Two varieties of lithiophorite in some Australian deposits

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ABSTRACT. Electron probe microanalyses carried out on thirty areas of lithiophorite $(Al,Li)MnO_2(OH)_2$ from five Australian localities indicate wide variations in its Ni, Co, Cu, and Zn content. The concentration of these elements varies inversely with the alumina content, though there is a marked change in their concentration at 18 % alumina, suggesting the existence of two varieties of lithiophorite with differing concentration of transition elements. EPMA line scans also indicate definite changes in Co content in lithiophorite grains less than 0.2 mm in dimension. The variations in alumina and transition elements may be explained if lithiophorite is considered to be an irregular mixed-layer-lattice intergrowth of pure lithiophorite with members of the recently discovered asbolane-type minerals.

THE aluminous manganese oxide lithiophorite is of widespread occurrence in soils and in the weathering zones of a variety of ore deposits. It is probably one of the major components of the poorly defined manganese oxides wads (Palache et al., 1944) in association with vernadite, birnessite, cryptomelane, etc., and possibly other unrecognized minerals. In contrast to some of these minerals, lithiophorite is readily identifiable, with well-defined optical properties and a crystalline structure which produces excellent X-ray and electron diffraction patterns. It has, however, two features which make it somewhat unusual. One is its Li content. The name means 'lithium-bearer', and the original material from Schneeberg, Saxony, investigated over a century ago by Frenzel, A. (1871) contained 1.23 % Li_2O. The name may have been an unfortunate choice, for, while some lithiophorites contain reasonable amounts of lithium [3.3 % Li_2O for lithiophorite at Postmasberg, South Africa (Villiers and Van Der Walt, 1945)], other lithiophorites contain only traces of Li_2O (Frenzel, G., 1980), and this element may not be essential to the structure. A second more unusual feature of the mineral, which is the subject of this paper, relates to its Cu, Ni, Co, etc., content. Not only are the contents of these elements highly variable, even in lithiophorite grains from a limited locality

(Ostwald, 1980), but the amounts sometimes recorded appear excessive if the elements are simply replacements in an aluminous manganese oxide structure. Even taking into account the confused state of the literature on manganese oxide wads (general term for an unidentified, soft, black, generally tetravalent manganese oxide of weathering origin) it is hard to imagine wad minerals containing 20.79 % CuO, cuproasbolane; 17.3 % CoO, cobalt wad, Idaho; 12 % Pb, plumbian wad from Baden (all figures from Palache et al., 1944). Minerals such as crednerite $CuMnO_2$, cesarolite $PbMn_3O_7 \cdot 3H_2O$, and the zinc-containing manganese oxides hetaerolite, hydrohetaerolite, and chalcophanite are possible explanations, but even here it is often difficult to reconcile the compositions of these minerals, especially non-manganese/manganese ratio, with the composition of the wads. Certainly, well-defined monomineralic manganese oxides containing major amounts of Ni and Cu are not apparent in ore deposits, though small amounts of these elements (1–2 %) are common in marine todorokite (Frenzel, G., 1980).

This paper results from an attempt to investigate the reasons for the variability in trace Cu, Ni, Co, etc., content of lithiophorites. Specimens were obtained from five Australian locations showing a wide range of mineralization types, and the mineral was examined by optical microscopy, electron probe microanalysis, and X-ray diffraction.

Specimen locations. Specimens of lithiophorite from the following locations were investigated.

1. Groote Eylandt 14° S, 136° 30′ E). Lithiophorite occurs in lateritized areas of the manganese oxide ore horizon and in manganiferous sandy soils away from the ore horizon (Ostwald, 1975). The Cu and Ni content of the mineral is generally low, but there is considerable variation in Ni + Cu + Co of lithiophorite grains even within small areas (Ostwald, 1980).

2. Kalgoorlie, Western Australia 31° S, 121° E). A specimen of cobalt-stained manganese oxide from the northern end of Golden Mile, Kalgoorlie, probably

equivalent to the asbolane described by Simpson (1948) from the same locality, proved to be lithiophorite containing 0.4–4.4% NiO and 2.8–8.6% CoO (Ostwald, 1977).

