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Studies on Manganese Oxide Minerals
VII. Lithiophorite[1]

By *Michael Fleischer* and *George T. Faust* (Washington)[2]

With 1 figure in the text and 7 tables

Abstract

The mineral lithiophorite, long considered to be a variety of "psilomelane" or "wad", is an independent species. Two new analyses, X-ray data, and differential thermal analyses are given and compared with those in the literature. The product formed by the firing of lithiophorite in the DTA experiments is a complex spinel-type structure. Chemical formulas and X-ray powder diffraction data for these spinels are given. The manganese oxides associated with "garnierite" and formed by the weathering of ultrabasic rocks commonly contain lithiophorite; available data indicate it to be a constituent of such material from the Urals, including the so-called elizavetinskite and buryktalskite.

Introduction

Manganese oxides containing small amounts of lithium were long ago described under the names lithiophorite (FRENZEL, 1870) and lithion-psilomelane (LASPEYRES, 1876). WEISBACH (1878) showed that the cobaltiferous manganese ore from Rengersdorf, Silesia, named kakochlor by BREITHHAUPT in 1832, also belongs here. These materials were, however, generally grouped with the large and varied group of "psilomelane" or "wad" for more than fifty years. Lithiophorite was shown by RAMSDELL (1932) by X-ray study to be an independent mineral with a characteristic X-ray powder pattern; he also showed the identity of kakochlor with lithiophorite. FLEISCHER and RICHMOND (1943) verified the

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[1] Publication authorized by the Director, U.S. Geological Survey.

[2] US. Geological Survey, Washington, D.C., U.S.A.

Table 1.

	A	B	C	1	2	3
MnO_2	55.85	42.22	49.99	52.93	51.07	51.56
MnO	9.55	15.42	2.67	—	4.61	3.88
CuO	1.74	0.96	0.53	trace	0.09	0.39
NiO	2.42	0.30	2.55^c	1.48	1.26	1.52
CoO		0.64		0.81	2.82	2.14
MgO	—	—	—	—	—	0.02
Al_2O_3	10.54	15.53	14.33	21.15	22.84	22.31
Fe_2O_3	1.48	2.43	0.83	0.88	0.32	0.45
Li_2O	1.23	1.42	0.91	0.79	1.59	1.48
Na_2O	—	—	—	0.03	0.10	0.12
K_2O	0.73	1.50	1.26	none	0.25	0.21
CaO	trace	trace	—	none	—	0.15
BaO	2.78	1.26	0.82	0.11	0.56	0.05
H_2O	12.64	15.42	(12.33)^d	14.40	0.67	0.26
H_2O^+					13.54	15.06
SiO_2	—	3.08^a	13.78	6.05^b	0.96	0.67
Total	98.96	100.18	100.00	98.83^e	100.68	100.27
G.	3.36	3.22	3.11	—	3.13	3.12
Analyst	WINKLER	WINKLER	IWAYA	E. P. HENDERSON, alkalies by J. I. DINNIN	V. NORTH	M. FLEISCHER

(a) also Bi_2O_3 trace. (b) Insol. (c) $Co_2O_3+Ni_2O_3$. (d) by difference. (e) including P_2O_5 0.20. (f) calculated from Mn 36.8. (g) calculated from Fe 0.2. (h) quoted as 47.24 by GINZBURG (1960). (i) = Co_2O_3. (j) including S 0.12; given as 99.38 in original, as 98.58 by GINZBURG (1960).

A–B From Schneeberg region, Saxony (FRENZEL, 1871, p. 353).
C Kakochlor from Rengersdorf, Silesia (WEISBACH, 1878).
1 "Pyrolusite" from Coble, Hickman County, Tennessee, quoted by WELLS (1937, p. 92), with new determinations of the alkalies.
2 Massive, fine-grained, from White Oak Mt., Bradley County, Tennessee, collected by W. G. Pierce.
3 Fine-grained botryoidal, from Greasy Cove, 6 miles S.W. of Attalla, Etowah County, Alabama, collected by W. G. Pierce.

conclusion that lithiophorite is an independent species, gave X-ray data and a provisional formula based on two unpublished analyses, and listed four new localities. Since, then, a number of papers have been published on the mineral. The name "oakite," provisionally used in this laboratory

Chemical analyses of lithiophorite

	D	E	F	G	H	I
MnO_2	48.95	44.0	35.71	58.2^f	49.35	47.94^h
MnO	8.21	9.0	2.92	—	4.29	7.95
CuO	—	—	—	2.1	—	—
NiO	—	—	—	1.5	4.80	1.60
CoO	—	—	6.99	2.0	1.97	3.05^i
MgO	—	—	—	—	1.17	1.20
Al_2O_3	23.84	22.0	19.22	24.3	5.07	12.21
Fe_2O_3	0.96	10.5	15.95	0.3^g	8.85	2.71
Li_2O	3.30	2.7	0.51	0.7	—	—
Na_2O	none	—	—	—	1.28	0.94
K_2O	none	—	—	0.1	0.62	—
CaO	trace	—	—	—	trace	2.32
BaO	—	—	—	0.003	2.49	2.04
H_2O	1.45	—	4.72	—	2.48	1.74
H_2O^+	13.15	11.7	11.97	—	11.20	11.34
SiO_2	0.30	0.1	1.63	0.7	—	4.12
Total	100.16	100.0	99.62	—	93.57	99.28^j
G.	3.37	—	—	—	—	—
Analyst	van der Walt	van der Walt				Arest-Yakubovich

D Cleavage flakes of crystals, Gloucester Farm, near Postmasburg, Union of South Africa (De Villiers and van der Walt, 1945).

