

PHYSICAL PROPERTIES OF SYNTHETIC LEPIDOLITES

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ABSTRACT

Natural lepidolites have 1M, 2M₂, and 3T structures and may contain up to 98 percent polyolithionite [KLi₂AlSi₄O₁₀F₂(Pl)], 60 percent trillithionite [KLi_{3/2}Al_{3/2}Si₃AlO₁₀(F,OH)₂, (Tl)], and 35 percent muscovite (Ms). They are separated from 2M₁ muscovites in the compositional triangle Pl-Tl-Ms by a region of mixed-layer micas. X-ray and optical properties of synthetic lithium micas were obtained from the crystallization of bulk compositions on the binary joins Pl-Tl, Pl-Ms, and Tl-Ms at 2 kbar.

Variable OH/F ratios in the starting materials showed the amount of F in polyolithionite necessarily equals four atoms per unit cell. In trillithionite, the OH/F ratio is a function of the amount of F available in the starting material, as indicated by shifts in the (005) spacing and average refractive index of the mica. No hydroxylepidolite end members could be synthesized.

Major discontinuities in the *c* dimension occur at compositions corresponding to *ca.* Pl₂₅Tl₇₅ and Pl₄₅Ms₅₅, and a less pronounced break in *c* may be present at Tl₃₅Ms₆₅ (mol %). In the first two cases, the breaks appear to be related to polymorphism; 2M₁ trillithionite is more stable than 1M trillithionite under all conditions investigated, and 2M₁ polymorphs are probably stable for the ranges Pl₂₅Tl₇₅-Tl₁₀₀, Pl₃₀Ms₇₀-Ms₁₀₀ and for all micas on the join Tl-Ms. Single phase 2M₂ lepidolites were not synthesized, however. The apparent absence of 2M₁ lepidolites in nature is evidently a function of composition. Extrapolation of the binary discontinuities into the ternary system Pl-Tl-Ms corresponds to an area represented in natural assemblages by mixed-layer lithium micas. No combination of X-ray and optical measurements can be used to provide satisfactory estimates of the composition of the ternary lepidolites.

INTRODUCTION

Lepidolite is a general name referring to lithium-rich aluminous micas of widely varying composition. They are a common constituent of many lithium-bearing granitic pegmatites. Previous investigations of lithium micas have been concerned primarily with chemical composition (Winchell, 1927, 1942; Stevens, 1938; Foster, 1960) and crystal structure (Levinson, 1953; Takeda and Donnay, 1965; Ross *et al.*, 1966) and have been restricted almost exclusively to natural specimens.

In order to treat the chemistry of natural lepidolites in systematic fashion, Foster (1960, p. 116) suggested several different stoichiometries and names as possible end members. According to Foster, the "essential" components of lepidolite can be plotted in the ternary system KLi₂AlSi₄O₁₀F₂ (polyolithionite, Pl)-KLi_{3/2}Al_{3/2}Si₃AlO₁₀(F,OH)₂ (trillithionite, Tl)-KAl₂Si₃AlO₁₀(OH)₂ (muscovite, Ms). From a study of 58 lepidolite and lithian muscovite analyses, Foster concluded that lepidolite can be

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derived from muscovite by progressive replacement of octahedral Al by Li in ratios ranging between two and three Li ions for one octahedral Al ion. The resultant net decrease in charge on the octahedral layer is counterbalanced by the substitution of Si for Al in the tetrahedral layer. Foster's compiled analyses, when plotted in terms of PL, TL, and Ms show the continuity in composition between lepidolite and muscovite (Fig. 1). Although PL is the most important lepidolite component, up to 60 per cent of TL may be present.

Concurrent with these ionic substitutions, the occupancy of the octa-

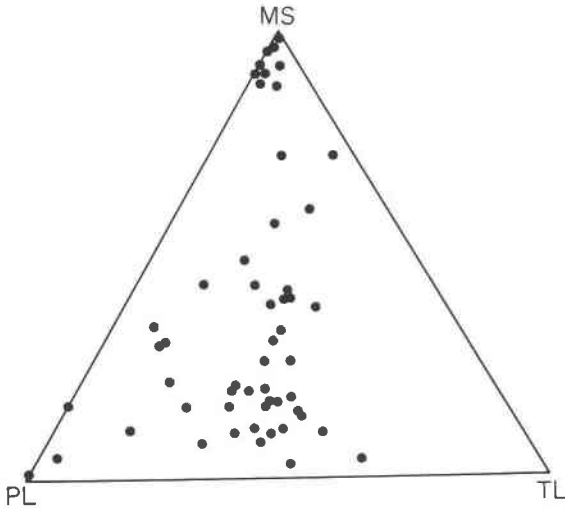


FIG. 1. Compositions of natural lithium muscovite and lepidolite in terms of mol % polyolithionite, trilithionite, and muscovite (all analyses from Foster 1960, p. 142).

hedral layer increases from 4.0 ions/cell in muscovite to nearly 6 ions/cell for some lepidolites, making the lepidolite group "transitional" between the dioctahedral and the trioctahedral micas. The interpretation of chemical analyses of these transitional micas has been a source of considerable argument. Lepidolites sampled from the same locality or even the same hand specimen that appear homogeneous may show widely divergent optical properties; X-ray studies show more than one polytype may be present (Ross *et al.*, 1966). Whether these differences actually reflect compositional changes within a homogeneous crystal (*i.e.* percent of Ms in "solid solution"; Foster, 1960) or represent two-phase aggregates of trioctahedral lepidolite and dioctahedral muscovite (Winchell, 1942) is unknown. Although Levinson (1953) confirmed the existence of mixed layer muscovite-lepidolite crystals in the compositional range 3.3 to 4

percent Li_2O , considerable confusion still exists as to both the nature and extent of this apparent miscibility gap.

The polymorphism of natural lepidolites has also received much attention in the literature. The only polymorphs reported to date are 1M, $2M_2$, and rarely, 3T (Levinson, 1953; Smith and Yoder, 1956). Muscovites may contain as much as 3.3 percent Li_2O while retaining the $2M_1$ structure (Levinson, *op. cit.*, who called such micas "lithian muscovites").

Previous attempts to correlate lepidolite polymorphism with specific

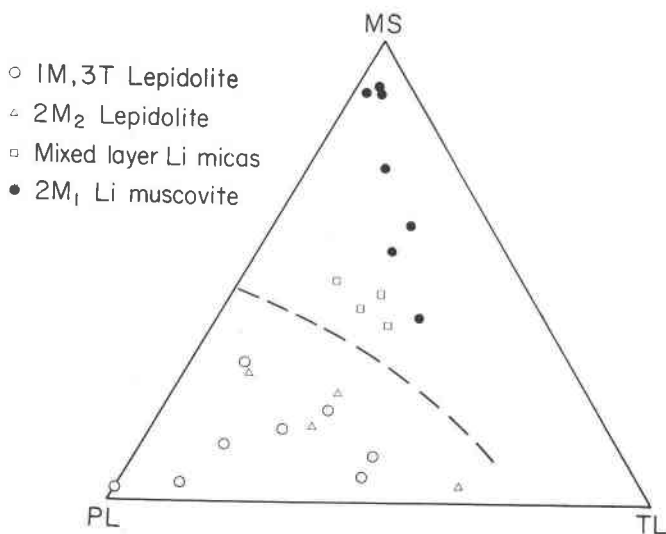


FIG. 2. Polymorphism of natural lithium micas as a function of composition (analyses and polymorphic type from Foster, 1960, p. 142).

compositions have enjoyed only limited success. Levinson found the general relationship, based solely on the percentage of Li_2O in the chemical analysis, to be: $<3.3\%$ Li_2O = "normal" muscovite ($2M_1$ polymorph), 3.3% to 4.0% Li_2O = transitional structures (mixed layer lepidolite-lithian muscovite), 4.0% to 5.1% Li_2O = $2M_2$ polymorph, and $>5.1\%$ Li_2O = 1M or 3T polymorph, the 1M polymorph being far more common. However, exceptions to this scheme can be found. The muscovite-epidolite "system" is not binary since two trioctahedral end members are involved: hence it is preferable to plot lepidolite compositions in terms of the three end members PL-TL-MS rather than using percentage of Li_2O as the only variable.

