Lithiophorite from the Lecht mines, Tomintoul, Banffshire

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SUMMARY. The constituent manganese minerals of an ore body located at the Lecht mines near Tomintoul include cryptomelane and lithiophorite. The latter, now known to occur extensively in soils, was characterized by X-ray, thermal, and electron microscope techniques. Lithiophorite yields a distinctive differential thermal curve and this was studied in some detail. A platy morphology is revealed under the electron microscope and from selected-area electron diffraction patterns it was concluded that the b parameter of the mineral is 8·73 Å, three times the value determined by Wadsley (1952). As suggested by Wadsley, this could arise from the distribution of lithium ions. Chemical analysis shows that the Lecht lithiophorite is slightly unusual in that it has a high iron and zinc content but is relatively low in cobalt. The associated cryptomelane contains a significant amount of thallium.

LITHIOPHORITE was first recognized as an individual mineral species by Ramsdell (1932), whose conclusions were subsequently confirmed by Fleischer and Richmond (1943). From single crystal studies Wadsley (1952) determined the structure of the mineral and suggested the formula $(Al,Li)MnO_2(OH)_2$. He showed that lithiophorite crystallized in the monoclinic system, with space group $C2/m$ and with unit cell parameters a 5·06, b 2·91, c 9·55 Å, and β 100° 31'. The mineral was found to have a layer structure with alternate sheets of MnO_6 and $(Al,Li)(OH)_6$ octahedra stacked so that O^{2-} and OH^- were situated above each other. Fleischer and Faust (1963) collected available X-ray and chemical data for lithiophorite and investigated its differential thermal curve.

Although lithiophorite has not been widely studied, it is becoming more extensively recognized in mineral deposits throughout the world. Recent work has shown that it is one of the major mineral forms of nodular manganese in Australian soils (Taylor, Mackenzie, and Norrish, 1964) and possibly in soils of other countries (Taylor, 1968). Manganese minerals in some soils are of agricultural significance since they may contain most of the soil cobalt in a strongly held form (Mackenzie, 1967) as well as appreciable concentrations of other trace elements of biological importance (Taylor and Mackenzie, 1966).

Occurrence. The material studied in the present investigation is from a deposit of manganese and iron ore, located at the Lecht mines, four and a half miles south-east of Tomintoul, Banffshire (NJ 238159). The ore occurs in a brecciated fracture zone, which extends for about 2 miles in a general north–south direction, in tightly folded schists of Dalradian age. Previously the mineralogy of the deposit has only been cursorily examined, the manganese ore being referred to by the general names of

psilomelane and wad (Hinxman, 1896). Samples of the ore were collected from out-crops and from waste tips of the old workings. It usually occurs as massive, black, fine-grained aggregates, occasionally showing a botryoidal form. X-ray examination shows that the aggregates are normally lithiophorite–cryptomelane mixtures, although pure samples of both minerals were obtained. Polished sections of the ore reveal a well-defined colloform texture in reflected light. Minerals found associated with the manganese oxides include hematite, goethite, and quartz.

Methods. X-ray diffraction photographs of randomly oriented powders were taken using Cu-$K\alpha$ radiation with a Ni filter. Differential thermal curves were obtained with the apparatus described by Mitchell and Mackenzie (1959) in a nitrogen atmosphere at a heating rate of 10 °C/min, and weight-loss data with a Stanton TR-01 thermobalance at 4 °C/min. For electron imcroscopy the material was ultrasonically dispersed in distilled water and a drop of the diluted suspension dried on a carbon-coated support grid. For electron diffraction studies a thin layer of aluminium was evaporated on to the specimen to act as a diffraction calibra-tion. A combination of spectrographic and other techniques was used for chemical analysis. Cobalt, Ni, Zn, and Ti were determined quantitatively after diluting the ashed minerals with $Al_2O_3/Fe_2O_3/CdO$ powder following the spectrographic method of Mitchell and Scott (1957.) Manganese, Zn, and Al were determined in a solution of 10 mg of the oxide in 4 % HNO_3, containing Li and Cr as internal standards, using the porous cup solution spark technique described by Mitchell (1964, p. 187). Iron was determined [on separate samples by the colorimetric method of Scott (1941). Larger portions (150 mg) of the oxide were used to prepare solutions for analysis of Ca, Na, and K by flame photometry and Mg was estimated in the same solutions by the porous cup technique described by Scott and Ure (1958). Silica was determined as insoluble residue remaining after HCl/HNO_3 dissolution of the minerals and ashing to constant weight. Other elements were estimated by a semi-quantitative technique using direct current arc excitation after dilution of the ashed oxides with the base mixture used to prepare the powder standards (Mitchell, 1964, p. 68). Manganese interference on the spectral line Cu 3247 Å precluded its use and Cu 3274 Å was used as an alternative.

