

The crystal structure of preiswerkite

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ABSTRACT

The structure of preiswerkite, ideally $\text{Na}(\text{Mg}_2\text{Al})(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$, from the type locality at Geisspfad in Switzerland, has been determined by single-crystal X-ray diffraction and refinement.

The polytype is $1M$ with space group $C2/m$. The unit-cell parameters are $a = 5.228(7)$, $b = 9.049(10)$, $c = 9.819(12)$ Å, $\beta = 100.42(13)^\circ$. As expected as a consequence of the tschermakitic substitution $^{6}\text{Mg} + ^{4}\text{Si} = ^{6}\text{Al} + ^{4}\text{Al}$, coupled with the $\text{K} = \text{Na}$ substitution, the ditrigonal distortion of the tetrahedral sheet is considerable ($\alpha = 20^\circ$), as in ephesite, clintonite, and margarite, because of a concomitant increase in tetrahedral dimensions, decrease in octahedral dimensions, and decrease in the $\langle \text{W-O} \rangle$ bond distance. The coordination of the interlayer cation becomes sixfold because of the very large value observed for the outer W-O distances, as in paragonite. The charge imbalance in the basal O atoms due to the high ^{4}Al content is compensated partly by a significant shortening of the $\text{T-O}_{\text{basal}}$ distances relative to the $\text{T-O}_{\text{apical}}$ distances and partly by some H bonding interactions that inhibit the replacement of OH by F. The O4-H bond is nearly parallel to c^* , as in phlogopite. Partial ordering can occur between the octahedral sites; long-range ordering in the tetrahedral sites has not been found.

Preiswerkite thus shares specific structural properties with a number of micas with very different compositions; apart from tetrahedral ordering, the closest structural analogue seems to be ephesite, ideally $\text{Na}(\text{LiAl}_2)(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$, which differs chemically only by the octahedral substitution $\text{Mg} + \text{Mg} = \text{Li} + \text{Al}$.

INTRODUCTION

Preiswerkite, a trioctahedral mica with the ideal formula $\text{Na}(\text{Mg}_2\text{Al})(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2$, was described in 1980 by Keusen and Peters; they found preiswerkite crystals with a small Fe component in a slightly schistose basic dike in the Geisspfad ultramafic complex in the Swiss Penninic Alps. In addition to the mineral description and chemical analysis, they reported X-ray powder diffraction data and determined, from Weissenberg photographs, that preiswerkite is a $2M_1$ -type mica with the likely space group $C2/c$, typical of the $2M_1$ polytype (cf. paragonite; see Table 3 in Bailey, 1984a).

Preiswerkite was subsequently reported at Allalinhorn, Switzerland (Meyer, 1983), Liset, Norway (Smith and Kechid, 1983; Kechid, 1984), and in Vendée, France (Godard and Smith, 1984; Godard, 1988). Smith (1988, p. 76) noted that all four localities display greenschist facies parageneses, three of them being retrogressed eclogite facies assemblages. In the four reported localities, as well as in a new, fifth, occurrence of preiswerkite, in ex-

tensively altered jadeitites from Guatemala (G. E. Harlow, personal communication), a pargasitic or magnesium aluminum taramite amphibole (\pm albite-rich plagioclase, zoisite, titanite, or a nepheline structure) is also present.

Ideal end-member aluminum silicon preiswerkite was synthesized by Franz and Althaus (1976), who called it "sodium-brittle mica," and by Liu (1989). They examined the solid solution between sodium end-member phlogopite and preiswerkite (corresponding to the tschermakitic substitution $^{6}\text{Mg} + ^{4}\text{Si} = ^{6}\text{Al} + ^{4}\text{Al}$) at different P and T conditions.

Tlili (1990) synthesized ferrous aluminum silicon preiswerkite and manganese aluminum silicon preiswerkite, as well as the Mg-Al-Si end-member at 1 and 2 kbar, 600 °C. However, the magnesium gallium silicon preiswerkite and Si-free magnesium aluminum germanium preiswerkite compositions yielded mineral mixtures at the same P - T conditions. Thus, the preiswerkite structure appears to accept large divalent octahedral cations (Fe^{2+} ,

Mn) but not large trivalent (Ga) or tetravalent (Ge) tetrahedral cations, in contrast to the structure of sodium end-member phlogopite, where the Ga or Ge equivalents were found to be readily synthesized, but not the Fe^{2+} or Mn equivalents (all in the same P - T range; Tlili, 1990). As noted below, these relationships are consistent with the increasing misfit between the diminishing octahedral dimensions and expanding tetrahedral dimensions of the tschermakitic substitution. The large Ga and Ge tetrahedral cations increase the misfit and reduce stability, whereas the larger Fe^{2+} and Mn octahedral cations attenuate distortions and enhance stability, in the direction toward preiswerkite.