The results of such a plot are shown in Figure 2. The analyses used (see also Fig. 1) are taken from Foster (1960), and represent all those micas for which single crystal X-ray data are available to determine the

polymorphic type. The location of the apparent break between homogeneous $1M$ or $2M_2$ lepidolite polymorphs and mixed layer structures (corresponding to the 3.3% to 4.0% Li_2O region of Levinson) is indefinite because of the paucity of lithium micas for which both composition and polymorphism are known. To provide insight into the chemical and structural complexities of the natural lithium micas, 35 idealized synthetic bulk compositions have been crystallized hydrothermally and their X-ray and optical properties have been measured. This work was carried out at the Johns Hopkins University, and comprised a part of the author's Ph.D. dissertation. The financial assistance of the National Science Foundation (grant GP-1796) is gratefully acknowledged.

EXPERIMENTAL PROCEDURE

Apparatus and experimental method. All hydrothermal experiments were performed using stellite "cold seal" pressure vessels (Tuttle, 1949). During heating, the vessels were open to a large water reservoir held at the desired pressure which was directly measured with a calibrated Heise bourdon tube gauge attached to the reservoir.

Honeywell Py-Ro-Vane on-off controllers fitted with external mercury relays provided temperature control. The temperature of the bombs was measured using chromel-alumel thermocouples which had been calibrated against the melting point of NaCl (800.5°C) and Zn (419.5°C). Temperatures are believed to be accurate to $\pm 5^\circ\text{C}$. Reactants were sealed with water in 0.12" O.D. gold capsules. Approximate proportions were 25 mg solids and 12 mg water. Runs were terminated by quenching the reaction vessel in a stream of compressed air. At the conclusion of each experiment, the charges were examined using standard X-ray diffractometer and optical methods.

Cell dimensions of both synthetic and natural micas were determined using the lattice constant least-squares refinement program written by Burnham (1962). X-ray reflections were measured against an internal Si standard; Ni-filtered Cu radiation was used exclusively. Only those reflections which could be uniquely indexed were refined; the final cell dimensions obtained were based on a refinement of 12 to 18 reflections.

Starting materials. Lepidolite compositions were prepared using both oxide-fluoride mixes and gels. Components of the mixes were: KHCO_3 (Fisher Certified Lot #791147); Li_2CO_3 (Baker's Analyzed Lot #24361); LiF (Fisher Certified Lot #785940); $\gamma\text{-Al}_2\text{O}_3$ (Prepared by firing $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Baker's Analyzed Lot #26373) in air at 1000°C for 30 minutes); SiO_2 (Prepared by firing silicic acid (Baker's Analyzed Lot #26001) overnight at 1200°C ; this yielded α -cristobalite).

LiF was used as the sole source for both lithia and fluorine in all the so-called "oxide-fluoride" mixes, in which Li/F was 1. For compositions with Li/F less than 1, K_2SiF_6 was added to the LiF , and the other components were varied accordingly to preserve the stoichiometry.

Fluorine-free mixes (hydroxy-lepidolite compositions) were prepared either by substituting Li_2CO_3 for LiF , or by preparing gels according to the "organic silica nitrate" method (Roy, 1956). Raw materials used in gel-making were KHCO_3 , Al wire, and previously standardized tetra-ethyl-ortho silicate.

In some cases, a natural kaolinite (for analysis see Velde, 1965, p. 438) was used as the sole alumina source, the other components remaining unchanged. This type of starting material will be referred to as a kaolinite mix.

F-OH RELATIONS IN SYNTHETIC LEPIDOLITES

Although fluorine is a common minor constituent of nearly all natural micas, it is by far most abundant in the lepidolites. Differences in the F/OH ratio effect the physical properties of micas. For example, the *c* dimension of synthetic 1M phlogopite shrinks from 10.314 Å to 10.136 Å when fluorine is entirely substituted for hydroxyl in the structure; concomitantly, γ falls from 1.588 to 1.549 (Yoder and Eugster, 1954). Thus, it is worthwhile to consider each lepidolite bulk composition in terms of F- and OH- "end members." Polyolithionite and trillithionite bulk compositions containing either the maximum amount of fluorine (FPl, FTl) or no fluorine (OHPl, OHTl) were reacted both in the presence and in the absence of H₂O. The synthesis conditions are given in Table 1, and the results may be summarized as follows: (1) mixes that lack fluorine when crystallized hydrothermally fail to yield any mica over a wide temperature range and at all pressures below 4 kbar. The composition of the mica synthesized in small amounts from OHTl mix at 5 kbar (Table 1) is unknown; judging from the compositions of the coexisting condensed phases it cannot be trillithionite and may well not be a lepidolite. Hence, synthesis of a hydroxylepidolite could not be demonstrated. It should be emphasized that these results do not necessarily reflect equilibrium conditions inasmuch as failure to synthesize hydroxylepidolite is not proof of its instability. (2) Polyolithionite grows in 100 percent yield from FPl mix both in the presence and absence of water. (3) Trillithionite could be grown from FTl mix only in the presence of water. This result is

TABLE 1. SYNTHESIS EXPERIMENTS FOR "PURE" F- AND OH-LEPIDOLITE COMPOSITIONS

Bulk Composition	FPl	OHPl	FTl	OHTl
Crystallized "dry"	mica (700°)	san+l ₂ s (700°)	q+ks+K ₂ LiAlF ₆ +LiF (600°)	euc+lc+ks (600°)
Excess H ₂ O present, P = 2 kbar	mica (250°-800°)	san+l ₂ s (250°-700°)	mica (400°-670°)	euc+lc+ks (300°-600°)
Excess H ₂ O present, P = 5 kbar	—	san+l ₂ s (400°)	—	euc+san+ (mica) (400°)

Explanation: Numbers in parentheses represent temperature or range of temperatures over which the given assemblage was observed. Run times at 2 kbar ranged from 3 days to 28 days. 5-kbar runs were 90 days duration.

Symbols: l₂s, Li₂SiO₃; q, SiO₂ (quartz); ks, KAlSiO₄; lc, KAlSi₂O₆; euc, LiAlSiO₄ (α -eucryptite); san, KAlSi₃O₈ (structural state not determined).