E Very fine-grained, contains a small amount of hematite, from Bishop, Postmasburg, Union of South Africa (De Villiers and van der Walt, 1945).

F From New Caledonia, contains goethite (Wadsley, 1950).

G From Mena district, Arkansas (Dressel and Kenworthy, 1961).

H "Cryptonickelmelane" from Buryktal massif, sample 5M/50 (Nikitin, 1960).

I From the Urals, sample 348 (Ginzburg and Rukavishnikova, 1951).

before the identity with lithiophorite was proved, unfortunately found its way into the literature (Gruner, 1943). It should be dropped.

The present paper summarizes the scattered literature and presents two unpublished chemical analyses, data of differential thermal analysis, and X-ray study of the heated material. Data given in recent Russian papers on manganese oxides from the Urals are shown to be consistent with the presence of lithiophorite in some of these samples.

Chemical Composition

Analyses of lithiophorite and related material are collected in Table 1, those from the literature being designated by letters and the three analyses made in this laboratory by numbers. All but A, B, C, and I have been x-rayed; samples from Rengersdorf, Silesia (locality of C), examined by us are lithiophorite. Other analyses in the literature appear to have been made on impure material; examples are analyses of "lithian wad" (Li_2O 0.35, K_2O 0.44, Al_2O_3 7.83%) from Appalachian Park, Tennessee (WHERRY, 1916), and of "lithion-psilomelan" (Li_2O 0.48, K_2O 3.38, Al_2O_3 2.53%) from Salm Chateau, Belgium (LASPEYRES, 1876); the latter appears to have consisted mainly of cryptomelane. These two analyses are quoted in DANA's "System of Mineralogy," 7th Ed., Vol. I, p. 568.

Formulas suggested for lithiophorite include:

$Li_2Al_8(Mn^{+2}, Co, Ni)_2Mn_{10}^{+4}O_{35} \cdot 14H_2O$	FLEISCHER and RICHMOND, 1943
$Li_2Al_4Mn_2^{+3}Mn_4^{+4}O_{18} \cdot 6H_2O$	DE VILLIERS and VAN DER WALT, 1945
$Li_2Al_4Mn^{+2}Mn_5^{+4}O_{18} \cdot 6H_2O$	
$(Li, Al, Mn)_2O_3 \cdot H_2O$	WADSLEY, 1950
$(Al, Li)MnO_2(OH)_2$	WADSLEY, 1952

The first of these was derived from analyses 2 and 3; it reduces reasonably well to the general formula proposed by WADSLEY (1952) on the basis of structural study, except for the presence of excess H_2O.

It will be noted that lithium is a minor constituent of lithiophorite, which is essentially an aluminum manganese oxide; even analysis D, much higher in lithium than any other, has a ratio $Al/Li = 2$. It would be interesting to establish whether a lithium-free lithiophorite exists, as suggested by analyses H and I; it seems more likely that the analyses are incorrect.

Physical Properties

Lithiophorite in distinct pseudohexagonal crystals has been described only by DE VILLIERS and VAN DER WALT (1945). These crystals show a perfect cleavage on (001), with laminae somewhat flexible and sectile. All other samples we have examined are massive, fine-grained to botryoidal, and do not show cleavage, but give uneven to subconchoidal fracture. The color varies from iron-black to distinctly bluish-black (especially on fresh fractures) for material of high cobalt content. The streak varies from blackish-gray to greenish-black. The hardness is usually 2—3, rarely higher; De Villiers and van der Walt reported 2½—3, lowest on the cleavage, for crystals. The specific gravity is 3.1—3.4.

X-ray Data

Published X-ray powder data for lithiophorite are assembled in Table 2. The patterns of Nos. 1 and 3 correspond to analysis No. 2 of Table 1; those of Nos. 2 and 6 to analysis D in Table 1; that of No. 9 to H of Table 1. The differences in contents of Li, Ni, and Co do not appear to have much effect on the X-ray pattern. The line in the patterns at about 3.13 Å coincides with strong lines of pyrolusite, cryptomelane, and hollandite, and that at 2.41 with a strong line of pyrolusite.

