tetrahedra and of larger divalent cations for Al in the octahedra has several effects. An increase in the number of smaller Si cations causes the tetrahedral sheet to become thinner and laterally smaller. It now fits the octahedral sheet (which has become thicker and laterally larger) much better, thus lessening the need for tetrahedral rotation. Therefore, alpha decreases as the composition become more phengitic. Corrugation of basal oxygens is also reduced. As larger cations in the octahedral sheet impinge upon and reduce the vacant site size, tetrahedra need not tilt as much in order to fit the large vacant site lateral edges. Less tilting of tetrahedra allows the basal oxygens to remain more nearly coplanar.

The tetrahedral composition of the Spanish Sahara phengite of this study is 54% along the series from the Rothbauer muscovite to the Güven phengite. Accordingly, five of its six tetrahedral parameters listed in

Table 7. Tetrahedral angles and distances.

T(1)–O bond lengths (Å)		T(2)–O bond lengths (Å)	
T(1)–O(1)	1.630(2)	T(2)–O(2)	1.628(2)
–O(3)	1.639(3)	–O(3)	1.643(3)
–O(4)	1.634(3)	–O(4)	1.633(3)
–O(5)	1.644(3)	–O(5)	1.638(3)
Mean	1.637(1)	Mean	1.636(1)
T(1) edge lengths (Å)		T(2) edge lengths (Å)	
O(1)–O(3)	2.693(3)	O(2)–O(3)	2.693(3)
O(1)–O(4)	2.719(3)	O(2)–O(4)	2.717(3)
O(1)–O(5)	2.696(4)	O(2)–O(5)	2.693(3)
O(3)–O(4)	2.662(4)	O(3)–O(4)	2.625(4)
O(3)–O(5)	2.635(3)	O(3)–O(5)	2.630(3)
O(4)–O(5)	2.623(3)	O(4)–O(5)	2.660(4)
Mean	2.671(1)	Mean	2.670(1)
T(1) bond angles (°)		T(2) bond angles (°)	
O(1)–T(1)–O(3)	110.9(1)	O(2)–T(2)–O(3)	110.8(1)
O(1)–T(1)–O(4)	112.9(1)	O(2)–T(2)–O(4)	112.9(1)
O(1)–T(1)–O(5)	110.9(1)	O(2)–T(2)–O(5)	111.0(1)
O(3)–T(1)–O(4)	108.9(1)	O(3)–T(2)–O(4)	106.5(1)
O(3)–T(1)–O(5)	106.7(1)	O(3)–T(2)–O(5)	106.6(1)
O(4)–T(1)–O(5)	106.3(1)	O(4)–T(2)–O(5)	108.8(1)
Mean	109.4(04)	Mean	109.4(04)
Tetrahedral rotation (°)			
O(4)–O(3)–O(5)		135.6(1)	
O(4)–O(3)–O(5)		104.2(1)	
O(3)–O(4)–O(5)		103.3(1)	
O(3)–O(4)–O(5)		135.8(1)	
O(3)–O(5)–O(4)		104.2(1)	
O(3)–O(5)–O(4)		135.5(1)	
Mean deviation from 120.0		15.87	
α		7.9	

Table 8. Tetrahedral and interlayer parameters.

	Muscovite-2M ₁ (Rothbauer, 1971)	Phengite-2M ₁ (this study)	Position in series	Phengite-2M ₁ (Güven, 1971)
Tetrahedral composition	(Si _{3.09} Al _{0.91})	(Si _{3.253} Al _{0.747})	0.54	(Si _{3.39} Al _{0.61})
Mean T-O bond length (Å)	T1 1.645 T2 1.644	1.637 1.636	0.47 ¹	1.621 1.633
Mean tetrahedral edge length (Å)	T1 2.685 T2 2.685	2.671 2.670	0.50 ¹	2.645 2.667
τ _{tet} (°)	T1 110.95 T2 110.93	111.56 111.56	1.31 ¹	111.48 111.35
α _{tet} (°)	11.33	7.93	0.64	5.99
Tetrahedral sheet thickness (Å)	2.245	2.236	0.35	2.219
Basal oxygen Δz (Å)	0.213	0.184	0.52	0.157
Intralayer shift	+0.376a _{2,3}	+0.376a _{2,3}	—	+0.376a _{2,3}
Layer offset	-0.005a ₁	-0.005a ₁	—	-0.004a ₁
Resultant shift	-0.386a ₁	-0.386a ₁	—	-0.385a ₁
Interlayer separation (Å)	3.393	3.342	1.50	3.359
Ideal β angle (°)	94.95	94.99	—	95.00
β angle observed (°)	95.7353	95.789	—	95.769

¹ Parameters for T1 and T2 were averaged.