Extensive spectroscopic data by Raman, infrared, and/or ^{29}Si MAS NMR techniques on natural and synthetic preiswerkite and related micas are available and provide information on geometrical distortion and order-disorder relationships in the tetrahedral and octahedral sites (Smith et al., 1987; Tlili et al., 1987, 1988, 1989; Tlili, 1990; Liu, 1989; Robert and Kodama, 1988; Circone et al., 1991; Sanz and Robert, 1992). Data from Circone et al. (1991), which supposedly relate to trioctahedral compositions close to the K equivalent of preiswerkite (there called "eastonite"), are not treated here. In fact their compositions, purported to lie on the join between phlogopite and potassium end-member preiswerkite, clearly do not. The compositions are either not truly trioctahedral because of octahedral vacancies (see Robert, 1976) and the presence of free corundum, as recorded by Circone et al., or the experimental products are imperfectly crystallized and possibly partly hydrated due to short experiment times. In addition, the given unit-cell parameters are incompatible (e.g., c too long) for any anhydrous purely trioctahedral $C2/m$ potassium mica.

Despite the interest in the crystal chemistry of micas (e.g., Bailey, 1984b), few structural data are available for Na-Al-rich compositions. Therefore, we present single-crystal X-ray structure refinements of preiswerkite from the type locality of Keusen and Peters (1980). An X-ray investigation of synthetic sodium end-member preiswerkite crystals obtained at 6 kbar, 475 °C (Tlili, 1990), failed because of small crystal size and poor quality. Crystals from other localities were also too small for this study.

ANALYTICAL TECHNIQUES

Several crystals from the type locality were extracted by the crushing and grinding of small rock fragments. In general, their crystal quality was low, and in all cases [310] twinning or polytypic sequences [$1M + 1M_d$ (d = disordered); $1M + 2M$,] affected the crystals. These features obliged us to select several different crystals and to use different data measurement conditions to check the implications of the crystal characteristics and of the experimental conditions on the crystal chemical results. The results of the two best structure refinements, representative of the most interesting features presented by the preiswerkite crystals, are reported in this work (Tables 1–4).

TABLE 1. Data measurement and structure refinement data for preiswerkite

	KP9	KP17
a (Å)	5.225(4)	5.228(7)
b (Å)	9.050(8)	9.049(10)
c (Å)	9.791(9)	9.819(12)
β (°)	100.27(6)	100.41(13)
V (Å ³)	455.6	456.9
Space group	$C2/m$	$C2/m$
θ range (°)	2–35	2–40
Scan mode	ω	$\omega/2\theta$
Scan width (°)	9.0	5.0
F_o	1112	1497
$F_o > 2\sigma(F_o)$	661	802*
R_{sym} (%)	6.3	7.0
R_{obs} (%)	3.8	4.6
R_{tot} (%)	10.2	10.2

* $F_o > 3(F_o)$.

X-ray data measurement

After selection for optical behavior and freedom from inclusions, crystals were mounted on a Philips PW 1100 automated four-circle diffractometer and studied with graphite-monochromated $\text{MoK}\alpha$ radiation; crystal quality was assessed by peak shape and width. Unit-cell dimensions were determined from least-squares refinement of d values obtained for 40 rows of the reciprocal lattice by measuring the barycenter of each reflection (1–4 in each row) in the θ range 2–35°, and the equivalent reflection at negative θ values. Ten crystals have been used for structure refinement, obtaining in all cases comparable crystal chemical results within the estimated standard deviations, with the exception of different ordering of the octahedral cations. The experimental conditions for data measurement for the two most representative crystals are listed in Table 1, together with selected crystal data.

All the examined preiswerkite crystals belong dominantly to the $1M$ polytype and have been refined in space group $C2/m$, as is the case with phlogopite and true "eastonite" (Ungaretti et al., 1990). Some crystals showed disordered stacking sequences, in agreement with the findings of Bailey (1984b, p. 582), who reported the $1M_d$ polytype for preiswerkite. This is also in agreement with Tlili (1990, p. 62 and 161), who, by means of X-ray powder diffraction on synthetic crystals of various magnesium-, iron-, manganese-, gallium- and/or germanium-phlogopite/eastonite/preiswerkite, found both $1M$ and $1M_d$ polytypes in various parts of these systems, depending upon the compositions and the presence or absence of hydrates.

Many crystals are characterized by a variable amount of [310] twinning (cf. Smith and Yoder, 1956; Brigatti and Davoli, 1990); crystal KP17, which is characterized by the absence of any [310] twinning, shows ordered $1M + 2M$, sequences (Bigi and Brigatti, in preparation). The two phenomena (twinning and coexistence of both polytypes) were examined by means of single-crystal four-circle diffractometry and long-exposure precession pho-

TABLE 2. Atomic coordinates, equivalent isotropic and anisotropic ($\times 10^4$) displacement parameters, and m.a.n.