Single-crystal studies by Wadsley (1952) on crystals from Postmasburg, Union of South Africa, show that lithiophorite is monoclinic, $C\,2/m$, $a = 5.06$, $b = 2.91$, $c = 9.55$ Å, $\beta = 100°30'$, cell contents $(Al, Li)_2\,Mn_2O_4\,(OH)_4$. There is a super-lattice which is dimensionally almost hexagonal. This is apparently responsible for the erroneous interpretation by J. McAndrew (quoted by Berry and Thompson, 1962) of single-crystal photographs of material from the same locality as being hexagonal. McAndrew's cell is related to the true cell described by Wadsley as follows: $a_{\text{McA.}} \approx 3b_{\text{W.}} \approx \frac{3a}{\sqrt{3}}{}_{\text{W.}}$; $c_{\text{McA.}} \approx 6c_{\text{W.}}$. Mikheev (1957, p. 409) gave an X-ray powder pattern (Table 2, No. 7) for "elizavetinskite" from the Sverdlovsk district, with the remark "The X-ray patterns of lithiophorite and elizavetinskite are very similar." He deduced a unit cell, orthorhombic, $a = 3.725$, $b = 12.38$, $c = 9.455$ Å; these unit-cell dimensions are quoted by Ginzburg (1960), but the mineral is given as hexagonal!

Differential Thermal Analysis

The differential thermal analysis studies (DTA) were made in an apparatus of the type developed by Alexander, Hendricks, and Nelson (1939). The technique used is described by Faust (1948, 1950). The samples were heated at the rate of 12° C per minute. The records were obtained as photographs. All the DTA experiments were made in the presence of air. The samples were crushed in a steel mortar of the Plattner type.

Table 2.

1		2		3		4		5	
I	d	I	d	I	d	I	d	I	d
—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
9.407	9	9.45	m	9.45	m	9.4	5	9.42	50
—	—	—	—	—	—	—	—	—	—
5.13	1	—	—	—	—	5.2	1	—	—
—	—	—	—	—	—	—	—	—	—
4.70	10	4.70	s	4.71	vs	4.73	10	4.72	100
—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
3.13	3	3.123	mw	3.14	w	3.15	3	—	—
2.48	1	—	—	2.49	w	2.49	1	2.52	10
—	—	—	—	—	—	2.41	3	—	—
2.35	9	2.385	mw	2.37	s	2.36	5	2.39	60
2.27	1	—	—	2.28	vw	2.27	1	—	—
2.12	1	—	—	2.13	vw	2.15	1	—	—
2.04	1	—	—	2.05	vw	2.03	1	—	—
1.87	8	1.882	m	1.88	s	1.88	5	1.89	40
—	—	—	—	—	—	1.65	0.5	—	—
1.55	6	1.508	w	1.57	m	1.58	3	1.58	10
—	—	1.459	vw	—	—	1.47	2	1.47	10
1.44	7	1.445	vw	1.45	m	1.45	2	—	—
—	—	—	—	—	—	1.43	1	—	—
—	—	1.396	vw	—	—	1.40	1	1.40	10
1.38	5	—	—	1.39	m	1.37	1	—	—
—	—	—	—	—	—	1.24	0.5	—	—
1.23	6	1.229	w	1.23	m	1.23	1	—	—
1.18	2	1.171	vw	1.18	w	1.18	0.5B	—	—
1.14	2	1.154	vw	1.15	w	1.14	0.5B	1.15	30[d]
—	—	—	—	1.07	vw	1.07	0.5B	—	—

(a) This line is given as "very weak" in Ginzburg and Rukavishnikova (1951).

(b) This line is given as 1.252 in Ginzburg and Rukavishnikova (1951).

* These lines are attributed to cryptomelane by Nikitin (1960).

1 Clifford Frondel, quoted by Fleischer and Richmond (1943), from White Oak Mt., Tennessee.

2 Wadsley (1950), crystals from Gloucester farm, Postmasburg, Union of South Africa.

3 Ramdohr and Frenzel (1956), from White Oak Mt., Tennessee.

4 Sorem and Cameron (1960), from Nsuta, Ghana.

5 Mouat (1962), from Artillery Mountains area, Arizona.

X-ray powder data (in Å) for lithiophorite and related materials

6		7		8		9		10	
I	d	I	d	I	d	I	d	I	d
—	—	12.3	3	—	—	—	—	—	—
—	—	—	—	—	—	—	—	9.54	2
9.27	4	9.68	6	9.399	6	9.17	7	9.17	7
—	—	—	—	—	—	6.92	3*	6.92	3
—	—	(5.24)	3	—	—	—	—	—	—
—	—	—	—	—	—	—	—	4.88	10
4.70	10	4.75	10	4.725	10	4.61	10	4.66	10
4.41	0.5	—	—	—	—	—	—	4.61	10
—	—	3.59	1	3.312	10[a]	3.46	1*	3.46	1
3.13	2	3.146	2	3.143	2	3.09	7*	3.09	7
2.52	2	(2.470)	3	2.483	4	—	—	—	—
2.40	0.5	—	—	—	—	—	—	—	—
2.38	8	2.350	10	2.348	10	2.35	7*	—	—
2.31	1	—	—	—	—	—	—	—	—
2.15	0.25	2.125	1	—	—	2.13	4*	—	—
2.06	0.25	—	—	—	—	—	—	—	—
1.886	7	1.872	10	1.878	10	1.872	5	1.834	7
—	—	—	—	—	—	—	—	1.689	7
1.579	4	1.574	5	1.572	3	1.535	2	—	—
1.462	5	1.485	2	—	—	—	—	1.482	10
1.446	1	1.442	7	1.447	4	—	—	—	—
—	—	—	—	—	—	—	—	—	—
1.396	4	—	—	—	—	—	—	1.408	4
—	—	1.380	6	1.376	4	—	—	—	—
1.245	2	—	—	—	—	—	—	1.305	3
1.232	3	1.235	6	1.232	4[b]	—	—	—	—
—	—	1.183	4	1.182	2	—	—	—	—
1.155	3	1.148	4	1.145	2	—	—	—	—
1.071	1	—	—	—	—	—	—	—	—