TABLE 2. CELL DIMENSIONS OF POLYLITHIONITE AND TRILITHIONITE

	<i>a</i>	<i>b</i>	<i>c</i>	β
(1)	5.186	8.968	10.029	100°24'
(2)	5.188	8.968	10.029	100°27'
(3)	5.189	8.974	10.067	100°27'
(4)	5.206	9.003	10.163	100°28'
(5)	5.18	9.00	20.12	95°20'
(6)	5.20	9.045	20.038	95°30'

- (1) FPl mix crystallized dry 750°C, 2 kbar
 (2) FPl mix crystallized wet 750°C, 2 kbar
 (3) Natural polyolithionite, Kangerdluarsuk, Greenland, USNM #94314
 (4) FTl mix crystallized wet 650°C, 2 kbar (1M polymorph)
 (5) FTl mix crystallized wet 665°C, 2 kbar (2M polymorph)
 (6) FTl crystallized dry 700°C, 1 atm (Hatch *et al.*, 1957 p. 66)

in disagreement with Hatch *et al.*, (1957) who reported the successful synthesis of fluorotrilithionite at one atmosphere (Table 2).

OPTICAL AND X-RAY PROPERTIES OF POLYLITHIONITE AND TRILITHIONITE

Polyolithionite crystallizes in colorless hexagonal plates that range from less than 0.005 to more than 2 mm in maximum dimension. Optical properties are: $\alpha = 1.529 \pm 0.003$, $\beta = 1.552 \pm 0.002$, $\gamma = 1.555 \pm 0.001$, and $(-)2V = ca. 30$. Trilithionite always forms very fine-grained mats (maximum crystal size *ca.* 5 μ); the average refractive index of crystal aggregates (white light) is *ca.* 1.55. These data compare well with refractive indices of iron-free natural lepidolites (Deer *et al.*, 1964).

Cell dimensions of polyolithionite synthesized "dry" are identical to those synthesized in the presence of water (Table 2, col. 1,2). Complete powder data appear in Table 3. Using single crystal techniques, Takeda and Donnay (1965) studied the crystal structure and twinning of polyolithionite crystals synthesized during this study, and confirmed that the mica is a 1M polymorph. The cell dimensions of synthetic polyolithionite are in surprisingly close agreement with those of "natural polyolithionite" from Kangerdluarsuk, Greenland (Table 2, col. 3), especially in view of the "excess" components in the natural mica including 0.79 percent MgO+FeO+MnO, 0.48 percent TiO₂, 1.14 percent Rb₂O, 0.53 percent Rb₂O, 0.53 percent Na₂O, and 1.52 percent Nb₂O₅ (Stevens, 1938).

Trilithionite crystallized for periods of less than a week, or at temperatures below 600°C appears to form the 1M polymorph exclusively (for cell dimensions, see Table 2, col. 4) although identifications of polymor-

TABLE 3. X-RAY DATA FOR SYNTHETIC POLYLITHIONITE MONOCLINIC $C2/m$
 Cu K_{α} = 1.5418 Å, Ni filter a = 5.186 Å, b = 8.968 Å, c = 10.029 Å,
 β = 100°24' V = 458.76 Å³, D_{calc} = 2.823 gm/cm³

Synthesized from an oxide-fluoride mix (sealed capsule) at 2000 bars, 750°C, 1 week

hkl	d_{obs}	d_{calc}	I	hkl	d_{obs}	d_{calc}	I
001	9.869	9.864	2	{203 220, 220}	2.217	{2.219 2.217}	2
002 ^a	4.930	4.932	9				
020 ^a	4.473	4.484	5	132		2.204	
110, 110 ^a	4.438	4.434	3	041 ^a	2.186	2.186	2
111 ^a	4.302	4.305	4	024		2.161	
021 ^a	4.078	4.082	3	222	ca. 2.15	2.152	1
111 ^a	3.821	3.825	3	133 ^a	2.125	2.126	3
112 ^a	3.589	3.589	10	202		2.115	
022 ^a	3.311	3.318	10	221	ca. 2.09	2.094	1
003 ^a	3.289	3.288	9	005 ^a	1.974	1.973	9
112 ^a	3.065	3.066	10	204		1.958	
113 ^a	2.867	2.865	7	133 ^a	1.944	1.945	2
023 ^a	2.651	2.652	5	224	ca. 1.79	1.795	1
{201 130, 130}	2.580	{2.585	7	205, 223	ca. 1.72	1.717	1
		{2.579		134, 115	ca. 1.71	1.706	1
{131 200, 200}	2.552	{2.553	5	{006 135}	1.641	{1.644 1.641}	4
		{2.550					
{004 113}	2.470	{2.466	2	313	ca. 1.61	1.609	0.5
		{2.462		243	ca. 1.58	1.577	1
202		2.453		152	ca. 1.57	1.572	1
131 ^a	2.441	2.441	2	{153 242}	ca. 1.54	{1.543 1.538}	0.5
132 ^a	2.372	2.376	5				
201		2.366		224		1.533	
114		2.315		314	ca. 1.51	1.514	
{040 221}	2.239	{2.242	2	{060 331}	1.497	{1.495 1.496}	4
		{2.239					

d in Å. Silicon (a = 5.4305 Å at 25°C) was used as internal standard. Intensities were measured on an arbitrary scale using peak heights.

^a Used in least-squares refinement.

phic type were made by powder data alone. Longer runs at temperatures near the upper stability limit of trilitionite (ca. 660°C at 2 kbar) produced small amounts of two-layer polymorph growing at the expense of the 1M polymorph. The conversion is sluggish; a run of 1000 hours pro-

duced a 50/50 mixture of the polymorphs, which represented the largest amount of two-layer trilithionite synthesized.

Since both $2M_1$ and $2M_2$ lithium micas are found in nature, it is important to be able to distinguish between these two polymorphic types using powder data alone if possible. Although powder data for examples of both polymorphs are available (Levinson, 1953), they are difficult to correlate since spacings are unindexed and the natural samples measured have different compositions. Accordingly, complete powder data were calculated for both a $2M_1$ and a $2M_2$ trilithionite using a computer program written by Burnham (1962) and using cell dimensions obtained in this study, in an attempt to ascertain which two-layer polymorph was synthesized. The cell dimensions were adjusted so that c and β would give the same basal spacing for both polymorphs, β for the $2M_2$ polymorph having been arbitrarily chosen as $98^\circ 30'$. The results are shown in Table 4.

Under ideal conditions, $2M_1$ micas may be readily distinguished from $1M$ micas because of the presence of certain strong reflections belonging only to the two-layer mica (such as 114, $1\bar{1}4$, and 025), and the absence of certain strong reflections (such as 112 and $1\bar{1}\bar{2}$) belonging only to the $1M$ mica (Yoder and Eugster, 1955). Although the lists of $2M_1$ and $2M_2$ spacings are similar, several strong reflections that appear for $2M_1$ (especially 022 at 4.105 Å, 023 at 3.732 Å, and 025 at 2.993 Å) are absent for $2M_2$. The $2M_2$ polymorph has no unique reflection which can distinguish it from a $2M_1$; the distinction can be made only on the absence of these key $2M_1$ reflections. Thus, whereas one can theoretically distinguish $1M$, $2M_1$, or $2M_2$ lepidolites either by themselves, or as mixtures of $1M+2M_1$ or $1M+2M_2$ using powder data alone, a mixture of $2M_1+2M_2$ polymorphs could not be detected because only reflections belonging to the $2M_1$ polymorph could be recognized.

The reflections noted by an asterisk in Table 4 are those reflections observed for the two-layer trilithionite and which could not be indexed on a $1M$ cell; hence, if only one polymorph is present, it is probably a $2M_1$ type. Approximate cell dimensions corresponding to the $2M_1$ structure are given in Table 2, col. 5.