Table 8 occupy positions in the series ranging between 35% and 64% with only the τ_{tet} parameter appearing as a deviation.

Interlayer

The amount of interlayer separation is less for the two phengites than for muscovite (Table 8). The smaller amount of tetrahedral rotation in phengite provides a larger opening in the tetrahedral ring so that the interlayer cation is able to fit more deeply into the ring. This arrangement brings the layers closer together and reduces the interlayer gap and d(001). The interlayer separation is especially small in the phengite of the present study because the balance of electrostatic forces has depressed the OH proton into the octahedral sheet and thereby allowed slightly deeper penetration of the interlayer cation.

Hydroxyl bond angle

The position of the hydrogen proton in micas is controlled by an interplay between electrostatic repulsion from the nearby M(1) and M(2) cations on one side of the OH group and repulsion from the interlayer cations and the tetrahedral cations on the other side (Giese, 1979; Bookin and Drits, 1982). In dioctahedral micas, such as muscovite and phengite, the hydroxyl bond is inclined away from the vertical toward the vacant M(1) site so that it makes some angle, ρ, to the (001) plane. This angle in muscovite-2M₁ was determined experimentally by Rothbauer (1971) to be +15° above (001), whereas in the present study the angle is -4° below (001) so that the hydrogen proton actually lies within the M(1) octahedron. Although the actual location of the hydrogen proton in the Güven phengite was not determined experimentally, Giese (1979) calculated ρ = +1.3° by minimization of electrostatic energy.

The negative ρ angle in the present study is unusual, but a negative angle has been observed previously in a further study of celadonite-1M (ρ = -14°) by Bookin *et al.* (1982) using the electron diffraction data of Tsi-pursky (1979). Celadonite has an even greater amount of Si⁴⁺ in the tetrahedral sheet than phengite; therefore the relative magnitudes of depression of the hydrogen proton into the octahedral sheet in celadonite and the phengite of this study may be accounted for by the relative amounts of repulsion of the hydrogen proton by the highly charged tetrahedral cations.

In contrast to the findings of the present study, two other refinements of phengites reported in the recent literature give observed hydrogen proton positions that lie outside the octahedral sheet. For phengite-1M Bookin *et al.* (1982) constructed difference electron-density maps from the electron diffraction data of Tsi-pursky and Drits (1977) to locate the hydrogen proton at ρ = +17°. For Li,Fe-phengite-1M Zhoukhlistov *et al.* (1983) found ρ = +9°. The wide range in position of the hydrogen proton is probably due to different distributions of octahedral cations as well as different tetrahedral compositions in different specimens. Bookin *et al.* (1982) reported a small occupancy of the *trans* M(1) octahedron in the phengite-1M above, and Bookin and Drits (1982) calculated that an occupancy of 0.04 atoms in that site could increase ρ by 6°. The Li,Fe-phengite-1M was found to have occupancy of Fe_{0.32} in M(1) by Zhoukhlistov *et al.* (1983). Partial M(1) occupancies of this sort would repel the proton slightly away from the octahedral sheet. The phengite-2M₁ of the present study also had a small electron density located at the M(1) site (equivalent to Mg_{0.14}), but this was not enough to counterbalance the repulsion due to the highly charged tetrahedral cations and the charge of the interlayer cation (normalized at +1.026).

Table 9. Other selected parameters.