Site	x	y	z	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	m.a.n.
Preiswerkite KP9											
O1	0.8546(5)	0.1971(3)	0.1593(2)	0.65(4)	68(7)	9(2)	26(2)	12(4)	13(5)	-3(2)	8.00
O2	0.4487(5)	0	0.1598(3)	0.58(6)	29(10)	10(3)	32(3)	0	21(6)	0	8.00
O3	0.6285(8)	0.1685(2)	0.3918(2)	0.90(6)	111(10)	24(4)	17(2)	3(4)	-5(7)	8(2)	8.00
O4	0.1335(10)	0	0.3970(4)	1.48(9)	122(13)	70(7)	23(2)	0	12(9)	0	8.00
T	0.5709(2)	0.1666	0.2126(1)	0.47(2)	34(3)	16(1)	14(1)	0(2)	4(2)	0(1)	13.50
M1	0	1/2	1/2	0.66(4)	32(6)	22(3)	25(2)	0	6(5)	0	14.05
M2	0	0.8291(1)	1/2	0.61(3)	61(5)	16(2)	17(1)	0	2(5)	0	13.28
W	0	0	0	1.22(7)	107(11)	42(5)	32(3)	0	14(7)	0	10.50
H	0.0749(5)	0	0.3042(3)	1.00							1.00
Preiswerkite KP17											
O1	0.8559(5)	0.1989(3)	0.1584(3)	1.09(5)	94(7)	36(2)	8(3)	2(4)	11(5)	-1(2)	8.00
O2	0.4530(7)	0	0.1651(4)	0.98(7)	105(12)	24(3)	7(4)	0	4(7)	0	8.00
O3	0.6348(5)	0.1703(3)	0.3905(3)	0.96(5)	94(6)	24(2)	7(3)	-3(4)	-1(4)	3(2)	8.00
O4	0.1252(7)	0	0.3989(4)	1.28(8)	71(11)	73(5)	4(4)	0	-1(6)	0	8.00
T	0.5740(2)	0.1672(1)	0.2139(1)	0.60(2)	52(2)	17(1)	5(1)	-2(2)	3(2)	-1(1)	13.50
M1	0	1/2	1/2	0.60(5)	40(7)	11(2)	7(3)	0	4(4)	0	13.20
M2	0	0.8302(2)	1/2	0.62(3)	49(4)	16(2)	6(2)	0	4(3)	0	13.31
W	0	0	0	1.83(9)	190(13)	60(4)	10(5)	0	7(8)	0	10.64
H	0.0831(4)	0	0.2950(3)	1.00							1.00

Note: displacement parameters are given in squared ångströms; m.a.n. are given in electrons.

tographs (see Fig. 1). The two cases can be distinguished by the presence of additional reflections occurring at $1/3$ or $1/2$, respectively, of the separation between two adjacent hkl and $hkl + 1$ reflections with $k \neq 3n$. The two selected refinements come from the most [310] twinned crystal (around 50% of each individual in IM_d sample KP9) and from a crystal with no [310] twinning, but with IM (90%) + $2M_1$ (10%) polytypes (sample KP17).

Intensity data were acquired for the monoclinic-equiv-

alent pairs hkl and $h\bar{k}l$ in the Laue group $2/m$; the θ range 2 to (35–40) $^\circ$ was explored using the step-scan profile technique of Lehman and Larsen (1974). The intensity data were corrected for Lorentz and polarization effects and for absorption by the method of North et al. (1968), averaged (the discrepancy factor, R_{sym} , is given in Table 1), and reduced to structure factors.

Structure refinement and correction for twinning and for ($IM + 2M_1$) coexisting polytypes

The unweighted structure refinements were performed without chemical constraints, starting from the published coordinates for IM phlogopite (Joswig, 1972).

Fully ionized scattering factors were used for nontetrahedral sites, whereas both neutral and ionized scattering factors were used for the tetrahedral sites and the O sites, as suggested by Ungaretti et al. (1983) in the case of amphiboles. In particular, the following scattering factors were calculated and used for various sites: $Al_{0.50}^{3+}Si_{0.50}^{4+}$ vs. $Al_{0.50}Si_{0.50}$ for T, $Mg_{0.85}^{2+}Al_{0.15}^{3+}$ vs. Fe^{2+} for M1, $Mg_{0.50}^{2+}Al_{0.50}^{3+}$ vs. Fe^{2+} for M2, and \square vs. Na^+ or K^+ vs. Na^+ for W; in any case, the refinement was done under the constraint that the occupancies of these sites must sum to 1.

Difference-Fourier maps calculated at the end of the refinement with anisotropic displacement factors showed some residual electron density peaks, the highest located between the standard W and H sites and almost at the center of the ditrigonal array of Si,Al tetrahedra, and another located between two back-to-back tetrahedral sheets. In the IM polytype, these features are compatible both with [310] twinning (Smith and Yoder, 1956; Brigatti and Davoli, 1990) and with the presence of some $2M_1$ ordered stacking sequences. In the IM polytype, a vector displacement of the upper half of a layer by $b/3$ with respect to the lower half, which significantly corresponds to a stacking error of 120 $^\circ$ rotation, produces twinning about

TABLE 3. Selected interatomic distances in preiswerkite

	KP9	KP17
T-O1 (b)	1.680(3)	1.686(3)
-O1 (b)	1.692(3)	1.685(3)
-O2 (b)	1.682(2)	1.684(2)
-O3 (a)	1.726(3)	1.705(3)
(T-O)	1.695	1.690
O1-O1	2.783(3)	2.772(4)
-O2	2.772(3)	2.770(4)
-O2	2.785(3)	2.775(4)
-O3	2.757(3)	2.748(4)
-O3	2.747(3)	2.742(4)
O2-O3	2.758(3)	2.750(5)
M1-O3 $\times 4$	2.038(3)	2.074(3)
-O4 $\times 2$	1.999(5)	2.030(5)
(M1-O)	2.025	2.060
M2-O3 $\times 2$	2.039(4)	2.015(3)
-O3 $\times 2$	1.985(3)	2.005(3)
-O4 $\times 2$	2.036(3)	2.002(3)
(M2-O)	2.020	2.007
((M-O))	2.022	2.025
W-O1 $\times 4$	2.572(3)	2.589(3)
-O1 $\times 4$	3.514(3)	3.501(4)
-O2 $\times 2$	2.576(4)	2.601(4)
-O2 $\times 2$	3.514(4)	3.512(5)
(W-O) ₁	2.573	2.586
(W-O) ₂	3.514	3.505
(W-O)	3.043	3.045
H-O4	0.906(4)	1.004(4)

Note: distances are given in ångströms; estimated standard deviations are in parentheses; a = apical, b = basal.