CRYSTALLIZATION OF LEPIDOLITE COMPOSITIONS WITH VARIABLE F CONTENT

The join FPl-OHPl. The lack of change in cell dimensions for polyolithionite synthesized in the presence and absence of water suggests, by analogy with F-OH phlogopites, that no detectable OH is allowed in the structure. This hypothesis was further investigated by crystallizing

TABLE 4. CALCULATED d (Å) FOR 1M, 2M₁, AND 2M₂ TRILITHIONITE POLYMORPHS

1M		2M ₁		2M ₂	
d	hkl	d	hkl	d	hkl
9.994	001	10.016	002	10.015	002
4.997	002	5.008	004	5.007	004
4.502	020	4.501	020		
4.450	110	4.473	110	4.448	110
—		4.443	$\bar{1}11$	4.451	$\left\{ \begin{array}{l} \bar{1}11 \\ 200 \end{array} \right\}$
—		4.392	021	4.451	
4.327	$\bar{1}11$	4.292	111	4.311	$\left\{ \begin{array}{l} 111 \\ 202 \end{array} \right\}$
—				4.310	
—		4.214	$\bar{1}12^a$	4.214	$\bar{1}12$
4.104	021	4.105	022	—	
—		3.966	112 ^a	3.968	112
3.846	111	3.864	$\bar{1}13$	3.861	$\left\{ \begin{array}{l} 202 \\ \bar{1}13 \end{array} \right\}$
—				3.860	
—		3.732	023 ^a	—	
3.619	$\bar{1}12$	3.584	113	3.602	$\left\{ \begin{array}{l} 113 \\ 204 \end{array} \right\}$
—				3.601	
—		3.480	$\bar{1}14^a$	3.473	$\bar{1}14$
3.345	022	3.348	024		
3.331	003	3.339	006	3.338	006
—		3.209	114 ^a	3.225	114
3.090	112	3.113	$\bar{1}15$	3.106	$\left\{ \begin{array}{l} 204 \\ \bar{1}15 \end{array} \right\}$
—				3.106	
—		2.993	025 ^a	—	
2.895	$\bar{1}13$	2.870	115	2.884	$\left\{ \begin{array}{l} 115 \\ 206 \end{array} \right\}$
—				2.883	
—		2.786	$\bar{1}16^a$	2.780	$\bar{1}16$
2.678	023	2.681	026	—	
2.596	201	2.593	130	2.598	020, $\bar{3}11$
2.589	130	2.587	$\bar{1}31$	2.587	116
2.563	$\bar{1}31$	2.577	200	2.577	021, 310, $\bar{3}12$

1M: calculated from synthetic 1M trilitlionite— $a=5.205$, $b=9.003$, $c=10.164$, $\beta=100^\circ 24'$.

2M₁: calculated from synthetic 2M₁ trilitlionite— $a=5.177$, $b=9.002$, $c=20.120$, $\beta=95^\circ 23'$.

2M₂: calculated to give same basal spacing as 2M₁— $a=9.000$, $b=5.197$, $c=20.252$, $\beta=98^\circ 30'$ ($b=9.0/\sqrt{3}$).

^a unique reflections observed for two-layer trilitlionite.

different proportions of FPl mix and OHPl gel. Resulting bulk compositions (*e.g.*, FPl₅₀OHPl₅₀) reflect only the Li/F ratio in the mix and do not necessarily relate to the F/OH ratio in any mica synthesized from them.

TABLE 5. RESULTS OBTAINED FROM CRYSTALLIZATION OF COMPOSITIONS ALONG JOINS

a. JOIN FPl-OHP1				
Composition	Phases	$2\theta(005)$	pl_{112}/san_{131}^b	
Pl ₁₀₀	pl	45.979	∞	
Pl ₈₀ OHP ₂₀	pl+san+(l ₂ s)	45.945	3.3	
Pl ₆₅ OHP ₃₅	pl+san+l ₂ s	45.950	1.5	
Pl ₅₀ OHP ₅₀	san+pl+l ₂ s	45.978	0.78	
Pl ₃₅ OHP ₆₅	san+l ₂ s+l ₂ s ₂ +pl	45.997	0.51	
Pl ₂₀ OHP ₈₀	san+l ₂ s ₂ +l ₂ s+(pl)	45.960	0.25	
OHP ₁₀₀	san+l ₂ s	—	0	

b. JOIN FTl-OHT1				
Composition	Condensed products	$2\theta(005)^a$	n^c	euc/tl ^d
FTl ₁₀₀	tl	45.392	—	—
FTl _{87.5} OHTl _{12.5}	tl	45.349	—	—
FTl ₇₅ OHTl ₂₅	tl	45.241	1.55	—
FTl _{62.5} OHTl _{37.5}	tl+(euc)	45.212	—	0.18
FTl ₅₀ OHTl ₅₀	tl+(euc)	45.106	1.56	0.23
FTl _{37.5} OHTl _{62.5}	euc+lc+ks+tl	45.070	—	2.2
FTl ₂₅ OHTl ₇₅	euc+lc+ks+(tl)	45.008	1.57	5.2
OHTl ₁₀₀	euc+lc+ks	—	—	—

Each assemblage is listed in approximately decreasing abundance of phases present, based on combined evidence of X-ray intensity and optical examination. Parentheses indicate trace amount of X ray, *i.e.* less than 10%. Pressure=2 Kbars, temperature = 600°C, run time=1 week.

^a Average of 4 oscillations (1°/2 minutes) using the (220) reflection of Si as an internal standard. Cu(K α) radiation.

^b Measured as a ratio of the relative intensities (peak heights) of the polyolithionite (112) and sanidine (131) reflections on an X-ray diffractogram.

^c Average refractive index of mica aggregates (white light).

^d Ratio of peak heights using the eucryptite (113) and the trillithionite (023) reflections.

Crystallization of several compositions at 2 kbar, 600°C for 1 week yielded mixtures of polyolithionite, sanidine, and lithium metasilicate (Table 5a). No significant shift in the positions of the 005 mica reflection occurs as the Li/F ratio changes. However, as Li/F increases, the percentage of mica obtained decreases proportionately with a concomitant increase in sanidine+lithium metasilicate (Fig. 3). Thus, the amount of polyolithionite obtained is directly proportional to the amount of available fluorine. This evidence, combined with the constancy of cell dimensions obtained from different F/OH environments, suggests that the

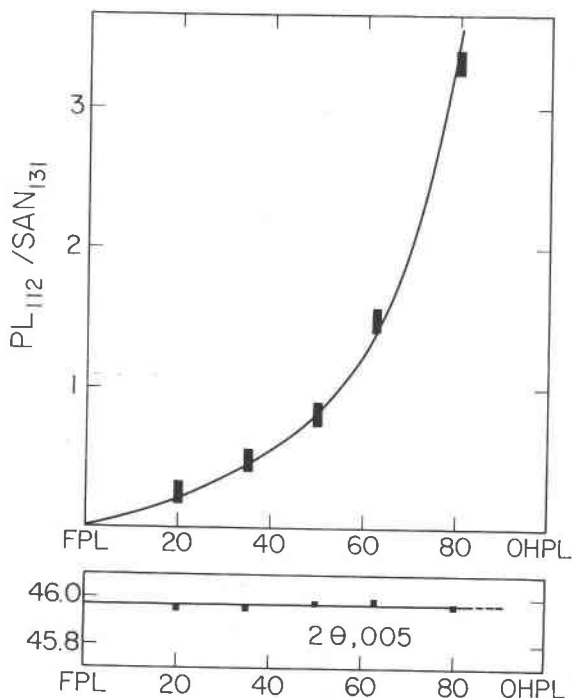


FIG. 3. upper: variation of the polyolithionite/sanidine ratio with fluorine content for the join FPL-OHPL. The ratio PL_{112}/SAN_{131} was obtained from the relative heights of those reflections on an X-ray diffractometer trace. lower: variation of the 005 spacing of polyolithionites obtained from the above bulk compositions, measured against an internal Si standard ($CuK\alpha$ radiation).

amount of F in polyolithionite does not significantly deviate from the ideal value of four atoms/cell.