	Muscovite-2M ₁ (Rothbauer, 1971)	Phengite-2M ₁ (this study)	Position in series	Phengite-2M ₁ (Güven, 1971)
a (Å)	5.19182	5.2153	1.21	5.2112
b (Å)	9.01535	9.043	1.20	9.0383
c (Å)	20.04577	19.973	0.74	19.9473
Avg. M(1) lat. edge (Å)	3.435	3.404	0.57	3.381
Avg. M(2) lat. edge (Å)	2.810	2.839	0.85	2.844
M(1)–M(2) diag. edges (Å)	2.852	2.869	0.74	2.875
	2.849	2.867	1.20	2.864
	2.941	2.938	0.14	2.919
M–O bond length (Å)	M(1) 2.241	2.233	0.42	2.222
	M(2) 1.930	1.952	0.81	1.957
ψ _{oct} (°)	M(1) 62.22	61.65	0.71	61.42
	M(2) 57.23	57.09	1.08	57.10

Although most structural parameters of the Spanish Sahara phengite are intermediate between those of the Rothbauer muscovite and the Güven phengite, its *a* and *b* cell dimensions are larger than those of either end member of this comparison series (Table 9). The larger cell dimensions are due primarily to the large size of M(1), as indicated by the anomalous positions in Table 9 of the mean M–O bond length of 2.233 Å for M(1), the M(1) lateral edge of 3.404 Å, and two large diagonal edges shared between M(1) and M(2). These anomalous bond lengths are consistent with, but do not prove, a hydrogen bond contact between the hydrogen proton inside M(1) with octahedral anion O(1), for which the contact distance is 2.574 Å. Octahedral anion O(2) is slightly more distant at 2.755 Å. Movement of O(1), and possibly of O(2) in a bifurcated bond, toward the proton of O(6) would explain the observed bond lengths and cell dimensions, but the existence of a hydrogen bond requires verification by other techniques.

Thermal ellipsoids

The thermal ellipsoids of the cations and apical oxygens are nearly isotropic. The ellipsoids for the basal oxygens, O(3), O(4), and O(5), however, are larger and more anisotropic with the major component of vibration normal to the two bonded tetrahedral cations. The anisotropy is considered to be true thermal vibration normal to the T–O bonds, whereas the sizes of the ellipsoids also incorporate the effects of positional disorder of the Si,Al tetrahedral cations.

CONCLUSIONS

In contrast to most other phengites described in the literature, the phengite in the present study shows no ordering of tetrahedral cations. Some phengites with reported tetrahedral ordering, particularly those studied with electron diffraction, have high residuals and may not represent reliable data, e.g., phengite-2M₂ (Zhoukhlistov *et al.*, 1973), R = 11.7%; Li,Fe-phengite-1M (Zhoukhlistov *et al.*, 1983), R = 10.2%; and phengite-1M (Sidorenko *et al.*, 1975), R = 10.9%. To

prove that tetrahedral ordering actually exists in these structures it is necessary to show that the T–O mean bond length differences are statistically significant with respect to the errors involved (Bailey, 1984) and, for the 1M phengites, that refinement in subgroup C2 yields a significantly lower residual R value than refinement in the ideal C2/m space group. Tsipursky and Drits (1977) illustrated the latter problem for another phengite-1M. They attempted refinement of electron diffraction data in both space groups C2/m and C2. The final residual for the refinement in space group C2/m in which all tetrahedra are equivalent by symmetry was 7.0%, whereas refinement in space group C2 indicated ordering of tetrahedral cations but yielded a higher residual of 9.3% and cannot be considered correct.

Ordering that occurs in the phengitic muscovite-3T (Güven and Burnham, 1967) may be due to its 3T stacking arrangement rather than its phengitic composition, as all other 3T micas also have shown tetrahedral ordering (Bailey, 1984). Nevertheless, the R-factor of Güven's (1971) phengite-2M₁ (4.5%) is low, and there is no reason to doubt the validity of the tetrahedral ordering found there. Therefore, some phengites must have tetrahedral cation ordering whereas others do not.

The environment of crystal formation may be the controlling factor of tetrahedral order or disorder in phengites. Güven's (1971) phengite-2M₁ formed in a low-grade glaucophane + actinolite + chlorite + aragonite + quartz schist under blueschist facies conditions. This high pressure environment would encourage ordering of cations. On the other hand, the phengite-2M₁ of the present study was associated with quartz + epidote + zoisite + magnetite and crystallized under lower-pressure, higher-temperature amphibolite facies conditions (Arribas, 1968, and personal communication, 1983), which would favor disorder. Additional

work on phengites from various environments may help to unravel the controls of tetrahedral order and disorder.

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