6 McAndrew quoted by Berry and Thompson (1962, p. 201), from Gloucester farm, Postmasburg, Union of South Africa, and Labrador Trough, Canada.

7 Mikheev (1957, p. 409), black powdery "elizavetinskite" from Sverdlovsk district, U.S.S.R.

8 N. N. Sludsko quoted by Ginzburg and Rukavishnikova (1951) and by Ginzburg (1960); intensities as given by Ginzburg (1960), from Urals, sample 164.

9 N. N. Sludsko quoted by Nikitin (1960), from Buryktal, sample 5M/50.

10 Lines assumed by Ginzburg (1960) to belong to the "new mineral buryktalskite".

The results of the DTA studies on lithiophorite are given in graphic form in Figure 1, and the numerical data are summarized in Table 3. The cryptocrystalline varieties of lithiophorite from Alabama and Tennessee yield almost identical DTA patterns with the minimum of the endothermal trough at 487° C ± 1° C. The endotherm is distinctly asymmetrical. Numerical values for the asymmetry of the troughs are

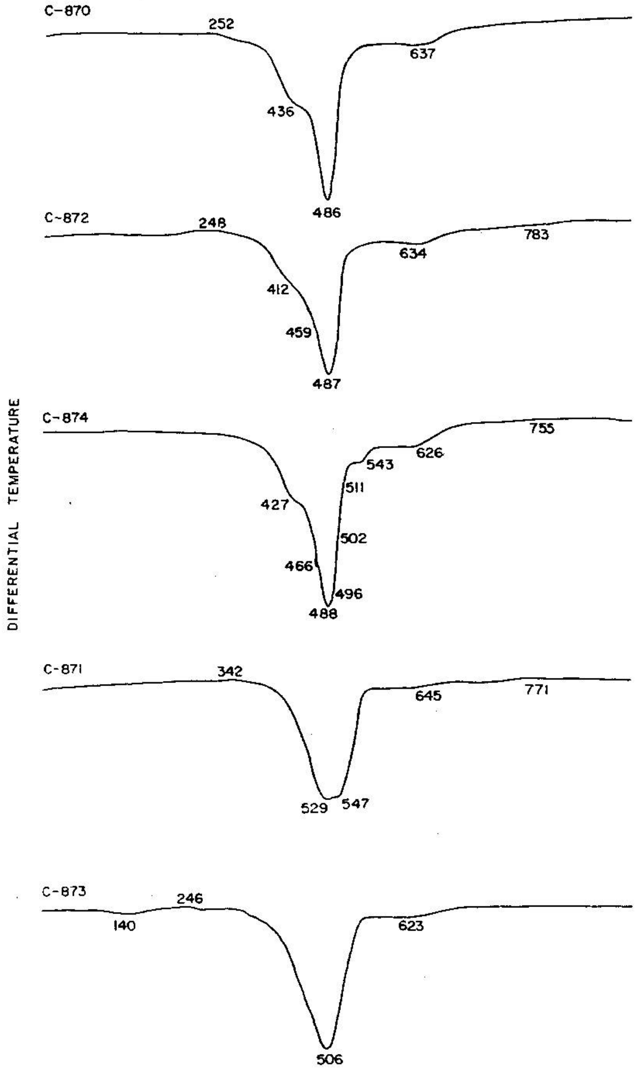

Fig. 1. Differential thermal analysis curves for pure lithiophorites. Curves C-870, made on material from Greasy Cove, Alabama; C-872, White Oak Mt., Tennessee; C-874, Coble, Tennessee; C-871, Postmasburg, Union of South Africa, were obtained from samples crushed through 66 mesh. Curve C-873, made on material from Postmasburg, Union of South Africa, was obtained on material crushed through 66 mesh and then ground to a finer grain size.

The temperature on the left of the diagram is about 25° C; the temperature at the termination of the curve, on the right, is about 1000° C.