X-ray and thermal studies. X-ray powder data clearly establish the identity of the lithiophorite (table 1). Apart from the absence of a few weak lines and some slight variations in visually estimated line intensities the powder pattern agrees with those published by previous authors (in Fleischer and Faust, 1963). The sample is pure apart from a small amount of quartz.

   The differential thermal curve for lithiophorite is shown in fig. 1a. It is distinctive and closely similar to those reproduced by Fleischer and Faust (1963). Its main feature is a pronounced endothermic peak at 433 °C, which is interrupted by a sub-sidiary endothermic reaction at 383 °C. Following this there is a broad endotherm at 600 °C succeeded by a minor one at 950 °C. Thermogravimetry (TG) shows a total weight loss of 17·3 % at 1000 °C, 14·8 % being lost before 500 °C (fig. 1b). Deriva-tive TG shows a broad weight-loss peak between 300 and 400 °C (fig. 1c). X-ray powder photographs of the heated samples (table I) yield the following information: Heating to 400 °C at a rate of 6 °C/min produces no change in the powder pattern but further heating at 500 °C for 2 hours results in the disappearance of the lithio-phorite pattern and the substitution of a weak pattern with only four lines. This photograph also shows that a small amount of quartz is present. Heating at 700 °C
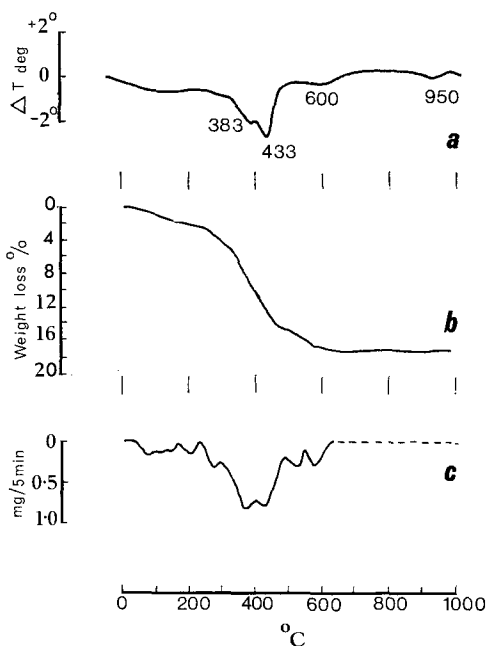
FIG. 1. Thermal curves for lithiophorite from the Lecht mines. *a*, Differential thermal curve. *b*, Thermogravimetric curve. *c*, Derivative thermogravimetric curve.

for 2 hours results in a rapid transition to a new phase identical to that found by Fleischer and Faust (1963) in their study of the fired products from DTA runs, and identified by them as a Li–Al–Mn oxide of the spinel type. This phase persists after heating at 1100 °C although some differences in the powder data may indicate slight modifications to it. The initial subsidiary reaction associated with the major endotherm on the DTA curve, therefore, appears to be due to loss of adsorbed water. This is followed by the dehydroxylation and decomposition of the lithiophorite structure, after which a new phase begins to form. The formation of the manganese-rich spinel may be indicated by the shallow endotherm at 600 °C whilst the reactions at the high-temperature end of the curve may be indicative of further minor changes.

