

## NEW STUDY OF CRYOPHYLLITE

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### ABSTRACT

New analyses confirm the composition shown for cryophyllite by analyses made 75 or more years ago. Optical and  $x$ -ray crystallographic data are given. The one-layer structure, the mean  $\text{Li}_2\text{O}$  content of 5.25 per cent, and the relation between Li, octahedral  $\text{R}^{3+}$ , and  $\text{R}^{2+}$  of the new analyses characterize cryophyllite as a lepidolite. The higher than usual FeO content warrants the distinguishing prefix "ferroan."

### INTRODUCTION

Cryophyllite, a lithium mica found in feldspar veins in the granite ledges of Rockport, Massachusetts, near the extremity of Cape Ann, was named and described by Cooke in 1867. The vein from which Cooke obtained his samples was covered up or blasted away, but other similar veins provided samples for new analyses by R. B. Riggs, which were reported by Clarke in 1886. Since that time, apparently, no work has been done on this unusual mica.

In the course of a study of the compositional relations of lithium micas (Foster, 1960), it was found that cryophyllite, according to the old analyses by Riggs, has the highest lithium content of any mica in the ferrous lithium mica series and that it extends this series into the lepidolite area. However, the constituents that give cryophyllite its unique position, FeO and  $\text{Li}_2\text{O}$ , are the most likely to be in error in such old analyses, and a new analysis was, therefore, considered desirable.

Through the courtesy of Drs. Clifford Frondel, Horace Winchell, and George Switzer, several specimens of the Cape Ann material were obtained. Associated with cryophyllite in the felspathic veins that constitute these specimens is another, more abundant mica, close to lepidomelane in composition. As the two micas resemble each other closely in appearance, qualitative tests for lithium were made on crystals from various areas of the specimens to try to locate the high lithium mica. No areas of high lithium mica were found in the Harvard or Yale specimens, nor in one of the specimens from the United States National Museum, but in two other National Museum specimens, both numbered 45960, mica having a content of  $\text{Li}_2\text{O}$  similar to that of cryophyllite was found. This material has permitted not only new analyses of cryophyllite to be made, but also optical and  $x$ -ray crystallographic studies, which had not previously been made on this mica.

## CHEMICAL DATA

Several grams of material were separated from each of these two specimens, which were designated A and B, respectively, as they had the same National Museum number. A portion of each sample for crystallographic and optical study was reserved; the remainder was reduced to pass 100 mesh by pounding rather than by grinding to avoid, as far as possible, oxidation of FeO. These samples were then analyzed in accordance with standard methods of rock analysis as outlined in Hillebrand *et al.* (1953) with the following exceptions: (1) SiO<sub>2</sub> was determined by the Berzelius method because of the high fluoride content of the sample, (2) the alkalis, Li<sub>2</sub>O, Na<sub>2</sub>O, K<sub>2</sub>O, Rb<sub>2</sub>O, and Cs<sub>2</sub>O were determined by flame photometer, and (3) F was determined by the Willard and Winter method (1933) as modified by Grimaldi, Ingram, and Cuttitta (1955). The results of these analyses, together with a mean of Cooke's analyses, and three analyses by Riggs with their mean, are given in Table 1.

Cooke found two distinct types of cryophyllite, one which he describes as "finely foliated and consisting of an aggregate of small crystals," and the other "in large distinct crystals imbedded in massive feldspar," but no other differences in character were observed, and the two types were found to be similar in composition. He made two fairly complete analyses of the large crystals, the mean of which is given in Table 1, but only partial analyses of the finely foliated type. Riggs' analyses were of three well-marked types, A, described as "broadly foliated brilliant, blackish green," B, described as "paler, dull-green, less lustrous, seemingly altered," and C, described as "an aggregation of minute six-sided prisms, dark green, almost granular in appearance, resembling some chlorite." The description of Riggs' sample A resembles that of Cooke's second type, and that of Riggs' sample C resembles Cooke's first type. Riggs' three analyses are almost identical. The greatest discrepancy is in the high Fe<sub>2</sub>O<sub>3</sub> and low FeO content reported in C, although the total iron as Fe<sub>2</sub>O<sub>3</sub> is almost the same in C as in B, 10.69 and 10.66 per cent, respectively. It is curious that the higher Fe<sub>2</sub>O<sub>3</sub> content should have been reported in C rather than in B, which was described as "seemingly altered."