3. Rockhampton, Queensland (23° S, 150° 30' E). Specimens from the superficial zones of lateritic nickel deposits of the Rockhampton area (INAL Staff, 1975) proved to be composed of lithiophorite (containing up to 4% CoO and 2% Ni) in close association with pisolitic goethite, gibbsite, clay, and quartz.

4. Gympie area, Queensland (26° S, 152° 40' E). A specimen of manganese wad from this location proved to be composed of romanechite, braunite, and lithiophorite containing 4.2% CoO.

5. Pilbara Manganese Province, Western Australia (21° to 23° S, 120° 26' to 121° 23' E), (Blockley, 1976). Specimens of manganese oxide, including minor cobalt-stained wad, were obtained from the Ripon Hills area of the Pilbara Manganese Province. The oxides are essentially superficial enrichments of Proterozoic man-

ganiferous shales. Mineralogy is essentially cryptomelane, pyrolusite, braunite, and lithiophorite.

Results. All the samples examined contained areas of optically homogeneous lithiophorite, often filling cavities or as irregular replacement areas. All showed the characteristic bireflection and extreme anisotropism of the mineral. Samples of lithiophorite were removed from polished specimens by the use of a diamond-pointed scriber, and powders examined by X-ray diffraction. In all cases the specimens showed reasonable crystallinity, with lines as recorded in JCPDS card 16-364.

Electron probe microanalyses carried out on thirty grains from the five localities are listed in Table I. All results are fully ZAF corrected and have not been normalized. The Li content of the lithiophorite grains was measured by ion microprobe mass analysis (IMMA). These analyses show that the Mn content (given as MnO_2 because

TABLE I. Electron probe microanalyses of lithiophorite (Wt. %)

Area	MnO_2	Al_2O_3	SiO_2	Fe_2O_3	K_2O	MgO	NiO	CoO	CuO	ZnO	H_2O^{+*}
1	62.2	23.6	0.3	0.3	0.1	ND	ND	ND	ND	0.1	13.4
2	60.7	23.2	0.8	0.6	ND	ND	0.1	0.2	ND	0.2	14.2
3	54.8	19.6	11.2	1.1	0.1	ND	0.2	ND	ND	0.2	12.8
4	57.4	18.0	3.4	3.8	0.4	ND	0.2	ND	ND	0.6	16.2
5	58.1	17.6	ND	4.6	2.3	0.5	2.0	ND	ND	0.8	14.1
6	58.0	17.2	6.5	1.4	0.4	0.2	1.4	ND	ND	0.2	14.7
7	59.3	19.0	1.7	0.8	1.8	3.2	0.6	ND	ND	ND	13.6
8	55.8	15.7	0.4	7.7	1.2	1.6	ND	3.2	ND	0.2	14.2
9	59.1	24.0	1.6	ND	0.1	ND	ND	ND	ND	0.1	15.1
10	57.4	13.7	1.4	6.8	2.6	ND	2.5	1.0	ND	ND	14.6
11	59.6	23.0	0.2	0.8	0.3	1.3	ND	ND	ND	ND	14.8
12	58.6	14.3	ND	7.2	ND	0.4	0.3	3.8	0.1	ND	15.3
13	58.7	14.7	ND	6.3	4.2	ND	0.1	3.4	ND	ND	12.6
14	60.2	16.2	5.4	1.2	ND	0.1	0.2	2.5	ND	ND	14.2
15	55.8	12.4	3.2	9.6	ND	1.2	1.6	2.0	0.6	ND	13.6
16	59.3	19.4	0.4	4.7	0.2	1.7	ND	ND	ND	ND	14.3
17	60.2	15.3	ND	4.8	0.3	0.6	ND	4.0	ND	0.1	14.7
18	55.8	19.1	5.3	4.3	ND	1.2	0.2	0.6	ND	ND	13.5
19	56.7	21.2	ND	7.2	ND	ND	ND	0.3	ND	ND	14.6
20	60.4	22.0	1.5	0.8	ND	0.6	0.3	0.2	ND	ND	14.2
21	57.3	20.2	0.6	3.8	ND	2.4	0.1	ND	ND	ND	15.6
22	59.4	17.0	5.2	0.6	ND	0.6	0.1	2.0	ND	0.3	14.8
23**	56.5	22.5	4.3	3.2	ND	0.4	ND	0.3	ND	ND	12.6
24	60.0	12.9	2.4	8.7	ND	0.4	0.3	4.0	ND	ND	11.3
25	61.6	21.5	0.7	0.1	0.1	1.2	0.1	0.5	ND	ND	14.2
26	58.2	20.8	3.2	0.6	0.8	ND	ND	ND	ND	ND	16.4
27	59.3	20.6	1.2	4.8	1.9	ND	0.2	0.3	ND	0.1	11.6
28	58.3	16.5	4.7	3.9	1.3	ND	0.1	2.7	0.2	ND	12.3
29	57.3	14.2	4.3	4.5	0.6	ND	2.8	ND	0.6	ND	15.7
30	60.8	18.5	0.6	3.1	2.8	ND	ND	0.5	0.1	ND	13.6