Table 3. *Observations of the differential-thermal-analysis curves of lithiophorite*

[These curves were made with a resistance of 600 ohms in the galvanometer circuit]

Record	Locality	Temperature (°C) of endotherms and exotherms										Weight of sample used (grams)	Habit
		Low temperature				Intermediate temperature Principal endotherm				High temperature			
		Endotherm			Exotherm	Beginning	First inflection	Other inflection	Minima	Plateau	Endotherm		
		Beginning	Minima	End									
C-870	Greasy Cove, 6 miles S.W. of Attalla, Etowah County, Alabama	90	165	218	252	348	—	436	486	637	—	0.6021	Fine-grained botryoidal
C-872	White Oak Mt., Bradley County, Tennessee	58	155	221	248	341	412	459	487	634	783	0.6087	Fine-grained massive
C-871	Gloucester farm, near Postmasburg, Union of South Africa	—	—	—	342	392	—	—	529 547	645	771	0.5675	Cleavage flakes from crystals
C-873	Gloucester farm, Postmasburg, Union of South Africa. Part of the same tube sample ground to a finer grain size	62	140	175	246	341	357	408	506	623	—	0.4007	Ditto
C-874	Coble, Hickman County, Tennessee	—	—	—	?	349	427	466 496 502 511	488	626	755	0.6666	Fine-grained

given in Table 4. The well-crystallized lithiophorite from Postmasburg, Union of South Africa, when ground to pass 66-mesh bolting cloth, yielded the rather different DTA pattern shown as curve C-871 in Figure 1. The endotherm is a well-pronounced doublet and is asymmetrical (see Table 4). A part of the same tube sample of this material was crushed to pass through 66-mesh bolting cloth and then ground in an agate mortar to further reduce the grain size. This more finely ground sample was studied by DTA, with the result shown as curve C-873 in Figure 1. Grinding has removed the doublet, introduced more asymmetry into the shape of the endotherm, and lowered the temperature of the minimum to 506° C. Further grinding to a still smaller average grain size will probably yield a DTA pattern close in shape to that of the cryptocrystalline varieties. This behavior of well-crystallized lithiophorite in DTA studies as related to its grain size is exactly what is to be expected in a non-equilibrium process.

Examined in more detail, these DTA curves of lithiophorite show a small exotherm at approximately 248° C, an inflection on the low-temperature side of the endotherm at approximately 425° C, and a vertical displacement of the base line at approximately 630° C. The small exotherm is not accounted for in this study, the inflection on the low-temperature side of the principal exotherm suggests a side-reaction or a two-stage process of dehydration, and the vertical displacement of the base line (offset) may be due to a measurable change in the specific heat or thermal conductivity of the products or to a combination of both of these thermal properties.

DTA studies on lithiophorite were made by DRESSEL and KENWORTHY (1961) using air and controlled atmospheres of helium, carbon dioxide, carbon monoxide, and hydrogen. They found a DTA pattern for the experiment performed in the presence of air, which is almost identical with those in Figure 1. The temperature of the minimum of the principal endotherm is 485° C. Their interpretation of the inflexion on the low-temperature side of the endotherm, at 418° C, is the same as suggested in this paper — "the reaction takes place in two steps." They investigated this process by performing the DTA experiment using a slower heating rate and observed the formation of two distinct troughs. NIKITIN (1960) gives a DTA curve for a manganese oxide mineral, here interpreted as lithiophorite, with a temperature for the minimum of 480° C.

The angular relationships of the principal endothermic trough of lithiophorite were measured in accordance with the procedure of DEAN (1947), in which the whole angle, designated as γ, is formed by the extension of the straight portions of the trough. The angle γ is subdivided into two angles, α and β, by a perpendicular bisector passing through the minimum point. The ratio of tan α to tan β is a measure of the asymmetry of the trough. When $\alpha = \beta$ the trough is symmetrical. The angular data for the DTA curves of the samples of lithiophorite are given in Table 4. All but one of the DTA curves show an inflection on the low-temperature side of the principal endotherm. The angle between the straight portion of the inflection and the straight portion on the high-temperature side of the principal endotherm is designated γ'.

Table 4. *Angular relationships of the principal endothermic trough of the lithiophorites*

Record	Locality	Angle γ (degrees)	Angle α (degrees)	Angle β (degrees)	$\frac{\tan\alpha}{\tan\beta}$	Angle γ' (degrees)
C-870	Greasy Cove, Alabama	15.5 (−)	8.5	7 (−)	1.22	25
C-872	White Oak Mt., Tennessee	16.5	12.5 (−)	4.5 (−)	2.82	43
C-874	Coble, Tennessee	15	10	4 (+)	2.52	57
C-871	Postmasburg, South Africa	28.5	19	8	2.45	not present
C-873	Postmasburg, South Africa	28	18.5	9.5	2.00	34.5

X-ray Study of the Fired Products from DTA Experiments

The fired products, obtained after the completion of the DTA experiments, were subjected to heating at the rate of 12° C per minute over a time interval of 80 minutes and a temperature span of approximately 1000° C. For many substances this rapid thermal process does not yield well-crystallized products, but for lithiophorite, conversion to a phase with the spinel structure was easily accomplished. The best X-ray powder diffraction pattern was obtained from the product resulting from the DTA experiment (C-871) on the well-crystallized lithiophorite from Postmasburg, Union of South Africa. The X-ray data for this sample are given in Table 5. From these data, the unit cell dimension