The analyses in Table 1 show a high degree of concordance. The greatest variance is in the values for the alkalis. Cooke's value for K is obviously much too high for a mica. On the other hand, he reports only a trace of Na<sub>2</sub>O, which is more in agreement with the flame photometer determinations than are Riggs' values for Na<sub>2</sub>O. He also detected the presence of Rb, which Clarke, reporting on Riggs' analyses, does not mention, but which is reported to be present in excess of 0.5 per cent in the recent

TABLE 1. ANALYSES OF CRYOPHYLLITE

	Cooke (1867)	Riggs (1886)			Foster (1960)			
	Mean	A	B	C	Mean	A	B	Mean
SiO <sub>2</sub>	51.54	51.96	51.46	52.17	51.86	52.28	51.84	52.06
Al <sub>2</sub> O <sub>3</sub>	16.76	16.89	16.22	16.39	16.50	15.56	15.96	15.76
Fe <sub>2</sub> O <sub>3</sub>	1.97	2.63	2.21	4.11	2.98	1.82	2.66	2.24
FeO	7.98	6.32	7.63	5.99	6.65	7.96	7.20	7.58
MnO	.31 <sup>1</sup>	.24	.06	.32	.21	.25	.27	.26
MgO	.76	.03	.17	Tr	.07	.00	.00	.00
ZnO <sup>2</sup>	—	—	—	—	—	.44	.40	.42
CaO	—	.12	Tr	Tr	.04	.08	.06	.07
Li <sub>2</sub> O	4.06	4.87	4.81	4.99	4.89	5.27 <sup>3</sup>	5.23 <sup>3</sup>	5.25
Na <sub>2</sub> O	Tr	.87	.89	.63	.80	.07 <sup>3</sup>	.09 <sup>3</sup>	.08
K <sub>2</sub> O	13.15	10.70	10.65	10.48	10.61	10.07 <sup>3</sup>	10.00 <sup>3</sup>	10.04
Rb <sub>2</sub> O	Tr	—	—	—	—	.68 <sup>3</sup>	.61 <sup>3</sup>	.64
Cs <sub>2</sub> O	—	—	—	—	—	<.03 <sup>3</sup>	<.03 <sup>3</sup>	<.03
TiO <sub>2</sub>	—	—	—	—	—	.10	.14	.12
H <sub>2</sub> O	—	1.31	1.12	1.46	1.30	1.28	1.50	1.39
F <sup>4</sup>	—	6.78	7.44	7.02	7.08	7.88	7.86	7.87
		102.72	102.66	103.56	102.99	103.74	103.82	103.78
—O=F		2.85	3.13	2.96	2.98	3.32	3.31	3.31
		99.87	99.53	100.60	100.01	100.42	100.51	100.47
Specific gravity <sup>5</sup>		—	—	—	—	2.936	2.921	

<sup>1</sup> Reported as Mn<sub>2</sub>O<sub>3</sub> 0.34.

<sup>2</sup> Quantitative spectrographic determination.

<sup>3</sup> Flame photometer determination by Blanche Ingram and Jesse J. Warr.

<sup>4</sup> Determined by Sara M. Berthold.

<sup>5</sup> Determined using a fused silica Adams-Johnston pycnometer.

flame photometer determinations. Riggs' values for Li<sub>2</sub>O are remarkably close to the flame photometer values considering the methods available at that time for the determination of Li.

Of particular interest are the Fe<sub>2</sub>O<sub>3</sub>:FeO ratios. In many old analyses Fe<sub>2</sub>O<sub>3</sub> is high and FeO is proportionately low because the oxidizing effect of grinding in preparing the sample was not realized until after 1900 and also because less accurate methods were available for the determination of FeO. However, Cooke's values for Fe<sub>2</sub>O<sub>3</sub> and FeO are very close to those made in 1960 (Anal. A). As the relative proportions of Fe<sub>2</sub>O<sub>3</sub> and FeO in Riggs' A and B analyses also compare favorably with those of the

1960 analyses, especially analysis B, it seems probable that the higher  $\text{Fe}_2\text{O}_3$  and lower FeO values reported in Riggs' analysis C truly indicate that in this sample a greater proportion of the iron was present as  $\text{Fe}_2\text{O}_3$ .

Quantitative spectrographic analyses of samples A and B are given in Table 2. The spectrographic values reported for Ca and Mg confirm the very low content of CaO and MgO found on analysis, and the spectrographic values for Li, converted to  $\text{Li}_2\text{O}$ , agree very well with results obtained by flame photometer: 4.95 and 5.27 per cent  $\text{Li}_2\text{O}$ , respectively, for sample no. 45960A, and 5.38 and 5.25 per cent  $\text{Li}_2\text{O}$ , respectively, for sample no. 45960B. Similarly, spectrographic Mn values, converted to MnO, agree very closely with the analytical values, 0.26 and 0.25 per cent, respectively, for sample A, and 0.23 and 0.27 per cent, respectively, for sample B. The spectrographic values for Rb, converted to  $\text{Rb}_2\text{O}$ , 0.43 and 0.54, are slightly lower than the respective flame photometer values, 0.68 and 0.61.