Analyses 1–10, Groote Eylandt; 11–14 Kalgoorlie; 15–21 Rockhampton;
22–25 Gympie; 26–30 Pilbara.

N.D. = not detected by EMPA

* by difference

** contains 0.2% PbO.

EPMA cannot distinguish between valency states) is reasonably constant though Al_2O_3 is more variable. In general, the lower values of Al_2O_3 appear to correlate with the maximum levels of $NiO + CoO + ZnO$. Totals are fairly constant, indicating a structural water content of 12–15%.

The Li analyses show a range of values, from a maximum of 2.3% to a minimum of 0.1%. The higher values occur in Kalgoorlie lithiophorite. A possible explanation for this lies in the occurrence of a concentration of Li-containing minerals, including spodumene, petalite, and lepidolite in a pegmatite at Londonderry, south of Coolgardie, only thirty miles from the area where the lithiophorite was collected. In Li content the Australian examples lie well within the range from high Li (3.3%, Postmasberg; Villiers and Van Der Walt, 1945) to low Li (0.04%, Serra do Navio, Brazil; Valarelli, 1975).

Alumina levels range from 24.0 to 12.9%. The lower value is outside the compositional ranges of 24.75–18.3% of Valarelli (1975) and 23.84–15.50% of Frenzel, G. (1980). The variation of $NiO + CoO + CuO + ZnO$ with alumina is shown in fig. 1. This indicates that lithiophorite with near
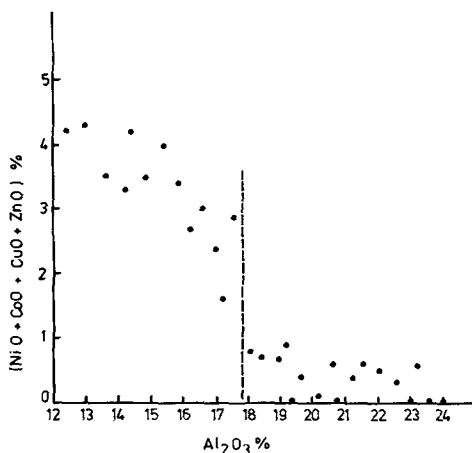

FIG. 1. Variation in $NiO + CoO + CuO + ZnO$ with Al_2O_3 in a collection of specimens of lithiophorite.

theoretical alumina level (20–24%) tends to be low in transition element* content, but that there appears, within the limits set by the number of analyses, to be an increase in transition element content with decrease in alumina. There is a steep increase in transition metal content below 18%.

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* The term 'transition element' is used as the elements commonly found in lithiophorite belong to the first transition series.

Al_2O_3, and on the basis of fig. 1 it is possible to classify the samples investigated into: (1) transition-metal poor lithiophorites, with about 24–18% Al_2O_3, and (2) transition-metal enriched lithiophorites, with Al_2O_3 ranging from 18 to 12%.

X-ray diffractograms of specimens from the two classes were essentially similar. Larsen (1970) commented that, in the Fort Payne lithiophorite, there was an apparent relationship between Co and Ni distribution and textural variations, with these elements being concentrated in crypto-crystalline rather than more coarsely crystalline material. A similar observation was made by Ostwald (1975). To follow this up in more detail, EPMA line scans were run (for Mn, Al, Co, Ni) across a number of micro-areas showing a range of crystallite sizes. While these studies, in general, confirmed the relation between crystallite size and metal content, this was not as interesting as the variations in Co which were observed in a single optically homogeneous area of lithiophorite from the Rockhampton district of Queensland.