TABLE 4. Indices of angular and polyhedral distortion in preiswerkite

	KP9	KP17
α (°)	20.0	19.5
τ (°)	107.7	108.2
ψ (°)	59.5	59.6
ρ (°)	99.2	92.0
t_1 (Å)	2.238	2.231
t_0 (Å)	2.051	2.051

Note: symbols are according to Bailey (1984a).

the [310] axis. The observed residual peaks in the difference-Fourier maps are therefore the consequence of some crystal domains shifted by $\pm b/3$ with respect to the dominant *IM* matrix.

Analogously to [310] twinning, the $2M_1$ polytype may derive from *IM* after a stacking error of 120° rotation. The coexistence of *IM* and $2M_1$ biotite has recently been reported in plutonic rocks by Bigi and Brigatti (in preparation), who studied the phenomenon by means of TEM and single-crystal structure refinement. Apart from evidence for [310] twinning in some biotite crystals, those authors found, on one hand, different amounts of *IM* and $2M_1$ polytypes within the same crystal and, on the other hand, coexisting crystals belonging to one or the other of these polytypes; in both cases they did not find differences in chemical composition between the two polytypes. Bigi and Brigatti concluded that, given the geometry of the mica layer, the boundary lines between twinning, polytypes, and disordered stacking sequences are ambiguous and depend on the scale of investigation. Twinning in fact derives from a single stacking fault in an ordered polytype, whereas a different polytype may be considered the result of a twinning operation periodically distributed along an ordered sequence.

Twinning about [310] and (*IM* + $2M_1$) polytypism imply that superposition of the diffraction peaks belonging to all the components affects the $k = 3n$ reflections, whereas no superposition occurs for $k \neq 3n$ reflections; this feature was in fact clearly visible, as mentioned above, when strong reflections with $k \neq 3n$ were scanned. Therefore, an approximate way of estimating the volume fraction (vf) of the prevailing twin or of the prevailing polytype is the following:

$$vf = (K_{\neq 3n}/K_{3n})^2$$

in which $K_{\neq 3n}$ and K_{3n} are the scale factors obtained after least-squares refinement of structure factors, when using the class of reflections as defined above.

A more accurate value for vf is obtained from a locally written program which allows the refinement of vf, along with the structure parameters. In this case, apparently because significant substitutions were present, high correlations were obtained between vf, the scale factor, and site occupancies. Therefore, different structure refinements were made for the same data by imposing different vf values around the approximate value obtained as above. In the case of the coexisting *IM* + $2M_1$ polytypes,

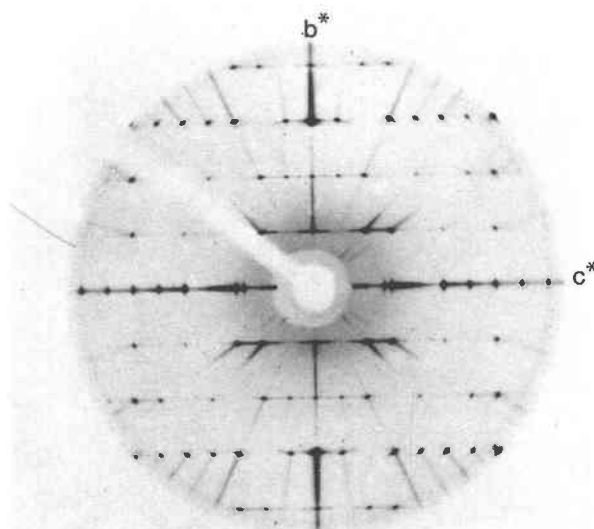


Fig. 1. The 0kl precession photograph of preiswerkite KP17; $\mu = 25^\circ$, MoK α (Zr-filtered) radiation. Some very weak but sharp extra reflections belonging to the $2M_1$ polytype are visible along the rows with $k \neq 3n$.

vf was optimized after the transformation of the coordinates of $2M_1$ into the *IM* unit cell. The vf value corresponding to the lowest *R* factor was chosen for each crystal. In the case of the *IM* [310]-twinning KP9 crystal, the optimized vf was 0.52; in the case of KP17 it was 0.90 (*IM* [+0.10 ($2M_1$)] (Table 2). After correction for 48% twinning or for 0.10 $2M_1$ polytype, the highest peak in the difference-Fourier map was in the expected position of the H site. It was given an equivalent isotropic displacement factor of 1 Å², added to the structural model, but the H parameters were not allowed to vary during subsequent cycles of refinement.