Zn, which escapes detection in the usual analytical procedure entailing double precipitations, was reported in the spectrographic analyses to be present in amounts in excess of 0.10 per cent, 0.35 per cent in A, and 0.32 per cent in B. These amounts of Zn, converted to ZnO, are included in the analyses in Table 1. The finding of Zn in these samples suggests that Zn should be more commonly looked for in micas, particularly if the analytical summation is low.

Attention is also directed to the presence of Sn and Nb in these samples. Sn is rather commonly found in micas, but Nb is rather uncommon. The amount of Nb reported in these samples, converted to

TABLE 2. QUANTITATIVE SPECTROGRAPHIC ANALYSES OF CRYOPHYLLITE  
(Sol Berman and Katherine Hazel, U. S. Geological Survey analysts)

U. S. National Museum No.	Cu	Sn	Pb	Zn	Mn	Ni	Fe	Cr	Ga	Y	
45960A	.048	.025	<.01	.35	.20	.0017	M	<.0003	.0059	<.004	
45960B	.012	.043	.03	.32	.18	<.0004	M	<.0003	.0059	.009	
	Yb	Ti	Zr	Nb	Be	Mg	Ca	Sr	Ba	Li	Rb
45960A	.0002	.040	.011	.12	.011	.0083	.017	.005	<.002	2.3	.39
45960B	.0003	.040	.011	.085	.011	.015	.016	.004	<.002	2.5	.49

Looked for but not found: Ag, Au, Hg, Ru, Rh, Pd, Os, Ir, Pt, Mo, W, Re, Ge, As, Sb, Bi, Te, Cd, Tl, In, Co, V, Sc, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu, Hf, Th, Ta, U, Cs, P and B.

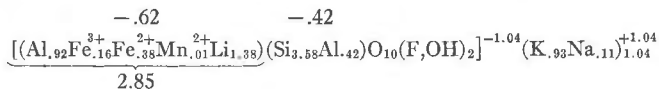
M = major constituent (>5%).

The sensitivity limit for cesium was 0.2%.

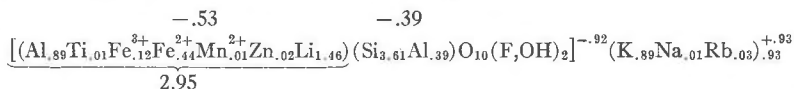
Note—The preceding results have an overall accuracy of  $\pm 15$  per cent except near limits of detection, where only one digit is reported.

Nb<sub>2</sub>O<sub>5</sub>, is about the same as that found by Stevens (1938) in a lepidolite from Madagascar.

Formulas calculated from the mean of Riggs' analyses,



and from the mean of the new analyses,



are similar in their content of the various cations. The formula for the mean of Riggs' analyses, however, has a higher negative charge on the unit layers, due principally to lower octahedral occupancy and to a higher negative charge on the octahedral layers; the negative charge on the tetrahedral layers in the two formulas is almost the same, 0.42 and 0.39, respectively.

#### OPTICAL DATA<sup>1</sup>

The indices of refraction were determined on samples A and B by the oil immersion method after checking the oils with the Abbe refractometer. The samples had been ground to pass a 100-mesh sieve. Glass that passed a 100 mesh and was retained on a 200-mesh sieve was used in the mount for the determination of the alpha index.

	A	B
$\alpha$	1.531	1.530
$\beta$	1.566	1.568
$\gamma$	1.569	1.572
2V (calc.)	32°6"	35°16"

The estimated accuracy attained in the determination of  $\beta$  and  $\gamma$  is  $\pm 0.002$ , and for  $\alpha$  is  $\pm 0.003$ .

#### X-RAY CRYSTALLOGRAPHIC DATA

Large single crystals of cryophyllite were available for crystallographic study, but they were soft and distorted and gave poor x-ray diffraction patterns, both by single crystal and powder methods. Nevertheless, by the use of careful mounting techniques it was possible to measure the unit cell of the crystal, identify its crystal structure, and index its powder pattern.

Powder diffraction patterns of the two samples, USNM 45960A and

<sup>1</sup> Optical determinations were made by Joseph J. Fahey, U. S. Geological Survey.