The area examined appeared to be a recrystallized single crystal, with maximum dimension 0.2 mm. It showed no evidence of growth zoning, etc. An X-ray energy dispersive analysis indicates the presence of major Mn and Al and minor Co. EPMA line scans for these elements (fig. 2) showed that the Co was very unevenly distributed, with some areas containing practically no Co while others contained up to 4%. Cobalt-enriched areas contained less Al than cobalt-free areas. The EPMA line scans thus suggest that the lithiophorite crystal contains discrete volumes of cobalt-depleted and cobalt-enriched lithiophorite.

Discussion. These investigations have shown what appears to be two varieties of lithiophorite, with similar X-ray diffraction patterns, in some Australian deposits. These could be termed transition metal-poor and transition metal-enriched. This distribution is further validated by the observations of rapid changes in cobalt content in essentially optically homogeneous lithiophorite. In general the metal content appears to be related to the relative proportions of MnO_2 and Al_2O_3 in the structure.

Under these circumstances mineralogical thinking turns to the concepts of atomic substitution and diadochy, concepts which initially developed in silicate mineralogy. Frenzel, G. (1980) describes the elements Cu, Ni, Co, Fe, Li, etc., as diadochically present in lithiophorite. Larsen (1970) in his studies of the manganese oxides of the Fort Payne formation, considers that crystallization of manganese oxide gels resulted in a partial lattice site substitution of Co^{3+} for Mn^{3+} in the resulting lithiophorite. He was not able to offer any interpretation
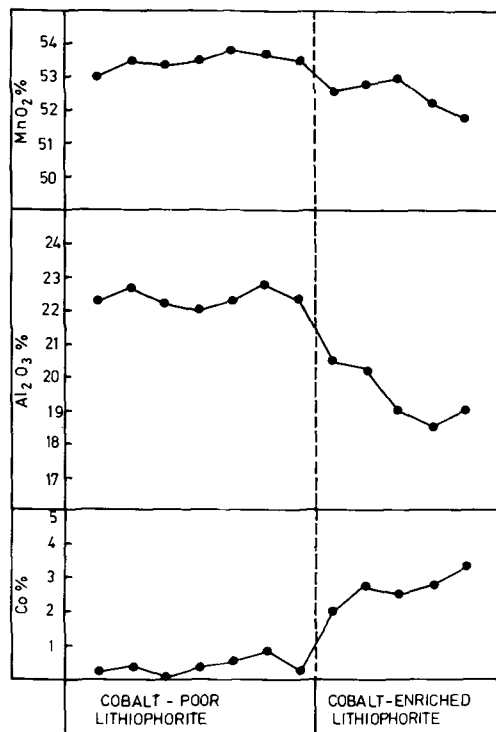
FIG. 2. EMPA line scans for Mn, Al, and Co in a specimen of single-crystal lithiophorite.

of the Cu and Ni of the mineral. McKenzie (1970) postulated that Co, Ni, and Cu atoms replaced Mn^{2+} in synthetic manganese oxides. The above-mentioned concepts of the diadochic replacement of Mn ions by Co ions do not appear to be in accord with the data in fig. 2, where a strong increase in Co is associated with a slight decrease in total Mn. Wagner et al. (1979) analysed forty-two samples of manganese oxides from Arkansas, USA, and deduced that the trace elements Co, Cu, and Ni were concentrated in lithiophorite because the replacement of Mn^{4+} (0.54 Å) by Al^{3+} (0.53 Å) requires the corresponding replacement of Li^+ (0.74 Å) by Co^{2+} (0.73 Å), Cu^{2+} (0.73 Å), and Ni (0.70 Å) for charge neutralization.

Cu and Ni are common components of marine manganese nodules, where they are considered to occur in isomorphous replacements in todorokite (Burns and Burns, 1977). Lithiophorite has not been detected in marine nodules. This fact—the concentration of Cu and Ni in marine todorokite and in terrestrial lithiophorite—was investigated by Giovanoli et al. (1973).

