Cation ordering in lepidolite

STEPHEN GUGGENHEIM

Department of Geological Sciences
University of Illinois at Chicago
Chicago, Illinois 60680

Abstract

Three lepidolite-1M and two lepidolite-$2M_2$ mica structures from three localities have been refined using single crystal X-ray data to determine cation ordering schemes in both ideal and subgroup symmetries. The 1M ($R_1 = 0.035$) and $2M_2$ ($R_1 = 0.048$) crystals from Radkovice, Czechoslovakia are ordered in their respective ideal space groups so that $M(1) = Li_{0.91}(Mn,Mg)_{0.09}$ for lepidolite-1M and $M(1) = Li_{1.0}$ for lepidolite-$2M_2$. In contrast, the lepidolite-1M from Tanakamiyama, Japan ($R_1 = 0.062$) is similar topologically to zinnwaldite in subgroup symmetry $C2$. The octahedra related by the pseudo-mirror plane are significantly different in size (mean M–O,F,OH = 1.88Å) and electron count (11.5 and 6.0). The difference in electron count between these two octahedral sites is more substantial than in zinnwaldite. The previous $2M_2$ refinement of Sartori *et al.* (1973) is confirmed but the 1M structure (Sartori, 1976) is better described as similar to that of the Tanakamiyama lepidolite, although due to systematic errors in the data an ordered model is not unequivocally established. Cation ordering similar to that found in the Tanakamiyama lepidolite is promoted by a high fluorine content, but parameters of crystallization other than fluorine content are important.

Introduction

Three recent refinements of layer silicate structures have shown that additional cation ordering may be present when symmetry constraints are relaxed from an assumed higher order space group to a lower one. Lower order space group refinements have shown that margarite-$2M_1$ (Guggenheim and Bailey, 1975, 1978) has an ordered arrangement of tetrahedral cations while zinnwaldite-1M (Guggenheim and Bailey, 1977) and a dioctahedral 1M mica (Sidorenko, *et al.*, 1975) showed both tetrahedral and octahedral ordering. In 1M polytypes of ideal space group ($C2/m$) symmetry, octahedral ordering is possible between the $M(1)$ site on the mirror plane and the two equivalent sites related by the mirror plane (both designated as $M(2)$). In zinnwaldite, the space group has been shown to be $C2$ and the two $M(2)$ sites are not symmetrically-related by a mirror plane as in space group $C2/m$. They are, therefore, designated as $M(2)$ and $M(3)$. The $M(2)$ site was shown to be occupied by aluminum whereas lithium, iron and vacancies are distributed randomly over the $M(1)$ and $M(3)$ sites.

The lepidolite micas have been shown to have several octahedral ordering schemes. The lepidolite-3T structure (Brown, 1978) crystallizes in space group $P3_112$ and has two sites that are large and lithium-rich and a small aluminum-rich third site. This type of ordering scheme is analogous to the zinnwaldite structure. In other lepidolite structures, when the ideal symmetry has been used in the refinement procedure, one large site is located in the *trans* arrangement at $M(1)$ and two smaller equivalent octahedra in *cis* orientation. This ordering pattern with $M(1)$ larger than the two $M(2)$ octahedra appears to be adopted even in structures where the octahedral composition might suggest alternate ordering models. Fluor-polylithionite-1M (Takeda and Burnham, 1969), lepidolite-1M (Sartori, 1976), lepidolite-$2M_2$ (Takeda, *et al.*, 1971; Sartori, *et al.*, 1973) and lepidolite-$2M_1$ (Sartori, 1977; Swanson and Bailey, 1981) are all lepidolite micas that appear to have such an ordering scheme where the $M(1)$ site contains the larger lithium ion and the two smaller symmetry-related $M(2)$ sites have an average composition near $Li_{0.5}Al_{0.5}$.

The novel ordering pattern for lepidolite-3T is significant in that such an ordering scheme indicates

there is no *a priori* reason why a similar scheme should not be found in the more common lepidolites. Experience has shown that some ordering schemes may not be observed because of refinement in the incorrect space group. Alternatively, crystallization history and environment may affect cation ordering. The purpose of this study is to examine cation ordering as a function of both possibilities. In addition, coexisting lepidolite polytypes ($1M$ and $2M_2$) are re-examined because systematic errors exist in data reported previously.

Preliminary refinements

Initially, Weissenberg film data (Sartori, 1976 and Sartori *et al.*, 1973) were used to refine the lepidolite-$1M$ and $2M_2$ structures in their respective centrosymmetric space groups and noncentric subgroups. Starting parameters were obtained for the $1M$ structure from the refinement by Sartori and for the $2M_2$ from Takeda *et al.* (1971). The scattering factor tables were from Cromer and Mann (1968). Each refinement in the ideal space group agrees with the results of Sartori (1976) and Sartori *et al.*, (1973); however, the isotropic thermal parameters of several atoms differ and the R values are considerably lower, presumably because of the effect of the different scattering factor tables.

The refinement procedure in subgroup symmetry in each case followed the method given by Guggenheim and Bailey (1975, 1977) and is reviewed below. For lepidolite-$1M$, starting models in $C2$ symmetry were obtained from zinnwaldite (Guggenheim and Bailey, 1977) or derived from the distance least-squares program OPTDIS written by W. A. Dollase of the University of California at Los Angeles. Each model was then refined by using the least-squares refinement program ORFLS (Busing *et al.*, 1962).

The model with the smaller M(3) site was rejected because it has more than double the R value of the alternate model. In addition, octahedral site compositions, as determined from bond lengths and scattering power, differ from the chemical analysis and those determined in the parent space group. However, convergence appeared successful for the model analogous to the zinnwaldite structure (Table 1). Calculated octahedral compositions based on bond distances are consistent with those determined from bond lengths in the parent space group, but bond lengths from the subgroup refinement are inconsistent with the chemical analysis (as was also noted in the supergroup refinement by Sartori, 1976). Differences in the T–O(2) bonds from within individual

tetrahedra in the supergroup refinement ($\Delta = 0.037$Å) and in the subgroup refinement ($\Delta = 0.05$Å) appear unreasonably large for chemically similar atoms in an identical chemical environment. These results suggest serious systematic errors in the data and therefore ordering cannot be unequivocally established in $C2$ symmetry. Two ordering models are possible in Cm symmetry, but were not investigated because the 1:3 ratio of Al to Si is not compatible with one Al ion per tetrahedral site (maximum possible ordering is $Al_{0.25} Si_{0.75}$).

All possible octahedral ordering models were considered for the subgroup refinement in Cc symmetry for lepidolite-$2M_2$ and involved varying the size of the M(2) site so that it was larger than its pseudosymmetry-related M(3) site and, in an alternate model, smaller than the M(3) site. Each refinement produced a large number of parameter interactions with correlation coefficients ranging from 0.80 to 0.99, which clearly indicate a centric structure. In addition, bond lengths involving the octahedral cations indicate that the coordination polyhedra were more highly distorted than is reasonable from a crystal chemical viewpoint. The R values for the isotropic refinement for Cc symmetry were $R_1 = 0.143$ and $R_2 = 0.188$ and $R_1 = 0.136$ and $R_2 = 0.200$.