Final unweighted *R* indices are listed in Table 1. Atomic coordinates, mean atomic numbers (m.a.n.) for cation sites, and equivalent isotropic and anisotropic atomic displacement factors are reported in Table 2. Details of the polyhedral geometry are reported in Table 3, whereas the traditional distortion parameters used in crystal chemical studies on micas are reported in Table 4.

Electron microprobe (EMP) and ion probe (SIMS) analysis

EMP analyses (Table 5, with all Fe as Fe²⁺) were obtained for the preiswerkite type material used in this study by either the Cameca Camebax electron microprobe at the Muséum National d'Histoire Naturelle (Paris) or the Jeol JXA-840A microprobe at the Centro Grandi Strumenti of the University of Pavia.

Because of the rather low m.a.n. at the W site found in

TABLE 5. Electron microprobe analyses of preiswerkite from the type locality

	1	2	3	4	5
SiO ₂	30.50	29.90	30.12	30.80	31.23
Al ₂ O ₃	35.00	35.40	34.05	35.06	35.09
TiO ₂	0.10	0.00	0.01	0.04	0.00
FeO	2.50	2.80	3.33	3.46	3.06
MgO	18.30	18.70	18.68	18.09	18.82
MnO	0.00	0.00	0.07	0.06	0.05
Cr ₂ O ₃	0.00	0.00	0.18	0.21	0.19
NiO	nd	nd	nd	0.09	0.00
CaO	0.10	0.09	0.11	0.10	0.05
Na ₂ O	7.70	7.35	7.56	7.39	6.33
K ₂ O	0.20	0.19	0.26	0.21	0.28
F	0.10	0.00	0.10	nd	0.00
H ₂ O	4.60*	4.60*	(4.30)	(4.39)	(4.43)
O = F	-0.04	0.00	-0.04	nd	0.00
Total	99.06	99.03	98.73	99.90	99.53
Atomic proportions based on 12 O atoms					
Si	2.084	2.047	2.083	2.101	2.123
¹⁴ Al	1.916	1.953	1.917	1.899	1.877
Total	4.000	4.000	4.000	4.000	4.000
¹⁹ Al	0.903	0.903	0.859	0.920	0.934
Ti	0.005	0.000	0.001	0.002	0.000
Fe	0.143	0.160	0.193	0.197	0.174
Mg	1.864	1.909	1.927	1.840	1.908
Mn	0.000	0.000	0.004	0.003	0.003
Cr	0.000	0.000	0.010	0.011	0.010
Ni	0.000	0.000	0.000	0.005	0.000
Total	2.915	2.972	2.994	2.978	3.029
Ca	0.007	0.007	0.008	0.007	0.004
Na	1.020	0.976	1.014	0.977	0.834
K	0.017	0.017	0.023	0.018	0.024
Total	1.044	1.000	1.045	1.002	0.862
F	0.023	0.000	0.023	0.000	0.000
OH	2.097	2.101	(1.984)	(1.997)	(2.009)

Note: numbered references are as follows: 1 = Basel (Keusen and Peters, 1980), 2 = Zurich (Keusen and Peters, 1980), 3 = Paris (this work, mean of 9), 4 = Paris (Tlili, 1990, mean of 6), 5 = Pavia (this work, mean of 4). Calculated values are in parentheses.

* Determined on impure concentrate.

some preiswerkite crystals by the structure refinements, a search for Li was performed by using the secondary ion mass spectrometry technique with the Cameca IMS4F ion probe at the CSCC. This analysis, performed as reported in Ottolini et al. (1993), showed the presence of a small and variable Li content (0.0–0.2 Li₂O wt%). This indicates that the various crystals used in the refinement may differ somewhat in their chemical compositions, whose range can be bracketed as the following: (Ca_{0.0–0.02}–K_{0.0–0.04}Li_{0.0–0.08}Na_{0.83–1.00})(Mg_{1.84–1.94}Fe_{0.15–0.21}Al_{0.85–0.95}–(Si_{2.03–2.12}Al_{1.88–1.97})O₁₀(OH)₂.

RESULTS AND DISCUSSION

Only descriptions of the most important features of the preiswerkite structure (Fig. 2) and their relations with the structure data available for phlogopite (Joswig, 1972) are given in this paper. This comparison is important because both preiswerkite and phlogopite belong to the *1M* polytype and are almost Fe-free trioctahedral micas. Thus we are in the ideal situation to examine the structural variations due to a combination of the Al + Al = Mg + Si and K = Na exchanges in trioctahedral micas.

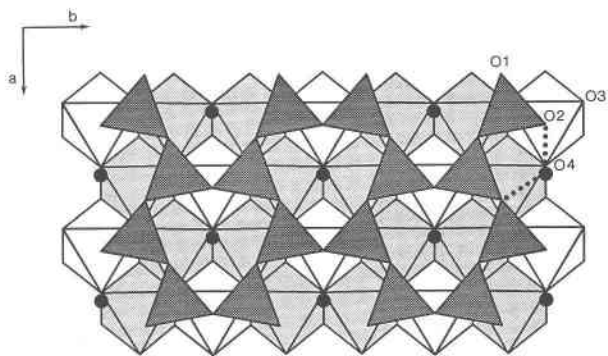


Fig. 2. An illustration of the preiswerkite structure projected on the (001) plane. The W cations at the center of the rings of tetrahedra have been omitted in order to show the positions of the H atoms (solid circles), which lie almost vertically above the O4 sites. Dotted lines indicate weak H-bonding interactions with the nearest O1 and O2 anions. In the octahedral sheet the M1 sites are blank, and the M2 sites are shaded.