Table 5. *X-ray powder diffraction data for a synthetic cubic lithium-manganese-aluminum oxide of the spinel type*[1]

I ($\sqrt{2}$ scale)	θ (obs)	hkl	d (obs) Å	d (calc.) Å
9	9.30	111	4.766	4.766
1 (br)	14.3[2]		3.11	
5	15.31	220	2.936	2.919
3	16.49[2]		2.714	
10	18.04	311	2.487	2.490
3	18.77	222	2.394	2.384
7	21.87	400	2.068	2.064
1	23.93	331	1.899	1.894
2	27.21	422	1.685	1.685
2	27.66[2]		1.659	
7	29.04	511 333	1.587	1.589
8	31.87	440	1.459	1.460
1	33.47	531	1.397	1.397
1	37.71	533	1.259	1.260
1	38.31	622	1.243	1.245
½	40.36	444	1.189	1.192
3 (br)	45.88	553 731	1.073	1.075
1 (band)	62.96	931	0.8648	0.8658
1 (band)	66.22	844	0.8417	0.8430

[1] Film 10871, Cu Kα Radiation, Ni filter, camera radius = 114.59 mm, cut off on d about 12 Å, Straumanis technique, film corrected for shrinkage.

[2] Extraneous.

a = 8.266 Å was calculated for this lithium-manganese-aluminum oxide of the spinel type.

The spinels synthesized in this research are related to the materials studied by Irani, Sinha, and Biswas (1960), who synthesized solid solutions of the spinel type involving Mn_3O_4 and $MgAl_2O_4$. They found that for a composition of Mn Mn_2O_4 : Mg Al_2O_4 of 11 : 5 the product is cubic and has the spinel structure with a = 8.34 Å, whereas, for the proportions of 8 : 8 the length of the edge of the unit cell is 8.26 Å. These authors investigated the state of oxidation of the manganese ions in their preparations by chemical analysis and, using these values, computed theoretical intensities from their X-ray powder diffraction data. The good agreement between the theoretical and calculated intensities permitted the determination of the cation distribution. With this knowledge as a basis, it was postulated that the cubic compound has long-range disorder with distorted octahedral sites occupied by Mn^{+3} ions.

The other specimens of lithiophorite studied are much more complex in their composition than the sample from Postmasburg and contain nickel, cobalt, barium, and copper in noteworthy amounts. The X-ray powder diffraction patterns of these samples were not as sharp as the pattern from the Postmasburg specimen, and this probably arises from the finer state of subdivision of the particles in these samples in contrast to the crushed crystals of the latter.

The X-ray powder diffraction data for these specimens are given in Table 6. These data were obtained from films prepared in Debye-Scheerer cameras of radius = 114.59 mm. The cutoff on *d* is about 12 Å. The data for the lithiophorites from Coble and White Oak, Tennessee, yield the unit cell dimension $a = 8.27$ Å, that from Greasy Cove, Alabama, a value of $a = 8.26$ Å.

HOLGERSSON and KARLSSON (1929) studied "cobaltites" of the spinel type. They synthesized copper, magnesium, zinc, manganese, and nickel end-members of the series such as $MnCo_2O_4$. Their X-ray powder

Table 6. *X-ray powder diffraction data for synthetic cubic Li-Ba-Cu-Ni-Co-Fe-Mn-Al oxide of the spinel type* 1)

I	hkl	Coble, Tenn. 2) d (obs) Å	Greasy Cove, Ala. d (obs) Å	White Oak, Tenn. 3) d(obs)Å
8	111	4.79	4.80	4.79
5	220	2.923	2.919	2.923
10	311	2.493	2.489	2.493
3	222	2.396		
7	400	2.065	2.062	2.065
7	422	1.689	1.691	1.691
2	511, 333	1.591	1.590	1.592
8	440	1.463	1.460	
1	533	1.2624		
1	642	1.106		
3	553, 731	1.076		1.078

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1) Cu $K\alpha$ Radiation, Ni Filter, camera radius = 114.59 mm, cutoff on d about 12 Å, Straumanis technique.

2) Extra line at 3.48 Å with I = 6.

3) Extra very weak lines at 3.49, 3.34, 3.07 and 2.74 Å; the intensity of the line at 3.34 Å is equal to 1, the rest are equal to ½.

diffraction data for the manganese compound, here called a manganese-cobalt oxide, are very similar to those of the compounds synthesized in this study. Their measurements have been recalculated in this study, into Å units, and are given, for comparison, in Table 7. The recalculated value for the unit cell dimension is, $a = 8.285$ Å.

Table 7. *X-ray powder diffraction data for synthetic cubic manganese-cobalt oxide. Data of* Holgersson *and* Karlsson (1929)[1])

I	hkl	d (obs) Å
W	220	2.933
VS	311	2.493
S	400	2.073
VW	(511) (333) β	1.756
W	422	1.692
VS	(511) (333)	1.588
VS	440	1.461
VW	533 β	1.391
W (diffuse)	(533) and (622)	1.261
W	444	1.196
S	642	1.108
VS	(553) (731)	1.076
S	800	1.036

[1]) Data of Holgersson and Karlsson recalculated to Å units.