Experimental procedures and refinement

Because of apparent systematic errors in the lepidolite-$1M$ data and the importance of an accurate comparison of coexisting lepidolite structures, intergrown $1M$ and $2M_2$ lepidolite polytypes (R1-43 in Černý *et al.*, 1970) from near Radkovice, Czechoslovakia were examined. Microprobe analyses of flakes of each did not show significant chemical differences. The resulting formula unit (Table 2) is assumed to be the same for both. In addition, a lepidolite-$1M$ (Genth and Penfield, 1892) obtained from the F. A. Genth Collection at The Pennsylvania State University was examined. The electron microprobe analysis (Table 2) is an average of nine individual analyses from an energy-dispersive system (from an ARL microprobe) and a wavelength-dispersive system (from a MAC-5 microprobe), both using the correction procedures of Bence and Albee (1968) and the alpha values of Albee and Ray (1970). In all cases the electron beam was broadened and the sample current kept as low as possible.

The three lepidolite samples were examined (Horsey, 1979, personal communication; Bish,

Table 1. Summary of residual values for the lepidolite models

	Total Reflections	Parameters	*R_1	**R_2	***Goodness-of-fit	Parameters	R_1	R_2	Goodness-of-fit
		Ideal $C2/m$ Symmetry				Subgroup $C2$: Zinnwaldite-type ordering model			
Lepidolite - 1M (reflection data from Sartori, 1976)									
isotropic	400	27	0.067	0.068	2.57	44	0.056	0.058	2.69
anisotropic	400	52	0.054	0.057	2.22				
Lepidolite - 1M (Radkovice)									
isotropic	1164	23	0.062	0.074	1.38	****40	0.043	0.052	1.11
anisotropic	1164	53	0.035	0.043	0.08				
Lepidolite - 1M (Tanakamiyama)									
isotropic	807	25	0.131	0.142	4.70	42	0.084	0.082	2.00
anisotropic	807	53	0.100	0.106	2.84	92	0.062	0.064	1.74
		Ideal $C2/c$ Symmetry							
Lepidolite - 2M_2 (Radkovice)									
isotropic	2764	40	0.082	0.078	5.37				
anisotropic	2764	93	0.048	0.050	3.42				

* $R_1 = (\Sigma||Fo|-|Fc||)/\Sigma|Fo|$

** $R_w = \{[\Sigma w(|Fo|-|Fc|)^2]/\Sigma w|Fo|^2\}^{\frac{1}{2}}$

*** Goodness-of-fit: $[\Sigma w||Fo|-|Fc||^2/\Sigma(n-m)]^{\frac{1}{2}}$ where n = number of independent data and m = number of parameters

**** based on a partial data set of 838 reflections

1979, personal communication) with a neodymium glass laser to observe second harmonic signals (SHG). A SHG signal was obtained for only the Tanakamiyama sample which indicates acentricity and, therefore, a reduction in symmetry from the ideal, centric space group to either $C2$, Cm or $C1$ symmetry. However, the lack of a SHG signal does not always indicate a centric structure if the cause of acentricity is subtle. Therefore, all three samples were studied in the reduced space group symmetries.

Approximately fifty crystals of the Radkovice material were examined by the precession method, from which a 2M_2 and 1M polytype were chosen for further work. Both crystals are transparent light purplish red flakes with the 1M rectangular in shape and measuring $0.31 \times 0.22 \times 0.075$ mm and the 2M_2 irregular in shape and measuring approximately $0.5 \times 0.5 \times 0.05$ mm. The 1M polytype was a cleavage fragment from an associated 2M_2 crystal. The Tanakamiyama sample was cleaved and cut to $0.30 \times$

0.35×0.03 mm size fragments. Ten specimens were examined before choosing one for study. The cleavage flake is transparent light brown.

No streaking was observed in precession photographs of the $0kl$ net of the Radkovice crystals indicating that they have regular stacking. However, in contrast to the Radkovice samples, the Tanakamiyama crystal does show some streaking parallel to Z^* indicating partial stacking disorder. The streaking was not judged serious enough to prevent a structure determination, although it was clear that the sample was of marginal quality.

Data were measured for the 2M_2 sample on a Syntex (Nicolet) $P2_1$ autodiffractometer and for both 1M crystals on a Picker FACS-1 diffractometer. Unit cell parameters were determined for each of the Radkovice crystals by least-squares refinement of fifteen high angle reflections. In the 1M case, the reflections were centered by hand. Unit cell parameters for the Tanakamiyama sample were calculated by the least-squares refinement of twenty-five mod-

Table 2. Chemical analyses of the Radkovice and Tanakamiyama lepidolites

Oxide	Radkovice [1]wet	Tanakamiyama [2]wet	probe	best		Radkovice Cations based on:	Tanakamiyama 11 oxygen (anhydrous)
		Weight Percent					
SiO_2	51.45	53.34	57.92	57.92	K	0.79	1.01
Al_2O_3	22.62	17.76	16.04	16.04	Rb	0.07	0.03
Ga_2O_3	0.0098	[3]na	na		Cs	0.03	
Cr_2O_3	0.0005	na	0.0	0.0	Na	0.03	0.01
Fe_2O_3	0.16	3.25			Ca	0.01	
FeO	0.036	na	[4]0.65	0.65			
TiO_2	na	na	0.013	0.013			
MnO	0.51	2.77	0.96	0.96	Li	1.48	1.41
MgO	0.53	0.05	0.0	0.0	Fe^{2+}	0.002	0.07
Li_2O	5.42	4.60	na	[5]5.25	Fe^{3+}	0.008	
CaO	0.20	0.37	0.015	0.015	Mg	0.05	
Na_2O	0.26	1.55	0.04	0.04	Mn	0.03	0.05
K_2O	9.09	10.90	11.90	11.90	Al	1.30	1.13
Rb_2O	1.69	na	0.787	0.787			
Cs_2O	0.94	na	0.176	0.176	Al	0.51	0.13
Tl_2O	0.0071	na	na		Si	3.49	3.87
F_2	7.40	7.78	9.08	9.08			
H_2O^+	2.36	na	na				
H_2O^-	0.84	0.65	na				
	103.52	103.02	97.58				
-O=2F	-3.11	-3.28	-3.82				
Total	100.41	99.74	93.76				

[1] from Černý et al. (1970), P. Povandra, analyst
[2] from Genth and Penfield (1892), F. A. Genth, analyst
[3] not analyzed
[4] all iron assumed FeO
[5] value based on refinement

erate to high angle reflections that were centered by computer. Cell parameters are given in Table 3. In all cases, graphite monochromatized $MoK\alpha$ radiation was used.