Chemical composition

A small degree of chemical variability is revealed by the analyses reported in Table 5 and by the range in crystal chemical formulae shown above and obtained by combining EMP + SIMS + X-ray refinement data. In any case, with the number of Si atoms close to 2 (2.05–2.1), Mg ≫ Fe²⁺, Na ≥ 0.83, F ≤ 0.03, and Cl ≤ 0.002, the samples all have compositions fairly close to that of the pure OH end-member.

Unit-cell parameters

The unit-cell parameters obtained for natural preiswerkite (Table 1) are close to the values determined for synthetic pure magnesium preiswerkite ($a = 5.218$, $b = 9.040$, $c = 9.793$ Å, $\beta = 100.26^\circ$; Tlili, 1990); the slightly larger values for the natural crystals can be attributed principally to the Fe content.

The unit-cell translations are significantly shorter than those reported for natural phlogopite ($a = 5.314$, $b = 9.202$, $c = 10.164$ Å; $\beta = 100.05^\circ$). This shortening is due to a combination of the effects of the two different substitutions involved: (1) the K → Na substitution, which reduces all the a , b , and c values, as can be seen by comparing muscovite (Güven, 1971) with paragonite (Lin and Bailey, 1984), and (2) the tschermakitic substitution, which reduces b with variable behavior for a and c for all the magnesium aluminum silicon sodian, iron aluminum silicon sodian, magnesium gallium silicon sodian, and magnesium aluminum germanium sodian series (Tlili, 1990, p. 161), as well as from phengite to muscovite (Güven, 1971).

Tetrahedral sheet

The presence of only one independent tetrahedral site in space group *C2/m* implies complete long-range Al,Si disorder in the tetrahedral sheet, even at this 1:1 composition. On the other hand, Raman spectra obtained from

various natural and synthetic mica samples (Smith et al., 1987; Tlili et al., 1987, 1988, 1989; Tlili, 1990, p. 174, 182, and 239) suggest the presence of strong short-range order in preiswerkite (i.e., alternating Al and Si tetrahedra). This is indicated by (1) a strong peak attributed to Si-O_b-Al vibration at 652 cm⁻¹, accompanied by relatively weak peaks attributed to Si-O_b-Si and Al-O_b-Al vibrations; and (2) in natural preiswerkite, two sharp peaks at 955 and 916 cm⁻¹, respectively, attributed to Si-O_a vibrations where Si is surrounded by three Al tetrahedra and to Al-O_a vibrations where Al is surrounded by three Si tetrahedra [in these expressions, subscript a indicates the apical O3 atom, whereas subscript b indicates the three basal O1 (×2) and O2 atoms]. The latter behavior is analogous to the strong peaks observed in margarite (which is long-range ordered with alternating Al and Si) and is in contrast to the wide clusters in the region in the range 850–1150 cm⁻¹ in disordered eastonite, phlogopite, muscovite, and phengite. Clintonite also shares this Raman behavior and hence may also be ordered.

Likewise, the ²⁹Si and ²⁷Al NMR study of synthetic preiswerkite and other phyllosilicates by Sanz and Robert (1992) clearly revealed a significant proportion of nearest-neighbor tetrahedral environments where Si is surrounded by Al₃ with a detectable number of Al₂Si environments but no detected AlSi₂ or Si₃ environments. Significantly, their data indicate a decrease not only of Si₃ and of AlSi₂ but also of Al₂Si environments at the expense of Al₃ environments as the mica composition approaches the composition of preiswerkite, thus again emphasizing the predominance of alternating Al and Si tetrahedra.

Long-range order of the tetrahedral cations would be responsible for the presence of weak, extra reflections determined by the change in periodicity or by the decrease of symmetry from C2/m to C2 or to C1. However, no extra reflections (with the exception of those due to [310] twinning or to some ordered 2M₁ stacking sequence) have been recognized in any of the several crystals submitted to X-ray analysis. As far as a non-centrosymmetric (monoclinic or triclinic) space group is concerned, this cannot be theoretically ruled out. However, although the equivalence of intensities of *hkl* and *h \bar{k} l* pairs is not fully satisfactory (cf. the rather high R_{sym} values), we mainly ascribe this to the low quality of the crystals and not to triclinic C1 symmetry. In fact the same R_{sym} factor calculated by using only the reflections with F_o > 3σ(F_o) and F_o > 5σ(F_o) reduces to 2.5 and 2.1 for crystal KP9 and 3.5 and 2.8 for crystal KP17. Furthermore, no systematic difference between the same *hkl* and *h \bar{k} l* pairs has been found when comparing the several sets of diffraction data measured with different preiswerkite crystals. Finally, a preiswerkite separate has not shown any piezoelectric effect when examined with Giebe-Schaube equipment, which gave a signal in the case of a mixture of 90% calcite + 10% quartz. Therefore the assumption of space group C2/m is definitely confirmed within the experimental accuracy of the available data.