Their researches were primarily concerned with possible relationships between the 10 Å phase of marine nodules [≡ todorokite of Burns and Burns (1977) or buserite of Giovanoli et al. (1975)] and lithiophorite, which also shows a major 10 Å reflection. To do this, pure lithiophorite was synthesized and characterized by X-ray and electron diffraction. This indicated a monoclinic structure with $a_0 = 5.06$, $b_0 = 8.70$, $c_0 = 9.61$ Å, and $\beta = 100°$ 7'. When, however, attempts were made to crystallize a sodium or a zinc-substituted lithiophorite, this mineral was not formed, and phases such as cryptomelane, hollandite, and hetaerolite were produced. Giovanoli et al. (1973) deduced that the lithiophorite structure was essentially stoichiometric, and that lattice substitution by foreign ions could not occur. The line scans on the sample of Rockhampton lithiophorite (fig. 2) and the studies of Giovanoli et al. (1973) on synthetic lithiophorite thus raise the possibility that the Co, Ni, and Cu commonly detected in lithiophorite exist in some form other than as diadochic replacements. An alternative explanation is that they exist as discrete layers in a mixed-layer-lattice lithiophorite, analogous to the mixed-layer clay minerals. Evidence in favour of this comes from recent work by Chukhrov et al. (1982) on asbolanes from the Ural Mountains deposits.

The complex cobalt- and nickel-containing wads of these ores were first described by Ginzburg and Rukavishnikova (1951), and detailed studies on the Buryktal deposit were carried out by Nikitin (1960). The mineralogy has been interpreted by Ginzburg (1960), who gives a series of new names to these manganese oxides: nickelomelane, cobaltomelane, nickel-cobaltomelane, cryptonickelomelane, alumocobaltomelane, buryktalskite.

Fleischer and Faust (1963) considered that some of these were actually varieties of lithiophorite, though others might have been new minerals. Little further work was done in this matter until the recent studies of Chukhrov et al. (1982). These investigators decided to follow up the suggestion of Ginzburg and Rukavishnikova (1951) that there might be a definite mineral, asbolane, in the deposits. Using analytical-electron microscopy, selected area electron diffraction, and X-ray diffraction, they were able to isolate a platy mineral, a Mn, Ni, Co, Ca hydroxide, showing the following X-ray characteristics.

d spacing (Å)	Relative intensity	hkl
9.6	weak	001
4.82	strong	002
2.445	medium	100
1.7	very weak	104
1.419	very weak	110

The electron diffraction studies indicated that the mineral consisted of two sub-lattices. Sub-lattice I consists of Mn–O octahedra and bound water molecules, and sub-lattice II consists of Ni–Co octahedra, with bound water. X-ray diffraction showed only the reflections of the Mn–O sub-lattice I, suggesting to Chukhrov et al. that sub-lattice II occurs as irregular 'islands' of small extent which alternate with the manganese oxygen layers in the c lattice direction.

Such a structure is remarkably similar to that of lithiophorite, which Wadsley (1952) and Pauling and Kamb (1982) have shown to consist of alternating layers of Mn_3^{2+} $Mn_{18}^{4+}O_{42}$ and $Al_{14}Li_6$ $(OH)_{42}$. This structural similarity between pure lithiophorite and the layer-lattice mineral asbolane is further demonstrated by their practically similar X-ray diffraction patterns (both have major lines at 9.5–9.6, 4.7–4.8, 2.4, 1.7–1.8, and 1.4 Å). Moreover, the postulated six-sheeted unit of the lithiophorite structure (Pauling and Kamb, 1982) is quite close to the thickness of the asbolane structure ($9.34 \times 3 = 28.02$ Å) of Chukhrov et al. (1982).

Although Chukhrov et al. (1982) have noted the similarity between normal lithiophorite and asbolane, they apparently consider them different minerals. Interpretation of their ideas is made more difficult by their earlier statements (Chukhrov and Gorshkov, 1981) that lithiophorite from the Urals contained 8.5 % CoO and 3.0 % NiO, and that they had identified cobalt- and nickel-free asbolanes (without the islands of sub-lattice II) in metalliferous sediments of the Bauer depression and the Chilean Plate. These latter structures would be non-stoichiometric manganese dioxides and possibly new minerals.