If it were desirable to have a source for industrial purposes of a complex manganese-rich spinel, such as prepared in this study, the controlled calcination of lithiophorite would be an inexpensive method of preparation.

The chemical composition of these spinels can be specified if an analysis is made of the lithiophorite sample before it is fired and an analytical determination of the manganese in its several valence states is made on the fired product. The loss of weight on firing of these samples is due only to the loss of water and to the change in valence of the manganese. It is, however, from crystal structural requirements, necessary to know the valence state and quantity of the two kinds of manganese ions present in the spinel. It is assumed that no other phase involving these ions is present in the fired product — a fact verified by the X-ray study. The small amount of silica present in the lithiophorite does not appear to react with the manganese oxides.

The amounts of total manganese and active oxygen in the fired products were determined by our colleague, Joseph J. Fahey. From these amounts the following contents (in weight percent) have been calculated:

	MnO	Mn_2O_3	MnO_2
C-871	—	63.6	2.2
C-873	—	62.3	1.8
C-870	14.1	48.1	—
C-872	12.5	47.5	—
C-874	14.3	42.9	—

Using these data and assuming that the small amount of Mn^{4+} present in the two fired samples from Postmasburg is in tetrahedral coordination and that the vacant sites $\square$ are tetrahedral sites, the following reasonable formulas with balanced charge on the octahedral positions may be calculated.

C-871
$$[\square_{.26}\,Li_{3.78}\,Mn^{4+}_{.36}\,Mn^{3+}_{3.60}]\,[Mn^{3+}_{7.77}\,Fe^{3+}_{.20}\,Al_{8.03}]\,O_{32}$$
$$\sum_{\text{tet}} = 7.47 \qquad \sum_{\text{oct}} = 16.00$$

C-873
$$[\square_{.12}\,Li_{3.95}\,Mn^{4+}_{.29}\,Mn^{3+}_{3.64}]\,[Mn^{3+}_{7.41}\,Fe^{3+}_{.22}\,Al_{8.37}]\,O_{32}$$
$$\sum_{\text{tet}} = 7.88 \qquad \sum_{\text{oct}} = 16.00$$

C-870
$$[Ba_{.01}\,Ca_{.05}\,K_{.09}\,Na_{.07}\,Li_{1.95}\,Co_{.56}\,Ni_{.40}\,Cu_{.10}\,Mn^{2+}_{2.99}\,Mn^{3+}_{1.88}]$$
$$\sum_{\text{tet}} = 8.10$$
$$[Mn^{3+}_{7.27}\,Fe^{3+}_{.11}\,Al_{8.62}]\,O_{32}$$
$$\sum_{\text{oct}} = 16.00$$

C-872
$$[Ba_{.04}\,K_{.10}\,Na_{.06}\,Li_{2.13}\,Co_{.75}\,Ni_{.33}\,Cu_{.02}\,Mn^{2+}_{2.63}\,Mn^{3+}_{2.03}]$$
$$\sum_{\text{tet}} = 8.09$$
$$[Mn^{3+}_{6.95}\,Fe^{3+}_{.08}\,Al_{8.97}]\,O_{32}$$
$$\sum_{\text{oct}} = 16.00$$

C-874
$$[\square_{.56}\,Ba_{.01}\,Na_{.01}\,Li_{1.31}\,Co_{.27}\,Ni_{.49}\,Mn^{2+}_{2.93}\,Mn^{3+}_{2.42}]$$
$$\sum_{\text{tet}} = 7.44$$
$$[Mn^{3+}_{5.49}\,Fe^{3+}_{.27}\,Al_{10.24}]\,O_{32}$$
$$\sum_{\text{oct}} = 16.00$$

These correspond to the inverse spinel arrangement (Barth and Posnjak, 1932). The stated cation distribution is purely formal.

For purposes of calculation it is not necessary to recompute the analysis to 100 percent, for the ratios of the constituents are maintained in the method. The calculation is made as follows: 1) it is assumed that the total negative valence is contributed by the 32 oxygen atoms giving a total negative valency of 64; 2) the analytically determined values of the metallic oxides are divided by their respective equivalent weights; 3) the sum of the values obtained in (2) is divided into 64 to yield a quotient, the factor F. The several values obtained in (2) are multiplied by this factor to adjust the positive valency to 64; 4) each of the adjusted values obtained in (3) is divided by the valence of the metal to get atomic ratios; 5) the atomic ratios are then apportioned according to the formula $X_8Y_{16}O_{32}$.

Occurrences. Nature of the Ural Manganese Oxides

Lithiophorite is a common mineral. With the single exception of the fine crystals from the Postmasburg district, South Africa, which are of hydrothermal origin (De Villiers and van der Walt, 1945), the mineral is of supergene origin. In addition to the localities listed in Tables 1 and 2, lithiophorite has been reported with dioptase from South Australia and with chalcophanite from the Buchan district, Victoria, by Wadsley (1950); it has been found at more than a dozen localities in the weathered zone in Alabama, Tennessee, Georgia, North Carolina, Virginia, and Puerto Rico by X-ray determinations made in this laboratory.