B, were prepared by M. E. Mrose, U. S. Geological Survey. The crystallinity of the soft flakes is easily destroyed by grinding, so that special care was required to prepare the powders for  $x$ -ray analysis by a scraping technique. The powder with the bonding material was formed into small spheres in order to reduce preferred orientation effects (Hildebrand, 1953). The  $x$ -ray mounts were built up by assembling these spheres into rod-shaped spindles. In this way, fairly sharp patterns were obtained.

The unit cell of the cryophyllite was established as monoclinic, space group  $C2/m$ , with  $a = 5.4 \text{ \AA}$ ,  $b = 9.3$ ,  $c = 10.3$  and  $\beta = 99\frac{1}{2}^\circ$ . It was found that these unit-cell dimensions gave a satisfactory indexing of the powder pattern of the USNM 45960A and B samples. Owing to the poor quality of the single-crystal patterns obtained, the unit-cell dimensions were determined more accurately from the powder patterns. The dimensions were adjusted by a rough least-squares analysis based only on the seven reflections: 110, 111,  $\bar{1}12$ , 112,  $\bar{1}13$ , 023 and 200. The results of the least-squares treatment gave the following cell dimensions:

$$\begin{aligned} a &= 5.25 \pm 0.02 \text{ \AA} \\ b &= 9.18 \pm 0.03 \\ c &= 10.02 \pm 0.03 \\ \beta &= 100^\circ 40' \pm 10' \end{aligned}$$

The powder data, which are identical for samples A and B within the errors of measurement, are given in Table 3, where they are compared with the  $d$ -spacings calculated on the basis of these latter cell constants.

The unit cell found corresponds to that of one of the polymorphs of biotite reported by Hendricks (1939). This form has a structure containing one phlogopite-type layer per unit cell. The content of the unit cell is therefore one formula unit as it is written in the section on chemical data. This accords with Levinson's (1953) finding that lithium micas (lepidolites) containing more than 5 per cent  $\text{Li}_2\text{O}$  generally have a one-layer octophyllite structure.

#### CRYOPHYLLITE = LEPIDOLITE (FERROAN)

Lepidolites are the high  $\text{Li}_2\text{O}$  members of two replacement series, one which starts with muscovite, and one which starts with siderophyllite (Foster, 1960). These relations are shown in Fig. 1. In this figure the lower limit of the lepidolite area with respect to the  $\text{Li}_2\text{O}$  content is based on Levinson's conclusion that micas with more than 4 per cent  $\text{Li}_2\text{O}$  have lepidolite (*i.e.*, octophyllite) structure.

In the muscovite-lepidolite series octahedral and tetrahedral Al are replaced by Li and Si, the theoretical relationship being expressed by the equation,  $2 \text{ Li} + \text{ Si} = 2 \text{ Al}$ . Thus, increase in Li content is accompanied

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR CRYOPHYLLITE

Calculated <sup>1</sup>				Measured <sup>2</sup>			
<i>hkl</i>	<i>d</i> <sub><i>hkl</i></sub>	<i>d</i> <sub><i>hkl</i></sub>	I	<i>hkl</i>	<i>d</i> <sub><i>hkl</i></sub>	<i>d</i> <sub><i>hkl</i></sub>	I
001	9.85	9.9	100	220	2.247		
002	4.93	4.97	9	203	2.240	2.236	4
020	4.58			132	2.232		
110	4.50	4.51	18	041	2.229		
111	4.36			222	2.182		
021	4.15	4.12	4	024	2.169		
111	3.86	3.86	3	133	2.153		
112	3.62	3.62	25	202	2.129	2.140	9
022	3.35	3.34	6	221	2.118		
003	3.28	3.30	70	042	2.076		
112	3.08	3.09	25	114	2.027		
113	2.882	2.89	18	223	2.012		
023	2.668	2.67	12	204	1.973	1.982	25
130	2.627			133	1.963		
201	2.617					1.956	3
131	2.600	2.61	12			1.779	12
200	2.580	2.58	35			1.721	4
131	2.480					1.562	3
202	2.482					1.525	3
113	2.469	2.47	9			1.509	18
004	2.463					1.493	2
132	2.414					1.416	2
201	2.389	2.395	25			1.379	3
040	2.288					1.351	6
114	2.324					1.338	6
221	2.272	2.261	6				

<sup>1</sup> Calculated *d*-spacings based on unit cell data: *a* = 5.25 Å, *b* = 9.18, *c* = 10.02,  $\beta = 100^\circ 40'$ .