The data for the $2M_2$ refinement were collected in the $2\theta:\theta$ variable-scan mode in four quadrants of the limiting sphere from $l = 0$ to 40 and from $0° < 2\theta < 90°$. Crystal and electronic stability were checked by monitoring two standard reflections after every fifty measurements. The standard deviation, $\sigma(I)$, was calculated from $\sigma(I) = T_r [S + (B_1 + B_2)/B_r^2 + q(I)^2]^{1/2}$, where S is the scan count, B_1 and B_2 the background counts, B_r the ratio of background time to scan time, T_r the 2θ scan rate in degrees per minute, and q is an estimate of the standard error squared, 0.003. Reflections were considered observed if $I > 2\sigma(I)$. Intensities were corrected for absorption by comparing to ψ scans taken at 10° intervals in ϕ for selected reflections at 2θ intervals of approximately 5° and for Lorentz-polarization effects. A maximum intensity decrease of 41% was observed for some ψ scans because of the platy

nature of the material. The 5363 non-zero reflections were symmetry averaged into two independent quadrants to produce a total of 2783 reflections after seven reflections were omitted because the intensity differences with their dependent counterparts were greater than $5/2 \sigma(I)$.

Data were collected for both 1M crystals in similar fashion using the moving-crystal, stationary-counter method (Lenhert, 1975) with an ω scan rate of 1°/min. Intensities for the entire limiting sphere were collected to $2\theta < 60°$ and in addition, for four quadrants from $60° < 2\theta < 90°$ from $k = 0$ to 26. Three reference reflections were used to monitor the crystal and diffractometer system after every fifty observations. The standard deviation of an intensity measurement was computed from $\sigma(I) = [CT + 0.25 (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$ where CT is the total integrated count in time t_c, B_1 and B_2 are the background counts in time t_b and p, the estimate of the standard error, is equal to 0.03. Reflections were considered observed if the intensities were more than twice the standard deviation. The data were corrected for Lorentz-polarization and absorption effects following similar procedures as given above. For the Radkovice data set, the 5151 reflections were symmetry averaged into two quadrants resulting in 1165 non-zero, independent intensities from which one reflection was rejected because the equivalent reflections differed in excess of $5/2 \sigma(I)$.

Equipment failure during the Tanakamiyama data collection required the use of two scale factors since the voltage applied to the X-ray tube was not identical throughout. A third scale factor was introduced for strong reflections collected with a scan width of 3.5° instead of the 2.5° used for the weaker reflections. For these data, 5485 reflections were

Table 3. Cell parameters of the lepidolites studied

	1M polytype			$2M_2$ polytype	
	*Sartori (1976)	Radkovice	Tanakamiyama	*Sartori, et al. (1973)	Radkovice
a(Å)	5.20(2)**	5.209(2)	5.242(3)	9.04(2)	9.023(2)
b(Å)	9.01(2)	9.011(5)	9.055(6)	5.22(2)	5.197(2)
c(Å)	10.09(1)	10.149(5)	10.097(7)	20.210(1)	20.171(3)
β(°)	99.3(3)	100.77(4)	100.77(5)	99.6(3)	99.48(2)

* specimen from Elba, Italy
** parenthesized figures represent estimated standard deviations (esd) in terms of the least units cited for the value to their immediate left, thus 5.20(2) indicates an esd of 0.02.

symmetry averaged into two independent quadrants to produce 986 non-zero reflections. However, averaging was not done between reflections with different scale factors. Final averaging was accomplished after the reflections were put on the same scale at the end of refinement. A total of 807 independent reflections were produced.

The refinement procedures were similar to those used for the data of Sartori. Both Radkovice and the Tanakamiyama crystals were first refined in the ideal space groups and then refined in all possible subgroups compatible with octahedral ordering schemes as derived from computer modeling. Only the Tanakamiyama sample proved to be acentric in agreement with the SHG results. Resultant R values for each refinement are given in Table 1. For the Tanakamiyama sample, the R values represent symmetry averaged data with reflections scaled appropriately at the final stage of each refinement. No significant correlation effects for the subgroup symmetry refinement for the Tanakamiyama sample were indicated. The largest parameter interaction of 0.92 was between the y positional coordinates of T(1) and T(11), but most interactions were considerably less.

Tables 4–6[1] list observed and calculated structure amplitudes for lepidolite-2M_2, Radkovice lepidolite-1M and Tanakamiyama lepidolite-1M, respectively. Final atomic coordinates are given in Table 7 and the calculated bond lengths and angles for the 2M_2 polytype are given in Table 8 and the 1M polytypes in Table 9. The correlation matrix was used as input in the calculation of bond lengths (Busing, *et al.*, 1964).

Subgroup refinements: review and suggestions

For space groups that have pseudo-inversion centers, Ermer and Dunitz (1970) warned that a simple expansion of the parameter set over the questionable inversion center leads to a singularity in the resulting normal equations matrix. Nor can the problem of symmetry reduction prior to the refinement be solved by introducing small, random shifts in atomic positions to make the starting acentric model only approximately centric, because the resulting set of normal equations does not

sufficiently describe the structure to allow convergence. In contrast to other uses of computer modeling to obtain starting coordinates prior to testing with X-ray data (see Baur, 1977 for a summary), the problem of testing a space group of lower symmetry without involving a change in the Laue symmetry is particularly difficult. A successful approach has been to move atoms away from their pseudosymmetrically-related positions by calculating new positions based on an ordering scheme. All possible models are generated from a distance least-squares program and the X-ray intensity data are then used for each model in a *full-matrix* least-squares refinement program (see Guggenheim and Bailey, 1975, 1977, 1978). Caution must be exercised in developing trial structures since unrealistic cases can force either a coupling or uncoupling of parameters (Geller, 1961). Likewise, few reflections or data containing large systematic errors may also couple or uncouple parameters, possibly explaining the ordering pattern established with the lepidolite-1M data set of Sartori. Since this refinement procedure has now been used several times for centric as well as acentric cases, difficulties regarding its use are described here.

The most difficult aspect is in determining successful convergence. Some problems that may relate to the determination of a successful refinement include (a) oscillations in parameters from one cycle to another (b) strong parameter interaction and (c) large shifts of parameters relative to their associated errors at the final stage of refinement. Trizinc diorthoborate (Baur and Tillmanns, 1970) proved to be an example illustrating such problems when refined in space group $I2/c$ and Ic. In Ic symmetry, many parameters oscillated around mean values and most x and z parameters related by the two fold axis had large correlations. Typically, because interacting parameters become increasingly indeterminant, refinements with correlations between atom pairs show correspondingly large estimated standard deviations for those pairs. The higher order space group was determined as the correct one in this case because bond lengths and angles conform to more reasonably acceptable values, the R value was nearly the same as that of the lower order space group but with half as many varied parameters, and there was an obvious lack of convergence in lower symmetry because parameter shifts were generally larger than one half the estimated standard deviation. In this particular instance the lack of convergence in subgroup symme-