Hence it is clear that although Si and Al tend to alternate (based on the avoidance principle, strong Si-O_b-Al Raman vibration, distinct Si-O_a and Al-O_a Raman vibration, and Al₃ and Si₃ environments by NMR), this feature is not extended in a periodic nature throughout the crystal (no extra reflections, no lowering of the average symmetry, no piezoelectric effect), such that the overall structure of the tetrahedral sheet is truly disordered (space group C2/m, 1M polytype). It is interesting to note that ephesite, ideally Na(LiAl₂)(Si₂Al₂)O₁₀(OH)₂, which differs chemically only by the octahedral Mg + Mg = Li + Al substitution, is strongly ordered with internal symmetry as low C1 (Slade et al., 1987). In the latter case, however, the presence of monovalent and trivalent octahedral cations requires ordering of the tetrahedral cations so as to achieve a suitable local charge balance.

A rather interesting result from these structure refinements concerns the geometry of the tetrahedral sheet. In micas this is generally described by two different parameters: α = 1/2(120° - <O_b-O_b-O_b>), which measures the deviation from ideality of the six-membered ring, and τ = <O_a-T-O_b>, which is a measure of the deviation from ideality of the T tetrahedron. In the case of preiswerkite, the observed values for both these indices (see Table 4) indicate (as expected: Bailey, 1984c; Tlili, 1990) a much more significant distortion than in phlogopite, in which α = 7.7° and τ = 110.6°, respectively. The ⁶⁰Mg + ⁴⁴Si = ⁶⁰Al + ⁴⁴Al substitution is in fact expected to cause an increase in the size of the tetrahedra [the ionic radii (ir) for ⁴⁴Si and ⁴⁴Al are 0.26 and 0.39 Å, respectively (Shannon, 1976)], and to decrease that of the octahedra (the ir are 0.72 and 0.535 Å for ⁶⁰Mg and ⁶⁰Al, respectively). The resulting misfit is minimized by means of the distortion of the tetrahedral sheet.

It is also to be noted here that τ in preiswerkite is smaller than the ideal tetrahedral value of 109.49°, in contrast to the situation in phlogopite, for which τ = 110.6° was reported.

Replacing ⁴⁴Si⁴⁺ with ⁴⁴Al³⁺ decreases the bond strength of all four T-O bonds [O1 (×2), O2, O3], whereas the coupled replacement of ⁶⁰Mg²⁺ by ⁶⁰Al³⁺ increases the bond strength of all M-O bonds [O3 (×4), O4 (×2)]. Therefore the combined effect in preiswerkite (as in ephesite, Slade et al., 1987) results in underbonding of the basal atoms O1 and O2 and overbonding of the apical atom O3. A partial compensation of this imbalance is obtained by the T cation being nearer to the plane formed by the basal O atoms such that T-O_a is considerably longer than T-O_b (T-O_a ≫ T-O_b, Table 3); both distances are larger than those in phlogopite, where T-O_a ~ T-O_b. Infrared and Raman observations also indicate this relative elongation of T-O_a (Tlili, 1990). Clearly this mechanism is appropriate in potassium or sodium micas, but not in calcium micas, where the higher charged interlayer cation satisfies the basal O charges and the T cation can therefore be closer to the apical O.

Although T-O_a ≫ T-O_b in preiswerkite, it is important to note that the tetrahedron is not elongated in the O_a

direction, as can be seen from the basal O_b-O_b distances, which exceed the lateral O_b-O_a distances. The tetrahedron is thus flattened relative to the tetrahedron of phlogopite and those of all Li-free potassium or sodium di- or trioctahedral micas, but this characteristic is not evident in much of the literature, where O-O distances are often not listed. Careful examination of the interdependence of the angle τ and the various T-O and O-O distances (Tlili, 1990) reveals that τ and T-O values alone are an unreliable guide to the outer shape of the tetrahedron.

Octahedral sheet

Inspection of the differing $\langle M1-O \rangle$ and $\langle M2-O \rangle$ distances and of the similar grand mean values in samples KP9 and KP17 clearly shows the presence of different degrees of Mg,Al ordering in the octahedral sheet (Table 3).

In sample KP9 the two octahedral mean distances are very similar, indicating nearly complete disorder of the octahedral cations. Since the structure refinements of other preiswerkite crystals did not reveal a distribution of the octahedral cations related to the [310] twinning, ordering appears to be independent of octahedral composition and also twinning or stacking sequences.

Compared with the $\langle M1-O \rangle$ and $\langle M2-O \rangle$ values of the pure Mg-bearing octahedra in phlogopite, which are virtually identical to each other (2.066 and 2.063 Å, respectively), the $\langle M1-O \rangle$ distance in the substantially ordered KP17 crystal is very similar (2.060 Å), whereas the (Mg + Al)-bearing $\langle M2-O \rangle$ distance is much smaller (2.007 Å) and is thus almost intermediate with respect to the $\langle M2-O \rangle$ distance in pure Al-bearing octahedra in muscovite and paragonite (1.900 and 1.940 Å, respectively) and in various potassium micas and lithium micas. On the other hand in the disordered KP9 crystal both $\langle M1-O \rangle$ and $\langle M2-O \rangle$ values (2.025 and 2.020 Å, respectively) are similar to those of clintonite (2.046 and 2.020 Å; Joswig et al., 1986), which has the same ideal octahedral composition (Mg_2Al). The $\langle M1-O \rangle$ value of crystal KP9 is the smallest $\langle M1-O \rangle$ value yet recorded for any potassium or sodium trioctahedral mica, and indeed it seems to be the smallest known for any kind of natural or synthetic mica (as reviewed in Tlili, 1990).