The results discussed in this paper suggest that the transition elements in lithiophorite do not occur as simple diadochic replacements of Mn ions in the structure. Their presence is apparently related to the amounts of alumina in the mineral. In view of the fact that this alumina occurs as hydrargillite layers, in part lithium-replaced, which alternate with manganese oxide layers, some process by which this aluminous layer is replaced by transition elements must be envisaged. The writer suggests that this process is the partial topotactic replacement of a pure lithiophorite structure by an asbolane-type mineral. Both are layer lattices and have unit cells with very similar c dimensions. This

LITHIOPHORITE STRUCTURE
(PAULING AND KAMB, 1982)

ASBOLANE STRUCTURE
(CHUKHROV et. al , 1982)

$Mn_{0.14}^{2+}$ $Mn_{0.86}^{4+}$ O_2

Al_{14} Li_6 $(OH)_{42}$

$(Ni_{0.28}Co_{0.17})$ $Ca_{0.05}(OH)_{1.5}$

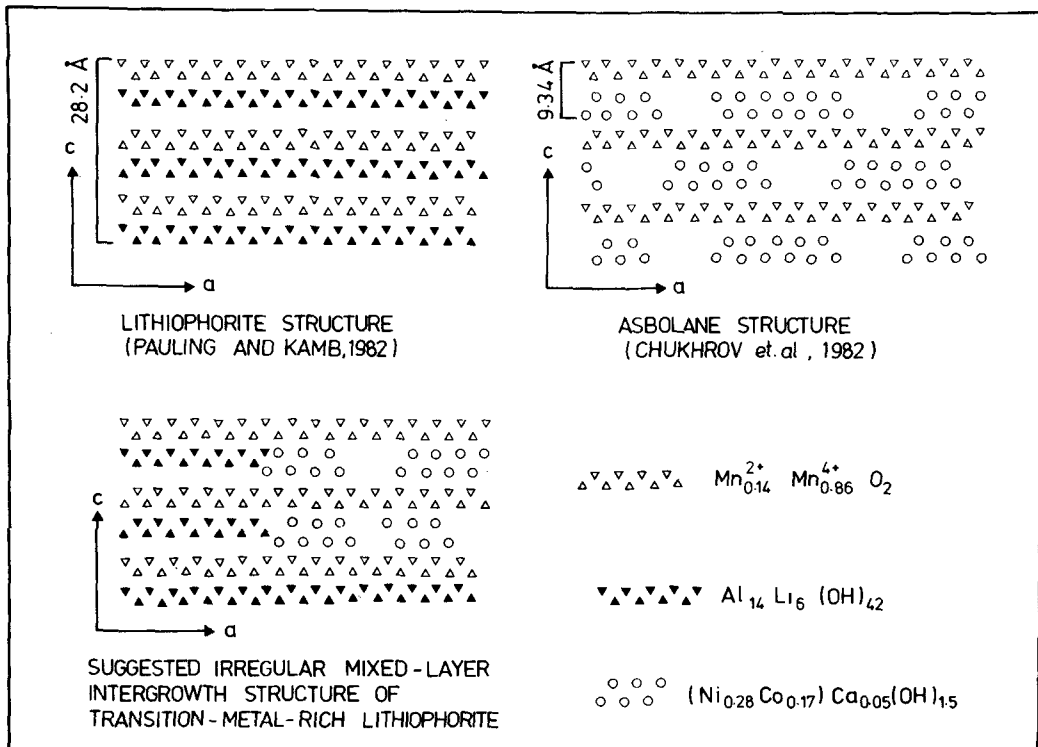SUGGESTED IRREGULAR MIXED-LAYER INTERGROWTH STRUCTURE OF TRANSITION-METAL-RICH LITHIOPHORITE

FIG. 3. Schematic diagram showing suggested structure of transition-metal-enriched lithiophorite.

concept is shown schematically, without balancing charges, in fig. 3. If this idea is correct the ordinary lithiophorite of the weathering zone of manganese-containing rocks and orebodies, which so commonly contains amounts of transition elements, is by no means a simple mineral. It is probably more correct to consider it a hybrid structure (Ubbelohde, 1966) or an intergrowth structure (Buseck and Cowley, 1983). Lithiophorite samples are currently being examined by high resolution transmission electron microscopy (HRTEM) in an attempt to validate the above suggestion, and to determine the reasons for the existence of the two varieties.

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