<sup>2</sup> Cu K $\alpha$  radiation:  $\lambda = 1.5418$  Å; camera diameter 114.6 mm; maximum *d*-spacing measurable,  $\sim 12$  Å. Sample taken from USNM 45960.

by increase in octahedral occupancy. Levinson found that increase in Li content in these aluminum lithium micas is also accompanied by changes in structure, with micas containing less than ca. 3.3 per cent Li<sub>2</sub>O having the normal muscovite structure, and those having more than 4.0 per cent Li<sub>2</sub>O having generally 6-layer lepidolite (up to 5.1 per cent Li<sub>2</sub>O) or 1-layer lepidolite (above 5.1 per cent Li<sub>2</sub>O) structure. Micas having from 3.4 to 4.0 per cent Li<sub>2</sub>O have mixed 2-layer muscovite and 6-layer lepidolite forms. Micas having such mixed-layer forms have an average octahedral occupancy of about 2.5, approximately halfway between dioctahedral muscovite and trioctahedral polyolithionite (Foster, 1960).

In the siderophyllite-lepidolite series to which cryophyllite belongs and

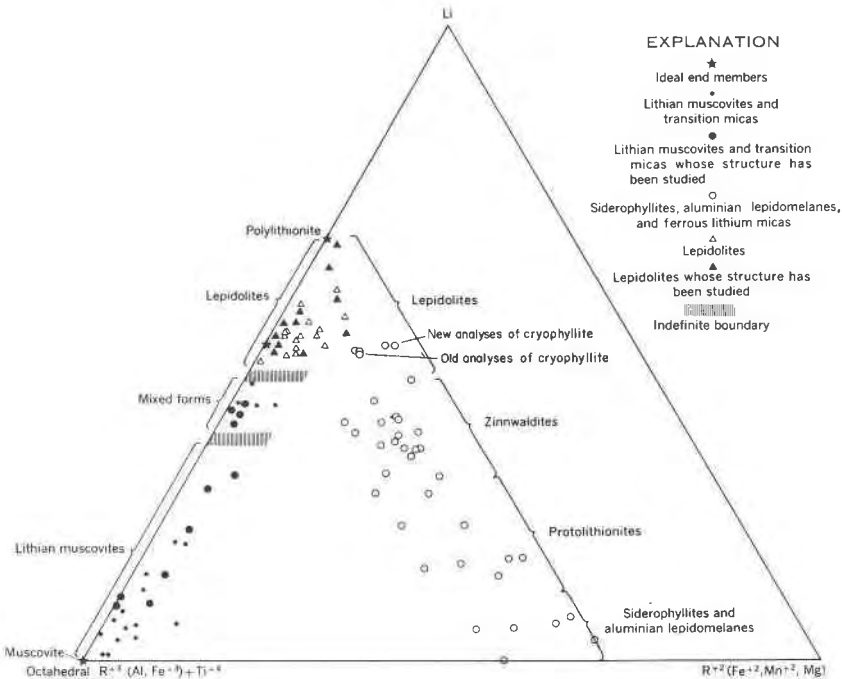


FIG. 1. Relation between Li,  $R^{2+}(\text{Fe}^{2+}, \text{Mn}^{2+}, \text{Mg})$  and octahedral  $R^{3+}(\text{Al}, \text{Fe}^{3+}) + \text{Ti}^{4+}$  in lithium micas (after Foster, 1960).

in which  $\text{Fe}^{2+}$  is replaced by Li, octahedral occupancy is greater than 2.50 throughout and the series is not characterized by changes in structural forms but is octophyllitic throughout. Thus, preliminary tests with micas associated with cryophyllite but having a lower  $\text{Li}_2\text{O}$  content show the presence only of the 1-layer structure.

#### CONCLUSION

The new analyses of cryophyllite show a high degree of concordance with the old analyses of Cooke and Riggs. The agreement is notably good for the important constituents  $\text{FeO}$  and  $\text{Li}_2\text{O}$ , which are often in error in such old analyses. The greatest disagreement between the new and old analyses is in the values for the alkalis. As the old analyses did not report  $\text{Rb}_2\text{O}$ , this is included in the  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  values reported, which are, accordingly, high.

The one-layer structure, the mean  $\text{Li}_2\text{O}$  content of 5.25 per cent, and the relation between Li, octahedral  $R^{3+}(\text{Al}, \text{Fe}^{3+}) + \text{Ti}$ , and  $R^{2+}(\text{Fe}^{2+}, \text{Mg}, \text{Mn})$  in the new analyses characterize cryophyllite as a lepidolite.



The somewhat higher FeO content than is usual in lepidolites justifies the designation of ferroan lepidolite.

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