Both lithium orthosilicate and lithium metasilicate were obtained in these runs, although the orthosilicate was never observed in the crystallization products of pure hydroxy-polyolithionite mixes. The presence of the orthosilicate implies loss of some Li_2O to the vapor.

The join FTl-OHTl. Crystallization of trilithionite bulk compositions with variable fluorine contents (prepared in analogous fashion to those described above) yielded quite different results (Table 5b). At 2 kbar, $600^\circ C$, 100 percent yield of trilithionite is obtained for bulk compositions with Li/F ratios ranging from 0.75 to 1. When this ratio exceeds 1, the mica yield begins to fall slightly below 100 percent up to a composition $FTl_{50}OHTl_{50}$ with the appearance of small amounts of eucryptite in the

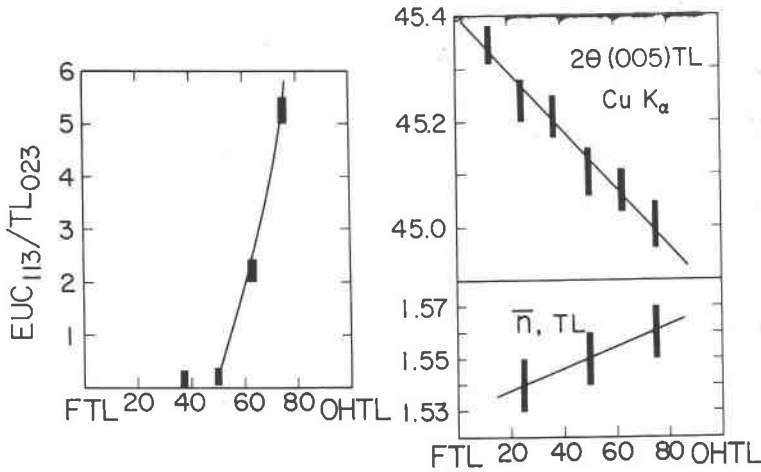


FIG. 4. left: variation of the eucryptite/trilithionite ratio with fluorine content for the join FTl-OHTl, based on ratios of peak heights for the two phases. upper right: variation of 005 spacing for trilithionites obtained from the indicated bulk compositions, measured against an internal Si standard ($CuK\alpha$ radiation). lower right: variation of average refractive index for trilithionites obtained from the indicated bulk compositions.

charge; however, beyond this point the percentage of mica obtained relative to eucryptite+leucite+kalsilite decreases very rapidly as is indicated by an arbitrary eucryptite/trilithionite ratio (Fig. 4). These intermediate trilithionites show both an expansion in the 005 spacing and an increase in the average of refractive index as the total amount of F is reduced (Fig. 4). The marked increase in basal spacing is indicative of substitution of OH for F, providing the mica is not allowed to change composition with respect to other components, and a positive correlation between refractive index and hydroxyl content for minerals having different OH/F ratios is well established.

Although the exact fluorine content of the trilithionites could not be measured, an approximation of the maximum changes in the F/OH ratio can nonetheless be made as follows. The maximum $\Delta d(005)$ observed for trilithionite is 0.017 \AA . Assuming a linear relation exists between fluorine content and basal spacing, a corresponding $\Delta d(005)$ in the F-OH phlogopite system would indicate a 50 percent change in the F/OH ratio of phlogopite because $\Delta d(005)$ for (OH phlogopite-F phlogopite) equals 0.034 \AA . Moreover, the observed change in average refractive index for trilithionite ($\Delta\gamma \approx 0.02$) when compared with optical measurements for F-OH phlogopites would also indicate about a 50 percent change ($\Delta\gamma$ for OH phlogopite-F phlogopite = 0.039). Therefore, although the

closeness of the approach of trilitionite to a pure FTI end member is not known, the most hydroxylated trilitionites probably have OH/F ratios of at least 1.

In summary, the two trioctahedral lepidolite end members differ with respect to fluorine content. Polyolithionite apparently contains practically no OH and may be synthesized in the absence of H₂O. Trilitionite crystallizes with a variable F/OH ratio depending on the amount of F present during synthesis, although a pure OH end member could not be grown. Thus whereas the formula for polyolithionite is properly written as a pure fluoro-end member, the general formula for trilitionite must always express the (F, OH) content as a variable ratio.

SYNTHESIS OF MICAS IN THE LEPIDOLITE SYSTEM



All lithium mica compositions were prepared using oxide-fluoride mixes, kaolinite mixes, and previously crystallized synthetic end members. The Li/F ratio in the starting materials was 1/1 in all cases. Compositions were restricted to the three limiting sidelines of the ternary system, *i.e.* Pl-Tl, Pl-Ms, and Tl-Ms.

X-ray properties of the micas.

1. The join Pl-Tl. All compositions along this join crystallize readily at 2 kbar, forming lepidolites in 100 percent yield at all temperatures below 630°C. Tl-rich compositions form extremely fine-grained aggregates, but very good diffractometer patterns with sharp high intensity reflections were obtained for all compositions. As determined from powder data, the 1M polymorph crystallizes exclusively throughout the range Pl₃₁Tl₆₉ to Pl₁₀₀ (mole %); for solid solutions richer in Tl, reflections indicating the presence of a two-layer polymorph appear. For the composition Pl₂₆Tl₇₆, small peaks having *d* values 3.49 Å and 3.22 Å appear in addition to the usual 1M reflections, corresponding to 114 and 11 $\bar{4}$ of the two-layer mica; however, no 025 (*d*=2.99 Å) characteristic of the 2M₁ polymorph was observed. Since these three reflections have approximately the same intensities for a 2M₁ mica, absence of the 025 reflection initially suggested the presence of a 2M₂ polymorph (see Table 3). Doubling the run time did not increase the amount of two-layer polymorph significantly, however, and increasing the total pressure to 4 kbar resulted in the presence of 025 in addition to 114 and 11 $\bar{4}$. Thus, the growth of a 2M₂ mica at 2 kbar cannot be confirmed, although mixtures of both polymorphs could well be present.

For all compositions between Pl₂₆Tl₇₆ and Tl₁₀₀, definite traces of

$2M_1$ polymorph are observed. The reflections present have very low intensity and do not interfere with the dominant $1M$ reflections; therefore, even though the two-layer polymorph is probably the stable one for these compositions (as was previously demonstrated by the progressive conversion of $1M \rightarrow 2M_1$ trilithionite), cell dimensions were computed solely on the basis of those strong reflections indexed according to a $1M$ cell. Based on the observed traces of a two-layer polymorph, however, the tentative conclusion is that the "stable" sequence of polymorphs along the join $Pl-Tl$ ($2k\bar{b}$, $600^\circ C$) is $1M-2M_2(?) - 2M_1$, with the break between one-layer and two-layer structures occurring around $Pl_{30}Tl_{70}$.