Electron microscopy and diffraction. Electron microscope examination of

TABLE I. *X-ray powder data for unheated and heated Lecht lithiophorite*

1		2		3		4	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
9·54 Å	s	—	—	4·83Å	vw	4·87Å	w
4·72	vs	—	—	—	—	3·48	w
3·13	w	—	—	3·11	vw	—	—
2·37	m	—	—	2·92	vw	2·95	s
1·87	m	—	—	2·73	vw	—	—
1·572	w	—	—	2·48	vs	2·51	vs
—	—	2·43 Å	vs	—	—	—	—
—	—	2·13	vw	—	—	—	—
1·469	w	—	—	2·04	w	2·08	m
—	—	1·83	vw	—	—	—	—
1·388	w	—	—	1·71	vw	1·72	m
1·240	w	—	—	1·586	vw	1·60	s
—	—	—	—	1·456	w	1·469	s
—	—	1·409	vw	—	—	—	—

1. Unheated
2. Heated at 500 °C for 2 hours
3. Heated at 700 °C for 2 hours
4. Heated at 1100 °C for 1 hour

finely divided lithiophorite reveals thin sharply defined flakes of irregular shape, rather similar to flakes of mica or chlorite (fig. 2a). They are typified by regions of intense moiré fringes. Selected area electron diffraction patterns of the mineral are precisely hexagonal (fig. 2b) so that a direct analogy with the patterns yielded by clay minerals can be drawn, following the principles outlined by Brindley and de Kimpe (1961).

Whereas spots in clay mineral patterns tend to be sharp with erratic variations in intensity from one crystal to another, the spots in lithiophorite patterns are broader, more diffuse, and are generally reproducible in intensity. The strongest spots occur just inside the 1·432 Å diffraction ring and yield a spacing of 1·455±0·01 Å. This corresponds with the 020 spacing of lithiophorite indexed by Mitchell and Meintzer (1967) and gives a b parameter of 2·91 Å. The weaker spots inside the 2·338 Å Al diffraction ring are at 2·50±0·02 Å and these could correspond either with the 110 (2·51 Å) or 200 (2·49 Å) reflections calculated by Mitchell and Meintzer. Thus far the pattern is in complete agreement with what would be expected from the structure of lithiophorite proposed by Wadsley (1952). However, many of the patterns reveal additional extremely weak spots indicating a spacing of 4·41±0·20 Å. This is three times the reciprocal spacing of the intense spots at 1·455 Å and thus indicates a b parameter of 8·73 Å, which is three

FIG. 2. a (top), Electron micrograph of a typical platy crystal of lithiophorite from the Lecht mines. b (bottom), Selected-area electron diffraction pattern from a crystal of lithiophorite. The rings are from aluminium metal evaporated on to the specimen support; the two strongest occur at 2·338 and 1·432 Å.

times that found by Wadsley. It should be noted that Wadsley described the conditions under which such a unit cell would be expected: either lithium ions could fit between the trigonal prisms formed by hydroxyls and oxygens of adjacent sheets, in which case the aluminium layer would be the normal gibbsite one, or the lithium ions could occur systematically in sites corresponding to 'holes' in the gibbsite layer. Wadsley discounted both possibilities since strongly exposed a axis Weissenberg films gave no evidence of higher spacings and concluded that the aluminium and lithium ions were randomly distributed over all sites in a layer of the brucite type. However, it may be that these reflections are too feeble to be recorded by the Weissenberg method; they are very weak even on the electron diffraction pattern.

Although morphologically the Lecht lithiophorite strongly resembles some clay minerals, its electron diffraction pattern is diagnostic. Apart from the characteristic
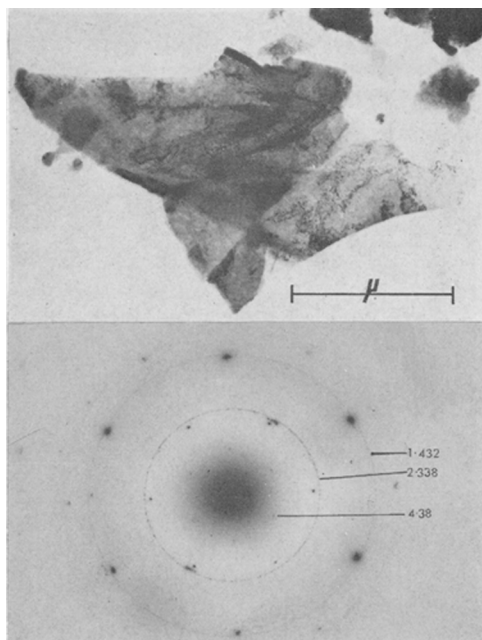
intensity distribution of the spots, the b parameter, whether it can be taken as 2·91 or 8·73 Å, is sufficiently far away from that of the clay minerals to avoid confusion.