The grand mean $\langle \langle M-O \rangle \rangle$ distances for all preiswerkite refinements is between 2.022 and 2.025 Å, in reasonable agreement with an ideal mean octahedral composition (Mg_2Al)/3. In fact, by using $\langle Mg-O \rangle = 2.078$ Å and $\langle Al-O \rangle = 1.925$ Å as in the crystal chemical studies of amphiboles (Ungaretti et al., 1983), a value of $(2 \times 2.078 + 1.925)/3 = 2.027$ Å is obtained.

The octahedral sheet thickness (see Table 4) is in reasonable agreement with the octahedral chemical composition of preiswerkite and seems to be independent of the Mg,Al ordering between M1 and M2.

Interlayer site

As is shown from both the EMP analyses and the results of the structure refinements, the interlayer site W in

preiswerkite is occupied mainly by Na (>93%, with minor Li, K, and Ca). Accordingly, the W site dimensions are much smaller than those in phlogopite. The difference between the $\langle W-O \rangle_o$ (outer) and the $\langle W-O \rangle_i$ (inner) distances in preiswerkite is 0.941 and 0.919 Å for the two samples of this work, significantly greater than that observed in phlogopite (0.349 Å) but near to the values (1.031 and 1.026 Å, respectively) observed for the two independent W sites in ephesite, which is the only other Na-Al-rich trioctahedral mica for which structural data are available (Slade et al., 1987).

The absolute values for $\langle W-O \rangle_o$ and $\langle W-O \rangle_i$ are similar not only in preiswerkite and ephesite, but also in clintonite and margarite, all of which have similar α values (between 19.8 and 23.1°; Tlili, 1990).

It should be noted that the coordination of the W site in preiswerkite is essentially sixfold, as indicated by the $\langle W-O \rangle_i$ distance (2.573–2.586 Å), which, again as in ephesite, tends to approach the expected $\langle Na-O \rangle$ value for true sixfold coordination, as in sodium nitrate (2.417 Å; Sass et al., 1957). In fact, the $\langle W-O \rangle_i$ values in preiswerkite are significantly shorter than those observed in nepheline, in which Na is eightfold coordinated (2.620 Å, Foreman and Peacor, 1970), and are the smallest recorded for any sodium or potassium trioctahedral or dioctahedral mica apart from ephesite, being smaller than the value observed for paragonite (2.624 Å). The $\langle W-O \rangle_o$ distances of preiswerkite, ephesite, and clintonite are the longest of any refined natural micas and can hardly be considered to be involved in any bonding interactions with W.

OH site

The position of the proton is of great interest in view of the numerous publications on the OH stretching frequencies determined by various spectroscopic methods (Bailey, 1984c; Giese, 1984; Guggenheim, 1984; Rossman, 1984; Robert and Kodama, 1988; Tlili et al., 1989).

The difference-Fourier maps, after the correction for [310] twinning or for the coexisting $2M$, polytype, revealed as the most prominent peak a rather sharp electron density residue approximately 1 Å from O4; this residue appeared at nearly the same coordinates in all ten structure refinements, indicating that the proton is really at this position and that it is not affected by significant positional disorder.

The distance of H^+ from the nearest O1 ($\times 2$) and O2 basal atoms (2.44 and 2.61 Å for sample KP9 and 2.42 and 2.52 Å for sample KP17), combined with the residual underbonding on the same O atoms (discussed above), strongly suggests the presence of some H-bonding interactions (Fig. 2). Bond strength contributions of 0.85 and 0.15 vu, respectively, to the O atom of the OH group and to the three involved basal O atoms (altogether) are exactly what permit a satisfactory local charge balance to the otherwise overbonded O4 and to the underbonded O1 and O2. Furthermore, the structural importance of these bonding contributions nicely explains why natural

preiswerkite does not show significant F contents, in contrast with most other micas, where the H-O_b distances are much longer (O1-H = 2.72 and O2-H = 2.74 Å in phlogopite), thus precluding significant bonding interactions. The same argument concerning local charge balance was employed to explain why ephesite is also F free (Robert and Bény, 1988; Robert et al., 1993).

That the proton approaches the three basal O atoms means that the O4-H bond is essentially vertical (i.e., parallel to c^* ; $\rho = 99.2$ and 92.0° , respectively, for KP9 and KP17) as in other Li-free trioctahedral micas (e.g., phlogopite), instead of being inclined as in Li-bearing trioctahedral micas [e.g., lepidolite (Guggenheim, 1981) and zinnwaldite (Guggenheim and Bailey, 1977)] or in dioctahedral micas [e.g., muscovite and margarite, where the O-H bond can be almost horizontal (Rothbauer, 1971; Guggenheim and Bailey, 1975, 1978; Joswig et al., 1983)]; the list of ρ angles calculated in Giese (1984, p. 119) is very useful in this connection.

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