Table 7. Final atomic parameters

Atom	x	y	z	*B	**β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
				Radkovice Lepidolite-$2M_2$						
K	0.5	0.4097(2)***	0.25	1.73(1)	0.00549(7)	0.0152(2)	0.00116(1)	0.0	0.00033(2)	0.0
M(1)	0.25	0.25	0.0	0.82(9)	0.0030(5)	0.007(1)	0.00049(9)	0.0003(7)	0.0004(2)	0.0005(3)
M(2)	0.58561(9)	0.2437(2)	0.00005(4)	0.67(1)	0.00210(7)	0.0057(2)	0.00050(1)	-0.0002(1)	0.00018(2)	-0.00001(4)
T(1)	0.79426(6)	0.4078(1)	0.13397(3)	0.572(9)	0.00182(4)	0.0044(1)	0.000439(9)	-0.00024(6)	0.00015(1)	-0.00003(3)
T(2)	0.12556(5)	0.4136(1)	0.13394(3)	0.562(9)	0.00164(4)	0.0049(1)	0.000436(9)	-0.00008(6)	0.00017(1)	-0.00000(3)
O(1)	0.7676(2)	0.3937(3)	0.05266(7)	1.13(3)	0.0057(2)	0.0085(4)	0.00042(2)	0.0006(2)	0.00007(5)	-0.00013(8)
O(2)	0.0905(2)	0.4261(3)	0.05283(7)	1.12(3)	0.0040(1)	0.0132(4)	0.00043(2)	0.0023(2)	0.00007(4)	0.00003(9)
O(3),F	0.4468(2)	0.4291(4)	0.04923(8)	1.90(4)	0.0060(2)	0.0334(8)	0.00061(3)	-0.0083(3)	0.00037(6)	0.0002(1)
O(4)	0.7058(2)	0.1774(3)	0.16634(9)	1.29(3)	0.0051(2)	0.0098(4)	0.00090(3)	-0.0032(2)	0.00043(6)	-0.0000(1)
O(5)	0.2380(2)	0.1785(3)	0.16219(8)	1.27(3)	0.0054(2)	0.0098(4)	0.00073(3)	0.0028(2)	0.00007(6)	-0.00026(9)
O(6)	0.9719(2)	0.3787(4)	0.16611(8)	1.27(3)	0.0024(1)	0.0185(6)	0.00086(3)	-0.0003(2)	0.00040(5)	0.0002(1)
				Radkovice Lepidolite-$1M$						
K	0.0	0.5	0.0	1.99(2)	0.0190(3)	0.00595(8)	0.00519(7)	0.0	0.0015(1)	0.0
M(1)	0.0	0.0	0.5	1.8(1)	0.019(2)	0.0050(5)	0.0052(5)	0.0	0.0033(8)	0.0
M(2)	0.0	0.3289(1)	0.5	0.73(2)	0.0062(2)	0.00231(8)	0.00213(7)	0.0	0.0005(1)	0.0
T	0.08100(8)	0.16860(5)	0.23203(4)	0.73(1)	0.0065(1)	0.00209(4)	0.00221(3)	-0.00012(6)	0.00058(4)	-0.00001(3)
O(1)	0.0218(4)	0.0	0.1750(2)	1.42(4)	0.0199(7)	0.0029(2)	0.0031(1)	0.0	-0.0001(2)	0.0
O(2)	0.3252(2)	0.2319(2)	0.1680(1)	1.46(3)	0.0113(4)	0.0056(1)	0.0038(1)	-0.0028(2)	0.0016(2)	-0.0003(1)
O(3)	0.1418(3)	0.1768(1)	0.3945(1)	1.26(3)	0.0170(4)	0.0037(1)	0.00223(8)	-0.0012(2)	0.0004(1)	-0.00010(8)
F	0.1076(3)	0.5	0.4017(2)	2.11(5)	0.0125(5)	0.0141(3)	0.0030(1)	0.0	0.0011(2)	0.0
				Tanakamiyama Lepidolite-$1M$						
K	0.0	0.5028	0.0	2.21(5)						
M(1)	0.0	-0.006(2)	0.5	0.3(1)						
M(2)	0.0	0.323(1)	0.5	0.66(8)						
M(3)	0.5	0.161(2)	0.5	1.3(2)						
T(1)	0.0756(7)	0.1704(8)	0.2309(4)	0.85(6)						
T(11)	0.5863(7)	0.3338(8)	0.2302(4)	0.87(6)						
O(1)	0.041(1)	0.002(2)	0.1708(5)	1.53(9)						
O(2)	0.319(2)	0.243(1)	0.169(1)	1.6(2)						
O(22)	0.813(2)	0.260(1)	0.162(1)	1.4(2)						
O(3)	0.114(2)	0.175(1)	0.394(1)	1.1(1)						
O(33)	0.663(1)	0.328(1)	0.3911(9)	0.9(1)						
F	0.110(1)	0.4729(9)	0.3985(5)	1.0(1)						

* Isotropic temperature factor as refined
** The anisotropic temperature factor form is exp $(-\Sigma_i \Sigma_j \beta_{ij} h_i h_j)$.
*** Parenthesized figures represent estimated standard deviations (esd) in terms of the least units cited for the value to their immediate left, thus 0.4097(2) indicates an esd of 0.0002.

try is obvious; however, this is not always the case.

A particularly disturbing aspect of the lepidolite subgroup refinements involving the Radkovice specimens is that each model appeared to converge; parameter shifts were less than a tenth of the associated estimated standard deviations at the end of the refinement process. In this case, high correlations between symmetry-related pairs suggested that the parent space group is the proper one. In addition, difference maps showed that the two "pseudosymmetry-related" octahedral sites in the subgroup refinement were identical in scattering power, which is in contradiction with results expected for ordered models. Such inconsistencies allow one to choose one space group over another.

However, a similar case is conceivable when the procedure is used to test for the ordering of two ions of similar scattering power, for example [IV]Si and [IV]Al. If the refinement behaves similarly to that described above, only the correlation matrix and a comparison of R values will be particularly useful. Such a circumstance was noted for margarite (Guggenheim and Bailey, 1978), and one must argue that the case for an acentric structure from X-ray data *alone* is less compelling for such examples. Alternate methods of determining centricity such as by infrared spectra or by SHG, in addition to diffraction data, strengthens the case considerably. Schomaker and Marsh (1979) suggest that weak reflections should be carefully examined in a non-centric

subgroup refinement since these are the most sensitive to the small imaginary component of the structure factor. Of course, the size of this component depends on how closely the structure approximates centricity and the need for a close inspection will vary depending on the problem.

In summary, the following criteria are used in evaluating the merit of a subgroup refinement: 1) correlation coefficients involving positional parameters cannot be above the (arbitrary) value of 0.90 for more than a few atoms for complex structures, 2) bond distances and angles must be compatible with commonly accepted values, 3) atom positions must be consistent with the average supergroup refinement, 4) the R value minimized in the full matrix refinement procedure for the subgroup refinement must approximate the corresponding supergroup refinement when nearly the same number of parameters are involved—this usually means a comparison of R values of the isotropic subgroup refinement with the anisotropic parent space group refinement, and 5) shifts in atomic parameters near the end of the refinement must be *much* smaller than the associated errors and with no oscillations about mean atomic positions observed.