By far the largest amount of data on such materials is contained in the monograph on the Urals by Ginzburg and Rukavishnikova (1951) and on the Buryktal deposit by Nikitin (1960). Many chemical analyses are given, along with optical, X-ray, and DTA data. The mineralogy has been interpreted by Ginzburg (1960), who gives a series of new names to these manganese oxides: nickelemelane, cobaltomelane, nickelcobaltomelane, cryptonickelemelane, alumocobaltomelane, buryktalskite. These have previously been commented on briefly (Fleischer, 1961); here we shall discuss only those samples that appear to be related to lithiophorite. Some of the samples are very high in NiO and probably contain new minerals, but they have yet to be described adequately.

The name elizavetinskite was given by Mikheev (1957) to material from the Sverdlovsk district, Table 2, No. 7. He stated that the assumed composition was (Mn, Co)O(OH); Ginzburg (1960) assumed it to be (Mn, Co, Ni)O(OH). The correspondence of the X-ray pattern of this material with that of lithiophorite is excellent except for the line at

12.3 Å, as MIKHEEV recognized; the name elizavetinskite should be discarded.

An X-ray pattern (Table 2, No. 8) given for Sample 164 by GINZBURG and RUKAVISHNIKOVA (1951) also is essentially the same as that of lithiophorite. Unfortunately no other data are given on this sample.

Sample No. 5M/50, "cryptonickelemelane" from the Buryktal massif (NIKITIN, 1960), is not as easy to decipher. The X-ray pattern (Table 2, No. 9) was considered by NIKITIN to show the presence of cryptomelane, despite the low K_2O in the analysis (Table 1, H). Both the chemical analysis and the X-ray pattern can be interpreted, with not much confidence, to correspond to a mixture of cryptomelane and lithiophorite. The DTA curve shows a single endothermic break at 480°, in good agreement with our data for lithiophorite, but with no indication of cryptomelane.

Sample 348 of GINZBURG and RUKAVISHNIKOVA (1951) gave an analysis (Table 1, I) very close to that of lithiophorite except that Li_2O was not determined. No X-ray data are given. The DTA curve shows a single endothermic break at 475°, in good agreement with our curves. It seems probable that this material is predominantly lithiophorite.

The data given on other samples cannot be deciphered with any assurance. GINZBURG (1960) takes the X-ray patterns, deducts lines of goethite, quartz, and other impurities, and arrives at the pattern given as No. 10, Table 2, as representing "a new mineral buryktalskite." Inspection shows that some of the lines correspond reasonably well with lines of lithiophorite and some with lines of cryptomelane; some cannot be assigned. In any case, the name is not acceptable in the complete absence of any physical or chemical properties except those measured on complex mixtures. The name was unanimously rejected in 1961 by the Commission on New Minerals and Mineral Names, I. M. A.

The occurrence of cobalt-rich manganese oxides in the weathering products of ultrabasic massifs has long been known; nine analyses of this type of material are given by DOELTER (Handb. Mineral-Chemie, v. 3, pt. 2, 1926; p. 875—876 and p. 881), including samples from New Caledonia and the Urals. Seven of these contain appreciable amounts of Al_2O_3 (6.3—20.4%), and it is likely that some, at least, contain lithiophorite, but neither determinations of Li_2O nor X-ray studies were made. The chemistry of the changes involved in the alteration of magnesium-rich ultrabasic rocks to the hydrous nickel silicate deposits ("garnierite") and the cobalt-rich manganese oxides associated with them are remarkable and deserve careful study. Nickel has been concentrated with respect to magnesium, most of the latter having been lost; most of the iron and silica has been removed, part of it appearing as hydrous iron oxide and quartz boxworks. Manganese has been precipitated as oxide and has apparently acted as an efficient concentrating agent for cobalt, copper, barium, lithium, and aluminum. Despite the predominance of nickel over cobalt in the parent rocks, the manganese oxides generally contain more cobalt than nickel, although the reverse relation is true of some samples. Occurrences of such material, with partial chemical analyses, are given by PECORA (1944) for deposits near São José do Tocantins, Goiaz, Brazil, in which the barium mineral, hollandite, predominates, and by KOSCHMANN and GORDON (1950) for samples from Loma Caribe, Dominican Republic, in which lithiophorite predominates.

In the Appalachians, lithiophorite occurs in surficial weathered zones in rocks ranging in age from Carboniferous to Early Cambrian, commonly as incrustations and fracture fillings in sandstones, quartzites, and cherts. Many of these deposits have been described by PIERCE (1944), including those from which the material of analyses 1, 2, and 3, Table 1, were collected. Lithiophorite is commonly one of the constituents of the black stains found on quartz on weathered surfaces in the southeastern United States.

In summary, lithiophorite is probably present in the manganese oxides derived from the weathering of the Ural ultrabasic rocks, even though the analyses given show a maximum Li_2O content of 0.13%, with most of the analyses showing traces to 0.02%. They should be checked.

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