Chemical data. The chemical analysis of the Lecht mineral together with formulae for other lithiophorite analyses from the literature are shown in table II. The structural formulae for the lithiophorite analyses are based upon a half unit cell containing 2 hydroxyls and 2 oxygens. The analyses are recalculated to a silica-free basis before deriving the formulae, which exclude alkalis and alkaline earths except lithium and

TABLE II *Chemical analyses of Lecht cryptomelane (A) and lithiophorite (B), together with half-unit-cell structural formulae for Lecht lithiophorite and lithiophorites quoted by Fleischer and Faust (1963)*

	A	B		Lecht	1	2	3	D	E	G
MnO_2	81·10	48·5	Mn^{4+}	0·87	0·89	0·84	0·83	0·80	0·80	1·24
MnO	—	—	Mn^{2+}	—	—	0·093	0·077	0·17	0·20	—
ZnO	0·91	2·71	Zn^{2+}	0·052	—	—	—	—	—	—
CuO	0·003	0·02	Cu^{2+}	0·0004	—	0·0016	0·0068	—	—	0·049
NiO	0·06	1·34	Ni^{2+}	0·028	0·029	0·024	0·028	—	—	0·037
CoO	0·01	0·07	Co^{2+}	0·001	0·016	0·054	0·040	—	—	0·050
MgO	1·27	0·49	Mg^{2+}	0·019	—	—	0·0007	—	—	—
Al_2O_3	1·29	18·3	Al^{3+}	0·56	0·61	0·64	0·61	0·67	0·68	0·89
Fe_2O_3	0·16	4·95	Fe^{3+}	0·096	0·016	0·006	0·008	0·017	—	0·007
Li_2O	0·02	0·86	Li^{+}	0·090	0·078	0·150	0·140	0·320	0·286	0·087
Na_2O	0·44	0·05								
K_2O	4·00	0·21	$\Sigma(Al^{3+}, Fe^{3+}, Li^{+})$							
CaO	0·35	0·20		2·06	1·96	2·09	1·99	2·37	2·34	
BaO	1·50	0·49	$\Sigma(Mn^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Mn^{4+})$							
SiO_2	1·96	8·25		3·68	3·68	3·70	3·64	3·54	3·71	
H_2O	6·10	13·20								
Tl_2O	0·017	0·003								
SrO	0·12	0·01								
TiO_2	0·04	0·07								
	99·35	99·72								

magnesium. Sample E of Fleischer and Faust (1963) was recalculated to an Fe_2O_3-free basis before deriving atomic ratios, as hematite was identified in this sample as a contaminant. Following Wadsley's structure all the aluminium and lithium are assigned to the hydroxyl layer and the remaining elements, except ferric iron, are allocated to the oxygen layer.

It is evident that the formulae are in close agreement. The Lecht mineral appears to be slightly unusual, however, in that it contains relatively small quantities of cobalt and large amounts of zinc. The presence of zinc is not reported at all in the analyses compiled by Fleischer and Faust (1963) although 0·6 and 1·0 % zinc are reported in two semi-quantitative analyses by Mitchell and Meintzer (1967). From considerations of atomic radii it might be anticipated that Co^{2+} (0·72 Å), Ni^{2+} (0·69 Å), and Zn^{2+} (0·74 Å) would be interchangeable with each other in the crystal lattice. This suggests the possibility that in soils zinc may be accommodated by lithiophorite in

the same way as cobalt. The Lecht lithiophorite also contains more ferric oxide than the other analyses quoted. It is thought that Fe^{3+} is located in the structure since no crystalline iron oxides were detected by X-ray diffraction in unheated or heated samples.

Table II also shows an analysis for the cryptomelane found in the Lecht ore deposit and which is normally closely associated with lithiophorite. This analysis is close to analyses for cryptomelane quoted by Faulring, Zwicker, and Forgeng (1960) although the relatively high barium content of the Lecht mineral may place it slightly towards the hollandite side of the cryptomelane–hollandite isostructural series. Comparing the analyses of the Lecht manganese minerals it may be seen that lithiophorite is much richer in the elements normally high in ferromagnesium minerals such as Fe, Li, Co, Ni, and Zn. The cryptomelane is richer in the alkali metals (excluding Li) and alkaline earth elements together with Tl. Thallium probably replaces potassium in the structure as in most geological processes the two elements behave similarly due to similarities in ionic size: $Tl^+ = 1\cdot47$ Å, $K^+ = 1\cdot33$ Å (Shaw, 1957).

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