Discussion

The relatively large standard errors associated with the atomic parameters (and bond lengths) for the Tanakamiyama refinement are related to the imperfect crystalline sample rather than a consequence of the parameter interactions between pseudosymmetry-related atoms; errors of similar magnitude were present in the ideal space group. Therefore, the errors associated with the scattering powers for the octahedral sites are probably high. Since the sample has not been analyzed for lithium, variations in assumed lithium content will affect the chemical proportions. However, an estimate for such errors is no more than ± 1.5 electrons per octahedral site. The quality of the data set suggests that the general features of the Tanakamiyama structure are correct, but the details may be somewhat uncertain.

Cation ordering

The Radkovice lepidolites (Figs. 1 and 2) have an octahedral ordering pattern quite different from the Tanakamiyama lepidolite (Fig. 3). For the Radkovice lepidolites, the octahedral cations are ordered in the typical pattern for micas with M(1) larger than M(2). The M–O,OH,F bond lengths calculated from

Table 8. Calculated bond lengths and angles for Radkovice lepidolite-$2M_2$

	Bond lengths (Å)				Bond angles (°)	
				Tetrahedron T(1)		
*O(1)	1.619(2)**	O(1)--O(4)	2.693(2)	O(1)--O(4)	111.77(9)	
O(4)	1.634(2)	O(5)	2.709(2)	O(5)	112.95(9)	
O(5)	1.630(2)	O(6)	2.693(2)	O(6)	111.71(8)	
O(6)	1.634(1)	O(4)--O(5)	2.623(2)	O(4)--O(5)	106.99(9)	
Mean	1.629	O(6)	2.620(2)	O(6)	106.59(9)	
		O(5)--O(6)	2.614(2)	O(5)--O(6)	106.44(9)	
		Mean	2.659	Mean	109.41	
				Tetrahedron T(2)		
*O(2)	1.616(2)	O(2)--O(4)	2.692(2)	O(2)--O(4)	111.76(9)	
O(4)	1.636(2)	O(5)	2.706(2)	O(5)	113.01(9)	
O(5)	1.630(2)	O(6)	2.690(2)	O(6)	111.67(8)	
O(6)	1.635(1)	O(4)--O(5)	2.612(2)	O(4)--O(5)	106.23(8)	
Mean	1.629	O(6)	2.619(2)	O(6)	106.43(9)	
		O(5)--O(6)	2.630(2)	O(5)--O(6)	107.33(9)	
		Mean	2.658	Mean	109.41	
	Interlayer cation K				**T(1) to T(2)**	
	inner	outer				
O(4)x2	2.964(2)	3.218(2)		around O(4)	131.9(1)	
O(5)x2	2.965(2)	3.310(2)		around O(5)	137.5(1)	
O(6)x2	2.954(2)	3.225(2)		around O(6)	132.3(1)	
Mean	2.961	3.251		Mean	133.9	
				Octahedron M(1)		
O(1)x2	2.127(2)	O(1)--O(2)x2	2.818(2)	O(1)--O(2)x2	82.81(6)	
O(2)x2	2.133(1)	O(3)x2	2.740(2)	O(3)x2	80.71(7)	
O(3),Fx2	2.103(2)	O(2)--O(3),Fx2	2.744(3)	O(2)--O(3),Fx2	80.75(6)	
Mean	2.121	Mean (shared)	2.767	Mean (shared)	81.42	
		O(1)--O(2)x2	3.195(2)	O(1)--O(2)x2	97.19(6)	
		O(3),Fx2	3.224(3)	O(3),Fx2	99.29(7)	
		O(2)--O(3),Fx2	3.227(2)	O(2)--O(3),Fx2	99.25(6)	
		Mean (unshared)	3.215	Mean (unshared)	98.58	
				Octahedron M(2)		
O(1)	1.964(2)	O(1)--O(1)	2.574(2)	O(1)--O(1)	81.87(7)	
	1.964(2)	O(2)	2.909(2)	O(2)	95.66(7)	
O(2)	1.960(2)	O(3),F	2.740(2)	O(3),F	88.34(7)	
	1.971(2)	O(2)--O(2)	2.580(2)	O(2)--O(2)	82.02(7)	
O(3),F	1.967(2)	O(3),F	2.744(3)	O(3)	88.20(7)	
	1.972(2)	O(3),F--O(3),F	2.457(2)	O(3),F--O(3),F	77.17(8)	
Mean	1.966	Mean (shared)	2.667	Mean (shared)	85.54	
		O(1)--O(2)	2.909(2)	O(1)--O(2)	95.66(7)	
		O(2)	2.918(2)	O(2)	95.73(7)	
		O(3),F	2.890(2)	O(3),F	94.47(8)	
		O(3),F	2.913(3)	O(3),F	95.63(7)	
		O(2)--O(3),F	2.913(3)	O(2)--O(3),F	95.60(8)	
		O(3),F	2.886(3)	O(3),F	94.25(8)	
		Mean (unshared)	2.905	Mean (unshared)	95.22	

* apical oxygen
** parenthesized figures represent estimated standard deviation (esd) in terms of the least units cited for the value to their immediate left, thus 1.619(2) indicates an esd of 0.002.

the radii given by Shannon (1976) are within 0.01Å of the observed values for a composition of M(1) = $Li_{1.0}$ and for each of M(2) = $Al_{0.65}$ $Li_{0.24}$ $\square_{0.07}$ $(Mn,Mg,Fe^{3+})_{0.05}$ for the $2M_2$ polytype and M(1) = $Li_{0.91}$ $(Mn,Mg)_{0.09}$ and for each of M(2) = $Al_{0.65}Li_{0.28}$ $\square_{0.07}$ $Fe^{3+}_{0.005}$ for the 1M form. The compositions derived from the structures are in excellent agreement with the chemical analysis. The slight difference in the compositions of the octahedral sites between the two polytypes appears to be real. Not
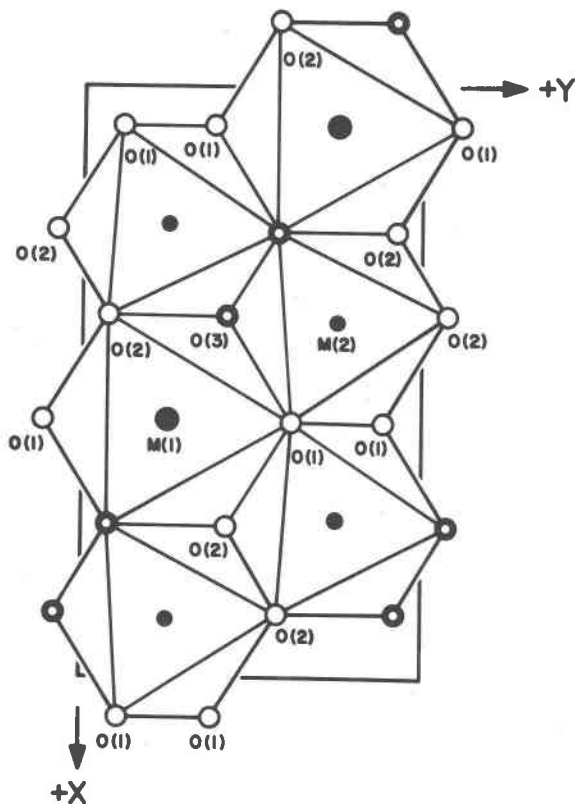
Table 9. Calculated bond lengths and angles for Radkovice and Tanakamiyama lepidolite-1M