Cell dimensions calculated for these micas are shown in Figure 5. The β angle remains essentially constant throughout the range of compositions ($100^\circ 26' \pm 10'$) and may be ignored. A unit-cell volume plot for the $Pl-Tl$ series shows a strikingly non-linear relationship. Sharp discontinuities exist in both the a and c dimensions around $Pl_{30}Tl_{70}$; moreover, throughout the compositional range $Pl_{40}Tl_{60}-Pl_{25}Tl_{75}$, reproducible cell dimensions cannot be obtained from identical starting materials under duplicate conditions. The sharp discontinuities observable for a and c are not reflected in the molar volume plot because the breaks are compensatory, that is, they occur in opposite senses over the same com-

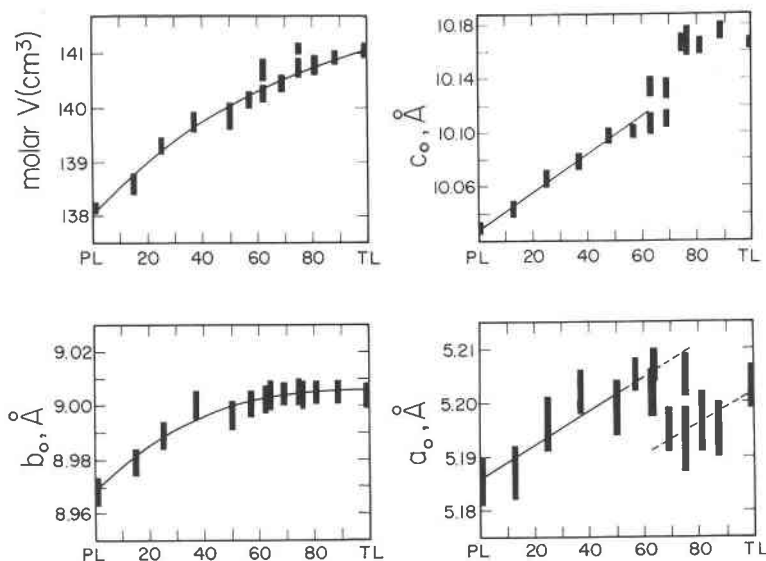


FIG. 5. Molar volume and unit-cell dimensions for micas belonging to the join $Pl-Tl$ (compositions in mol %). The β angle equals $100^\circ 26' \pm 10'$ for all compositions. The size of the symbols indicates the standard error obtained from the refinement of the parameter by computer.

positional range. It is not possible to prove the presence of a similar break for *b*, although the possibility of a discontinuity in the range $\text{Pl}_{40}\text{Tl}_{60}$ - $\text{Pl}_{50}\text{Tl}_{50}$ does exist. A smooth curve has been drawn through all the data points, however.

2. The join Pl-Ms. Apart from end member compositions, single phases could not be crystallized from intermediate compositions along the join Pl-Ms since, although mica was always the dominant phase obtained, significant amounts of sanidine were also observed. The percentage of sanidine reached a maximum value for compositions near the center of the series (up to 30 percent based on optical estimates), and fell off proportionately toward both end members, amounts as small as 5 percent being readily detected. Apart from mica, the only Li-bearing phase which consistently appeared was eucryptite, although its appearance was restricted to compositions between $\text{Pl}_{60}\text{Ms}_{40}$ and $\text{Pl}_{20}\text{Ms}_{80}$ (mole %), and mostly to higher temperatures. Eucryptite never exceeded 5 percent of the total phases present, and was only rarely detected by X rays. The presence of a β -spodumene of unknown composition was suspected in two runs near 750°C and a trace of petalite ($\text{LiAlSi}_4\text{O}_{10}$) was found in one run only. Thus, the bulk of the subsolidus products consisted of mixtures of mica and feldspar.

The recalcitrance of muscovite to crystallize in high yields from oxide mixes or glasses is well known (Yoder and Eugster, 1955; whereas 100 percent muscovite yields can be readily obtained hydrothermally using stoichiometric mixtures of either kaolinite+kalsilite (*ibid.*) or kaolinite + KOH (Velde, 1965). Accordingly, binary compositions were prepared using kaolinite as the sole alumina source in the hope that the presence of a layered structure in the starting material would promote nucleation of the mica. Using this technique, no improvement resulted; in fact, the charges obtained from these mixes appeared essentially identical to those with respect to mica/sanidine ratios as the oxide mixes.

Because micas on this join could not be synthesized in 100 percent yields, any analysis of the X-ray data obtained requires some discussion. Two interpretations are possible: the first is that the compositions of the micas synthesized do lie on the join Pl-Ms, and correspond closely to the bulk composition of the starting material; thus, all the other phases that appear in the run products (*i.e.*, sanidine \pm LiAl silicates \pm corundum + vapor) must also add up to the same original bulk composition. However, because of the large proportion of sanidine observed relative to LiAl silicates, this implies considerable transport of lithia into the vapor phase. In this regard, most charges did contain isotropic fragments having low refractive index, and these were interpreted as a quenched vapor

phase; however, generally the proportion of these fragments was much less than 5 percent of the total charge volume. Of course, the proportion of undetected vapor which may not have quenched is not known; however there was no indication that this problem caused significant departures of bulk composition in the Pl-Tl join in which the compositions were even more enriched in lithia.

The second possibility is that the composition of the micas obtained do not lie on the Pl-Ms join. Withdrawal of $KAlSi_3O_8$ from all the bulk compositions would yield a mica relatively enriched in Tl but lying somewhat off the Pl-Tl-Ms plane. If this procedure obtained for all compositions between Pl and Ms, the resultant path of mica compositions would describe a curved path between Pl and Ms situated away from the Pl-Tl-Ms plane, but with the convex edge pointing towards Tl. Lepidolite compositions lying off the plane are evidently rare in nature, however.

Although the author could not choose between these two alternatives, it is apparent that both choices can nonetheless be described in terms of a continuous series of mica compositions between Pl and Ms, and thus data obtained should be representative of the solid solution behavior of lepidolite (*sensu vasto*)—muscovite, even though the composition of the lepidolite component may not be exactly Pl. Thus, the resulting plots of d -values of the micas obtained are given in terms of bulk composition of the starting material: the reader is cautioned that these compositions may not correspond to the compositions of the micas themselves.

Based on analysis of powder data of micas crystallized from Pl-Ms bulk compositions, $2M_1$ polymorphs were obtained from $Pl_{10}Ms_{90}$, $Pl_{20}Ms_{80}$, and $Pl_{30}Ms_{70}$. Complete conversion to the $2M_1$ polymorph was observed only for $Pl_{10}Ms_{90}$, the other two compositions producing mixtures of polymorphs. As is usually the case, higher temperature and longer run time favor the two-layer structure. Thus, by analogy with both muscovite and trillithionite, it is assumed that presence of $2M_1$ reflections indicates stability of that polymorph relative to $1M$. All compositions between Pl_{100} and $Pl_{40}Ms_{60}$ produced $1M$ polymorphs only. The sequence of polymorphs encountered experimentally corresponds approximately to the natural sequence except that $2M_2$ micas were not recognized.