Tetrahedron T: (Radkovice)

	Bond lengths (Å)			Bond angles (°)	
O(1)	1.6342(8)*	O(1)--O(2)	2.629(2)	O(1)--O(2)	107.02(9)
O(2)	1.635(1)	O(2)	2.620(2)	O(2)	106.43(8)
O(2)	1.637(1)	O(3)	2.715(2)	O(3)	112.99(8)
**O(3)	1.622(1)	O(2)--O(2)	2.625(1)	O(2)--O(2)	106.69(7)
Mean	1.632	O(3)	2.695(2)	O(3)	111.68(6)
		O(2)--O(3)	2.695(2)	O(2)--O(3)	111.63(6)
		Mean	2.663	Mean	109.41

Tetrahedron T(1): (Tanakamiyama)

	Bond lengths (Å)			Bond angles (°)	
O(1)	1.64(1)	O(1)--O(2)	2.62(2)	O(1)--O(2)	105.7(5)
O(2)	1.66(1)	O(22)	2.62(1)	O(22)	106.1(5)
O(22)	1.64(1)	O(3)	2.71(1)	O(3)	112.7(5)
**O(3)	1.62(1)	O(2)--O(22)	2.64(2)	O(2)--O(3)	114.2(5)
Mean	1.64	O(3)	2.75(1)	O(22)--O(3)	110.9(6)
		O(22)--O(3)	2.68(2)	Mean	109.4
		Mean	2.67		

Tetrahedron T(11): (Tanakamiyama)

	Bond lengths (Å)			Bond angles (°)	
O(1)	1.64(1)	O(1)--O(2)	2.62(1)	O(1)--O(2)	105.8(5)
O(2)	1.64(1)	O(22)	2.63(1)	O(22)	107.1(5)
O(22)	1.63(1)	O(33)	2.70(1)	O(33)	113.1(5)
**O(33)	1.60(1)	O(2)--O(22)	2.61(2)	O(2)--O(22)	106.0(6)
Mean	1.63	O(33)	2.71(1)	O(33)	113.8(6)
		O(22)--O(33)	2.65(1)	O(22)--O(33)	110.6(6)
		Mean	2.65	Mean	109.4

Interlayer cation K — Radkovice / T to T

		Radkovice		T to T	
O(1)x2	2.956(2)	3.319(2)	around O(1)		136.7(1)
O(2)x4	2.947(1)	3.246(2)	around O(2)		132.02(7)
Mean	2.952	3.283	Mean		134.4
	inner	outer			

Interlayer cation K — Tanakamiyama / T(1) to T(11)

		Tanakamiyama		T(1) to T(11)	
O(1)x2	3.036(6)	3.205(6)	around O(1)		137.0(4)
O(2)x2	3.03(1)	3.19(1)	around O(2)		136.1(8)
O(22)x2	3.01(1)	3.13(1)	around O(22)		130.2(8)
Mean	3.03	3.18	Mean		134.4
	inner	outer			

Octahedron M(1): Radkovice

	Bond lengths (Å)			Bond angles (°)	
O(3)x4	2.127(1)	O(3)--O(3)x2	2.820(2)	O(3)--O(3)x2	83.01(4)
Fx2	2.100(1)	Fx4	2.741(2)	Fx4	80.82(5)
Mean	2.114	Mean (shared)	2.781	Mean (shared)	81.92
		O(3)--O(3)x2	3.186(1)	O(3)--O(3)x2	96.99(4)
		Fx4	3.219(2)	Fx4	99.18(5)
		Mean (unshared)	3.203	Mean (unshared)	98.09

Octahedron M(1): Tanakamiyama

	Bond lengths (Å)			Bond angles (°)	
O(3)x2	2.11(2)	O(3)--O(3)	2.64(2)	O(3)--O(3)	77.5(8)
O(33)x2	2.13(1)	Fx2	2.95(1)	Fx2	88.7(4)
Fx2	2.117(5)	O(33)--O(33)	3.02(2)	O(33)--O(33)	90.5(8)
Mean	2.12	Fx2	2.59(1)	Fx2	75.1(3)
		Mean (shared)	2.80	Mean (shared)	83.0
		O(3)--O(33)x2	3.152(8)	O(3)--O(33)x2	96.2(2)
		Fx2	3.22(1)	Fx2	99.3(4)
		O(33)--Fx2	3.191(9)	O(33)--Fx2	97.5(5)
		Mean (unshared)	3.19	Mean (unshared)	97.7

Octahedron M(2): Radkovice

	Bond lengths (Å)			Bond angles (°)	
O(3)x2	1.966(1)	O(3)--O(3)	2.820(2)	O(3)--O(3)	91.62(6)
O(3)x2	1.971(1)	O(3)x2	2.587(1)	O(3)x2	82.17(5)
Fx2	1.974(1)	F--O(3)x2	2.741(2)	F--O(3)x2	88.02(6)
Mean	1.970	F	2.464(3)	F	77.27(6)
		Mean (shared)	2.653	Mean (shared)	84.77
		O(3)--O(3)x2	2.920(2)	O(3)--O(3)x2	95.73(5)
		Fx2	2.919(1)	Fx2	95.63(5)
		F--O(3)x2	2.892(2)	F--Fx2	94.31(6)
		Mean (unshared)	2.910	Mean (unshared)	95.22

Octahedron M(2): Tanakamiyama

	Bond lengths (Å)			Bond angles (°)	
O(3)x2	1.88(1)	O(3)--O(3)	2.64(2)	O(3)--O(3)	89.0(8)
O(33)x2	1.901(8)	O(33)x2	2.660(7)	O(33)x2	89.3(4)
Fx2	1.853(8)	O(33)--Fx2	2.59(1)	O(33)--Fx2	87.1(4)
Mean	1.88	F--F	2.53(1)	F--F	86.2(5)
		Mean (shared)	3.47	Mean (shared)	87.9
		O(3)--O(33)x2	2.74(1)	O(3)--O(33)x2	92.6(4)
		Fx2	2.70(1)	Fx2	92.4(3)
		O(33)--Fx2	2.67(1)	O(33)--Fx2	90.9(5)
		Mean (unshared)	2.70	Mean (unshared)	92.0

Octahedron M(3): Tanakamiyama

	Bond lengths (Å)			Bond angles (°)	
O(3)x2	2.116(8)	O(3)--O(33)x2	2.660(7)	O(3)--O(33)x2	77.3(4)
O(33)x2	2.14(2)	Fx2	2.95(1)	Fx2	88.5(5)
Fx2	2.12(1)	O(33)--O(33)	3.02(1)	O(33)--O(33)	89.6(8)
Mean	2.13	F--F	2.53(1)	F--F	73.3(6)
		Mean (shared)	2.79	Mean (shared)	82.2
		O(3)--O(33)x2	3.20(1)	O(3)--O(33)x2	97.5(6)
		Fx2	3.18(1)	Fx2	97.2(5)
		O(33)--Fx2	3.23(2)	O(33)--Fx2	98.7(3)
		Mean (unshared)	3.20	Mean (unshared)	97.8

* parenthesized figures represent estimated standard deviations (esd) in terms of the least units cited for the value to their immediate left, thus 1.6342(8) indicates an esd of 0.0008.

** apical oxygen

only are the mean bond distances consistent with the respective chemistries, but the *R* values also improved for the 1M refinement when the scattering factor for M(1) was increased by 0.75 electrons to reflect the greater scattering power of manganese and magnesium. Difference maps for both final structures were featureless. The full complement of lithium to the M(1) site of the 2M₂ form appears

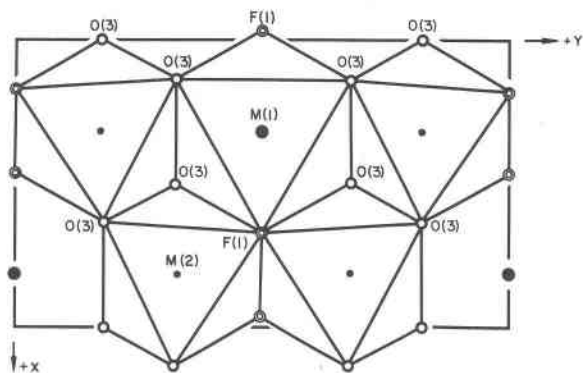Fig. 1. Octahedral ordering pattern of Radkovice lepidolite-2M$_2$.

Fig. 2. Octahedral ordering pattern of Radkovice lepidolite-1M.

1.63Å, respectively. Apparent differences in tetra-hedral composition as derived from average bond lengths are not significant because of high estimated standard deviations. It is interesting to note that the apical O(3) anion of the apparently larger tetrahe-dral T(1) site is more closely coordinated to the aluminum-rich M(2) site in contrast with the apical O(33) anion of the T(11) tetrahedron. A similar topology exists in lepidolite-3T and zinnwaldite. An Al concentration in T(1) would cause the apical O(3) anion to be undersaturated and would favor a more highly charged cation in M(2) and a closer M(2)–O(3) approach. In addition, two (F,OH) anions are in the *cis* orientation along a shared edge between M(2) and M(3) and, because of the smaller fluorine radius, may approach each other more closely than any other anion pair along the shared edge around M(1). The combination of both effects probably contributes to the accommodation of Al in M(2).

The Radkovice structures

There are major differences between the struc-tures of the 1M and 2M$_2$ polytypes caused by the

unique for the lepidolites. All previous lepidolite refinements show minor substitution for lithium in M(1) similar to the 1M refinement results.

For the Tanakamiyama lepidolite, the mean octa-hedral bond lengths for the cation–anion distances are M(1):2.12Å, M(2):1.88 Å and M(3):2.13 Å, and the scattering powers are 6, 11.5 and 6 electrons, respectively. Even with the large estimated stan-dard errors, there is no doubt that M(2) and M(3), which are related by the pseudo-mirror plane, are quite different in both size and scattering power. Within the estimated standard errors, M(1) and M(3) are identical in both size and scattering power. The size and scattering power of the M(2) site are consistent with complete or nearly complete order-ing of alumium into this site. The remaining ele-ments and vacancies may be allocated equally be-tween M(1) and M(3). However, the estimated standard errors and the large number of substituting elements prevent a unique solution from being determined.

For the Tanakamiyama lepidolite, the mean T–O bond lengths for T(1) and T(11) are 1.64Å and

Fig. 3. Octahedral ordering pattern of Tanakamiyama lepidolite-1M.

fundamental variations in stacking. This variation accounts for the differences in coordination around the interlayer cations and has been discussed in detail by Takeda and Burnham (1969) and Takeda, *et al.* (1971). Takeda *et al.* (1971) suggested that the octahedral coordination around the potassium ion in the 1M form produces an energetically more stable structure than the $2M_2$ form, which involves a trigonal prism coordination about the interlayer cation, because of the staggered arrangement of oxygens. However, they suggested that the $2M_2$ polytype may be stabilized at small tetrahedral rotation angles, α. The tetrahedral rotation angle, which is a measure of the deviation of the tetrahedral ring from hexagonal symmetry, is 7.25° in the 1M polytype and 6.57° in the $2M_2$ form. The potassium coordination reflects this difference also with mean inner K–O distances of 2.952Å for the 1M and 2.961Å for the $2M_2$ form and mean outer K–O distances of 3.283Å and 3.251Å, respectively. Since the tetrahedral–octahedral sheet misfit and the size and charge of the interlayer cation are similar in both structures, such differences must be attributed to the variation in stacking and the resulting environment about the interlayer cation.

The smaller angular rotation of tetrahedra in the $2M_2$ structure accounts for the larger inner and smaller outer mean K–O distances of the $2M_2$ polytype when compared to the 1M form. Consequently, the hole formed in the ditrigonal ring is slightly larger in the $2M_2$ structure allowing for a small decrease in interlayer separation when compared to the 1M form (see Table 10).

Tables 11 and 12 list the magnitudes and orientations of the apparent atomic vibration ellipsoids. The ellipsoids of the two structures are remarkably similar. The r_3/r_1 ratio for the cations vary from 1.05 to 1.22 indicating their nearly spherical shape. The only exception to this trend is the M(1) cation in the $2M_2$ polytype which is elongate as indicated by a ratio of 1.48. The ratios for oxygen atoms range from 1.49 to 1.74 with the average value of 1.63, whereas the hydroxyl/fluorine sites have values of 1.98 in the 1M and 2.35 in the $2M_2$ polytypes. The major axes of the ellipsoids for all anions in the $2M_2$ polytype are oriented approximately parallel to the layers. The trend is also approximated in the 1M polytype although to a lesser degree.

Similar to zinnwaldite (Guggenheim and Bailey, 1977) and phlogopite (Hazen and Burnham, 1973), the magnitudes of the oxygen vibration ellipsoids are quite large and may suggest that there is a

Table 10. Important structural features

Parameter	Radkovice $2M_2$	Radkovice 1M	Tanakamiyama 1M
α_{tet} (°) ($\frac{1}{2}$|120°-mean O_b-O_b-O_b angle|)	6.57	7.25	3.4
*τ_{tet} (°) (mean O_{apical}-T-O_{basal} angle)	T(1):112.14 T(2):112.15	112.10	T(1): 112.6 T(11):112.5
β_{ideal} (°) [180°-cos⁻¹(a/3c)]	98.58	99.85	99.97
**ψ (°)	K:	52.36	56.7
[cos ψ = oct. thickness/2(M--O,F,OH)] M(1):	61.07	61.34	60.4
M(2):	58.54	58.96	56.1
M(3):			60.5
Mean	59.38	59.75	59.0
Sheet thickness (Å) tetrahedral	2.254	2.259	2.26
octahedral	2.052	2.032	2.10
Interlayer separation (Å)	3.387	3.420	3.32
Basal oxygen Δz_{ave} (Å)	0.080	0.007	0.08