Because the presence of considerable amounts of sanidine interfered with several important mica reflections, the only meaningful X-ray parameter which could be measured was the basal spacing based on the position of the 005 (for $1M$), or 00.10 (for $2M_1$) reflection. This particular peak is very sharp for the end member compositions but becomes pro-

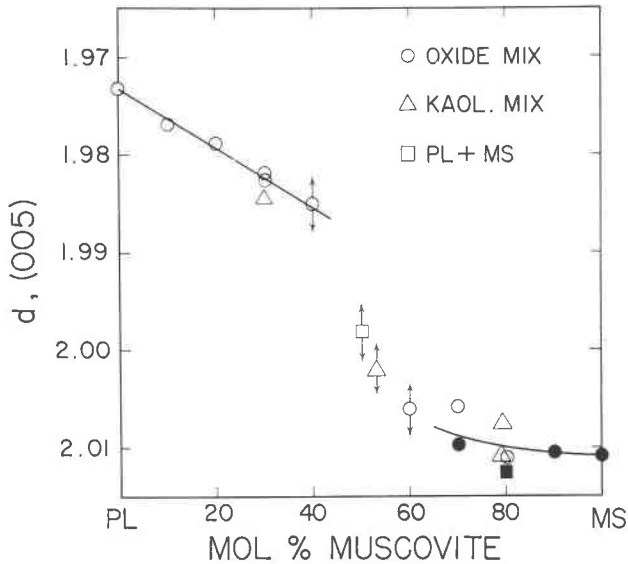


FIG. 6. Basal spacing of micas crystallized from bulk compositions on the join Pl-Ms. Open symbols: 1M polymorph, d (005) measured; dark symbols: 2M₁ polymorph, d (00.10) measured. Square symbols: starting material was polyolithionite + muscovite. Vertical arrows indicate greater measurement uncertainty for compositions near center of join.

gressively broader and weaker for intermediate compositions. The results of these measurements plotted for different types of starting materials are shown in Figure 6.

Three facts are apparent. The basal spacing for Pl-rich compositions increases regularly, presumably indicating a change in composition of the lepidolite with decreasing average octahedral occupancy. Second, the basal spacings of the muscovite-rich compositions are nearly constant. Third, a striking discontinuity in basal spacing exists at a composition around Pl₅₅Ms₄₅ ± 5 (mole %) on either side of which the basal spacings are extremely broad, diffuse and of rather low intensity.

3. The join Tl-Ms. Micas along the join Tl-Ms grew in much better yields than found for Pl-Ms. In the range Tl₁₀₀-Tl₅₀Ms₅₀, mica was the only product obtained. Small amounts of sanidine appeared in more Ms rich compositions, with the amount increasing toward the muscovite end. Based on optical estimates, the amount of sanidine present did not exceed 15 percent and was generally much less.

Compositions between Tl₃₀Ms₇₀ and Ms₁₀₀ crystallized as the 2M₁ polymorph exclusively. Toward Tl, the amount of 2M₁ polymorph obtained in a six-week run decreased at the expense of the 1M polymorph,

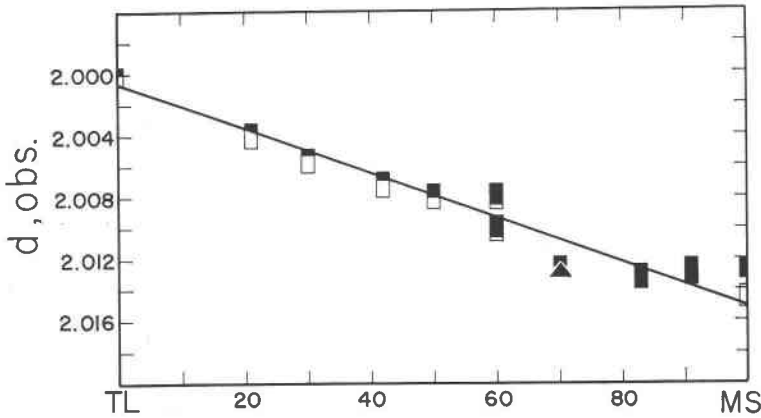


FIG. 7. Basal spacing of micas crystallized from bulk compositions on the join TL-Ms. Ratio of dark to light area on symbol reflects estimated proportions of $2M_1$ mica (dark) to $1M$ mica (light). In most cases a mixture of polymorphs was present; thus the measured reflection combined (005) and (00.10). Triangle: Composition $Tl_{30}Ms_{70}$ rerun for additional six weeks.

although $2M_1$ reflections are present for all micas along the join. From prior knowledge of the preferred stability of the $2M_1$ polymorph for both end members, it is tentatively concluded that the $2M_1$ polymorph is the more stable form for all binary compositions.

The relationship of basal spacing to composition is shown in Figure 7. There is a hint of a break between $Tl_{40}Ms_{60}$ and $Tl_{30}Ms_{70}$; as was observed for Pl-Ms compositions, the basal spacings of the Ms-rich micas are relatively insensitive to change although the relatively small difference between the basal spacings of trilithionite and muscovite make the distinction between a true break and normal data scatter difficult. The critical composition $Tl_{40}Ms_{60}$ gave two significantly different spacings from two exactly duplicate six-week runs (*cf.* the micas within the discontinuous region of the Pl-Tl join); however, a mica crystallized six weeks from bulk composition $Tl_{28}Ms_{72}$ did not change its basal spacing when rerun for an additional six weeks. Moreover, the basal spacing of a $1M$ muscovite crystallized from an oxide mix is somewhat greater than that of a $2M_1$ muscovite synthesized from kaolinite+KOH. Thus, from powder data alone, it is not possible to demonstrate with certainty that a discontinuity exists between $Tl_{40}Ms_{60}$ and $Tl_{30}Ms_{70}$, although the possibility of such a break cannot be ruled out.

Optical properties of synthetic Li micas. Refractive index measurements of natural lepidolites cannot be used as an indication of either Li content or

polymorphic type. For iron-free lepidolites the values are relatively constant with γ near 1.55 (Winchell, 1942). Optical data regarding lithian muscovites are not plentiful and, although "lepidolite" optical constants can be obtained for micas with as little as 3 percent Li_2O , lithian muscovite refractive indices are in general higher than lepidolites, but slightly lower than pure muscovites (Levinson, 1953). As an example of this, Rimal (1962) cites γ values for lithian muscovites from the Harding pegmatite, New Mexico, ranging from 1.599 to 1.602 and corresponding to lithia contents between 0.15 and 1.6 percent, although no correlation between Li_2O content and γ was evident.

Detailed optical measurements could not be made on synthetic binary

TABLE 6. AVERAGE REFRACTIVE INDEX OF SYNTHETIC LITHIUM MICAS (WHITE LIGHT)

Composition	$\bar{n}(\pm 0.01)$
Tl ₁₀₀	1.545
Pl ₁₀₀	1.54
Pl ₈₀ Ms ₂₀	1.55
Pl ₆₀ Ms ₄₀	1.54
Pl ₄₇ Ms ₅₃	1.54
Pl ₄₀ Ms ₆₀	1.54
Pl ₂₀ Ms ₈₀	1.55
Pl ₁₀ Ms ₉₀	1.54
Ms ₁₀₀	1.575

micas synthesized in this study because the grain size of all the micas obtained was so fine (av. $< 5 \mu\text{m}$) that only an average refractive index could be measured. Regardless of composition, these averages ranged from 1.54 to 1.55 (Table 6). However, these values are significantly lower than similar determinations made on a synthetic muscovite ($n = 1.575$). No intermediate values exist, even for composition Pl₁₀Ms₉₀. Because of the extremely low refractive energy of fluorine (Larsen and Berman, 1934, p. 31), it is likely that the sharp difference between the average refractive indices of pure muscovite and Pl₁₀Ms₉₀ is more a reflection of small amounts of fluorine entering the mica structure than lithium. The fact that these refractive indices are lower than values for comparable natural lithian muscovites may be a reflection of the small amounts of Fe and Mn invariably present in the natural micas.