* ideal value: 109.47°
** ideal value: 54.73°

contribution to the temperature factor from positional disorder caused by differences in Al–O and Si–O bond distances and the lack of tetrahedral cation order. However, unlike these other structures, there is no appreciable difference between the vibration ellipsoids of the apical and basal oxygens. Although the M(1) site of the $2M_2$ polytype is more elliptical than that of the 1M form, its magnitude is considerably less. Any positional disorder of cations in M(1) of the 1M polytype must conform to the $2/m$ point group symmetry of that site, thereby producing a larger ellipsoid. The large magnitudes of the (F,OH) ellipsoids for both polytypes also suggest positional disorder. The orientation of the major axis of the vibration ellipsoid for this site is similar in both structures, each perpendicular to the plane established by the M(1) site and the shared edge between the M(2) octahedra. The elongation of the ellipsoid is not directed along bonds to the nearby cations. However, the three octahedral cations around the (OH,F) site and the Al + Li disorder in M(2) would be expected to influence the (OH,F) position in a complex way.

Conclusions

It is apparent that not all lepidolites have similar octahedral ordering schemes and some may differ slightly in tetrahedral ordering patterns. Based on

crystal chemical arguments, high fluorine content may promote the ordering of aluminum into either M(2) or M(3). Such a conclusion is consistent with the ordering observed in the Tanakamiyama lepidolite, lepidolite-3T (Brown, 1978) and zinnwaldite (Guggenheim and Bailey, 1977). However, high fluorine content cannot be the sole cause for this phenomenon. The Radkovice lepidolites are nearly as fluorine-rich as the Tanakamiyama sample and more fluorine-rich than either the Sadisdorf zinnwaldite or lepidolite-3T. Parameters of crystalliza-

Table 11. Magnitudes and orientations of thermal ellipsoids for Radkovice lepidolite-$2M_2$

Atom	Axis	rms (Å) displacement	Angle (°) with respect to X	Y	Z
K	r_1	0.1440(9)*	90	0	90
	r_2	0.1476(9)	149(7)	90	111(7)
	r_3	0.1539(9)	121(7)	90	21(7)
M(1)	r_1	0.08(1)	109(18)	125(18)	38(14)
	r_2	0.10(1)	137(26)	49(24)	73(22)
	r_3	0.118(9)	53(25)	61(22)	58(14)
M(2)	r_1	0.087(2)	59(10)	31(10)	93(5)
	r_2	0.094(2)	149(10)	59(10)	82(10)
	r_3	0.100(1)	91(9)	91(7)	8(9)
T(1)	r_1	0.077(1)	69(5)	22(5)	90(3)
	r_2	0.087(1)	159(5)	69(5)	82(6)
	r_3	0.0939(9)	92(6)	93(4)	8(6)
T(2)	r_1	0.080(1)	31(8)	59(18)	99(4)
	r_2	0.083(1)	121(18)	31(18)	85(5)
	r_3	0.0935(9)	89(3)	90(4)	11(3)
O(1)	r_1	0.091(3)	88(2)	79(8)	16(5)
	r_2	0.108(2)	82(2)	169(6)	81(7)
	r_3	0.154(2)	8(2)	83(2)	103(2)
O(2)	r_1	0.092(3)	80(5)	97(5)	21(6)
	r_2	0.109(3)	43(3)	131(3)	109(7)
	r_3	0.151(2)	48(2)	42(2)	98(2)
O(3),F	r_1	0.102(3)	128(6)	112(3)	38(7)
	r_2	0.118(3)	127(6)	111(3)	127(7)
	r_3	0.240(3)	59.5(8)	149.5(8)	95.0(9)
O(4)	r_1	0.092(3)	57(2)	33(2)	98(3)
	r_2	0.134(2)	86(4)	96(3)	172(3)
	r_3	0.159(3)	33(2)	122(2)	91(4)
O(5)	r_1	0.099(3)	117(2)	28(2)	81(5)
	r_2	0.120(3)	101(4)	91(5)	159(3)
	r_3	0.163(2)	30(2)	62(2)	109(2)
O(6)	r_1	0.092(3)	6(3)	87(2)	105(3)
	r_2	0.132(2)	96(3)	84(4)	164(3)
	r_3	0.160(3)	93(2)	7(4)	83(4)

* parenthesized figures represent estimated standard deviations (esd) in terms of the least units cited for the value to their immediate left, thus 0.1440(9) indicates an esd of 0.0009.

Table 12. Magnitudes and orientations of thermal ellipsoids for Radkovice lepidolite-1M

Atom	Axis	rms (Å) displacement	Angle (°) with respect to X	Y	Z
K	r_1	0.156(1)*	90	0	90
	r_2	0.158(1)	142(8)	90	117(8)
	r_3	0.164(1)	128(8)	90	27(7)
M(1)	r_1	0.143(8)	90	0	90
	r_2	0.146(8)	38(14)	90	139(14)
	r_3	0.171(7)	52(14)	90	49(14)
M(2)	r_1	0.091(2)	17(6)	90	84(6)
	r_2	0.097(2)	90	180	90
	r_3	0.105(2)	107(6)	90	6(6)
T	r_1	0.0915(9)	51(11)	40(12)	89(3)
	r_2	0.0944(9)	42(11)	130(12)	88(3)
	r_3	0.1062(7)	103(3)	90(3)	3(3)
O(1)	r_1	0.109(3)	90	0	90
	r_2	0.122(3)	104(3)	90	155(3)
	r_3	0.170(3)	14(3)	90	115(3)
O(2)	r_1	0.106(2)	29(2)	61(2)	98(3)
	r_2	0.138(2)	83(3)	100(3)	169(3)
	r_3	0.163(2)	118(2)	30(2)	97(3)
O(3)	r_1	0.105(2)	83(2)	80(6)	21(4)
	r_2	0.121(2)	105(3)	160(4)	75(6)
	r_3	0.156(2)	17(2)	107(3)	104(2)
F	r_1	0.122(3)	96(19)	90	5(19)
	r_2	0.129(3)	174(19)	90	85(19)
	r_3	0.241(3)	90	0	90

* parenthesized figures represent estimated standard deviations (esd) in terms of the least units cited for the value to their immediate left, thus 0.156(1) indicates an esd of 0.001.

tion other than fluorine content may be important in determining cation ordering patterns in the lepidolites and zinnwaldites. The conclusion that zinnwaldite is not ordered in $C2$ symmetry reached by Levillain et al., (1981) from Mössbauer spectra of Zinnwald and Madagascar specimens suggests that cation ordering schemes may be variable in zinnwaldite as well.

A comparison of octahedral sizes and scattering power between the Radkovice 1M and $2M_2$ polytypes indicates very small differences that cannot greatly affect the limits of lepidolite stability. Octahedral and tetrahedral sheet units are remarkably similar and, as suggested by Sartori (1976), structural unit variations do not apparently control the stacking sequence.

Acknowledgments

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