DISCUSSION AND CONCLUSIONS

Although many of the observations noted above cannot be satisfactorily explained without adequate single-crystal X-ray analysis, a few speculations seem appropriate nonetheless.

1. A chemically continuous series of micas can be synthesized over the compositional ranges $Pl_{100}Tl_0$ - Pl_0Tl_{100} and $Tl_{100}Ms_0$ - $Tl_{50}Ms_{50}$. Because more than one polymorph may be present, it is not possible to demonstrate that the micas crystallized from any given composition are chemically homogeneous. The fact that micas in the compositional ranges $Tl_{50}Ms_{50}$ - Ms_{100} and Pl_{100} - $Ms_{100}Pl_0$ cannot be synthesized free from other phases is probably best explained by differences in nucleation rate of mica relative to sanidine for the given bulk compositions and starting materials, although use of different starting materials did not significantly change the result. Another explanation is that binary micas of those compositions are not stable; however, analyses of natural micas approach the polyolithionite-muscovite join rather closely (Fig. 1); thus it would be difficult to explain why synthetic compositions which differ only very slightly from the natural micas should be unstable.

2. A sharp discontinuity in the basal spacing of lepidolite was found along both the Pl-Tl and Pl-Ms joins. The breaks appear to be related to polymorphism, since they separate 1M micas (on the Pl end) from micas which show the presence of $2M_1$ reflections (on the Ms and Tl end).

The Pl-Tl lepidolites are ideally trioctahedral; thus the discontinuity in that series cannot be related to changes in the occupancy of the octahedral layer. Possible explanations may be found either in the ordering of cations in the octahedral sites or in the grosser structural differences between the polymorphic types. Regarding the last possibility, it is interesting to note that even in those compositions which showed traces of the $2M_1$ polymorph ($Pl_{25}Tl_{75}$ - Tl_{100}), the anomalous c dimensions were determined from the dominant reflections indexed according to a 1M cell. The fact that $2M_1$ lepidolites are not found in nature appears to be a function of bulk composition—*i.e.* natural lepidolites containing more than 60 percent Tl in solid solution have not been reported.

Polyolithionite crystallized hydrothermally apparently does not take significant amounts of OH into its structure: trillithionite, on the other hand, crystallizes with a variable (F/OH) content, with the exact composition dependent on the bulk composition of the starting material. This different behavior is persuasive evidence that the structures of these two micas (regardless of polymorphic type) must be significantly different. Even though the fluorine content of a mica has a strong effect on the size of the basal spacing, it is unlikely that these discontinuities can be attributed solely to fluorine contents because, for all bulk compositions, the Li/F ratio was invariant. Trillithionites with variable F/OH contents were synthesized only when the Li/F ratio in the starting material was altered.

The Pl-Ms discontinuity is complicated by the inability to synthesize sanidine-free assemblages. Thus, although the compositions of the micas

which were synthesized may be in doubt, the observed break in basal spacing may be significant in relation to solid solution between trioctahedral lepidolite and muscovite. It is particularly interesting to compare the location of this break with available data on natural lepidolites. Based on single-crystal studies and chemical analyses, a region of mixed-layer lepidolites exists which separates the muscovite-type structure from the lepidolite-type structure, and "in which octahedral occupancy is about 2.50 to 2.60 sites" (Foster, 1960, p. 126). Inasmuch as the theoretical octahedral occupancy of a mica near the center of the discontinuity

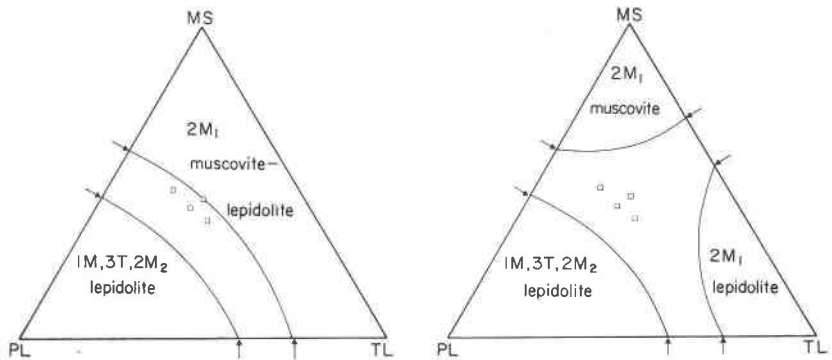


FIG. 8. Two possible interpretations of the relationship between polymorphism and composition in lepidolite and lithian muscovites. Arrows point to boundaries of discontinuities in cell dimensions found in synthetic binary systems; squares are compositions of natural mixed layer Li micas (see Fig. 2). Left: Tl-Ms join is a continuous series of $2M_1$ solid solutions. Right: Tl-Ms join is a discontinuous series.

observed in the synthetic micas is about 2.55 sites, it is tempting to conclude that this break separates 1M lepidolite-type structures from $2M_1$ muscovite-type structures. Unfortunately, the powder technique is not sensitive enough to distinguish between single-phase micas and two-phase micas in this case.

3. Applications of information gained from the binary systems can be applied to the system Pl-Tl-Ms with the aid of analyzed natural micas. Figure 8 shows two possible interpretations of the available data. The arrows indicate the boundaries of the discontinuities found on the binary joins; the ternary compositions represent natural micas of known polymorphic type (see also Fig. 2). In the first case, a break in the trilithionite-muscovite join is assumed; in the second case a homogeneous series of $2M_1$ micas is postulated for that join. As stated earlier, it is not possible to decide between these two alternatives based on present data. In either interpretation, however, a large field of $2M_1$ lepidolites are stable near

the trilithionite corner; in the first case these lepidolites are separated from $2M_1$ muscovite structures (presumably by a two-phase region) and in the second case this field merges with that of $2M_1$ muscovite. In both cases, the $2M_1$ structures are separated from the $1M$, $3T$ and $2M_2$ lepidolites by a two-phase region. Unfortunately, the confirmed synthesis of a $2M_2$ lepidolite was not achieved and thus no information regarding its stability relative to the other polymorphic types could be obtained.

This study has demonstrated the structural complexities inherent in even the simplified lepidolite system. Final answers to the problems raised here will depend on obtaining more information regarding the polymorphism of natural lepidolites, and on crystal structure analysis. For instance, of utmost importance to this study would be a single-crystal analysis of a $2M_1$ trilithionite so that its structure could be compared with that of $2M_1$ muscovite; alternatively, perhaps a natural $2M_1$ lepidolite whose composition lies near the trilithionite corner can be found.

The chemical complexity of the natural micas presents several problems which could be amenable to the synthetic approach; hence, a study of the effect of Rb, Cs, Fe or F on the polymorphism of these micas might prove worthwhile. In the meantime, apparently no combinations of standard X-ray or optical technique can be used to indicate the compositions of either the natural or the synthetic lepidolites.

ACKNOWLEDGEMENTS

I am indebted to Hans P. Eugster who suggested the problem and guided critical phases of the research, and to Hiroshi Takeda for fruitful discussions concerning problems of the lithium micas. D. H. Lindsley and D. R. Wones read early drafts of the manuscript and made many helpful suggestions.

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Manuscript received, January 31, 1968; accepted for publication, June 14, 1968.