# LITHIOPHORITE FROM THE POSTMASBURG MANGANESE DEPOSITS

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With Chemical Analyses by C. F. J. van der Walt

## Introduction

In Dana's *System of Mineralogy* lithiophorite is described as a hydrated manganese ore containing 10–15% $Al_2O_3$, 1.2–1.4% $Li_2O$ and 12.6–15.4% $H_2O$. In the past it has generally been looked upon as a variety of "psilomelane" but in 1932 Ramsdell (1) found that it gives a distinctive *x*-ray photograph and is thus an independent mineral species. The formula has been given by Fleischer and Richmond (2) as possibly $Li_2(Mn^{II}, Co, Ni)_2Al_8Mn_{10}^{IV}O_{35} \cdot 14H_2O$. Up to the present no ore-microscopical or crystallographic data for the mineral have, as far as I know, been published.

Lithiophorite was first recognised in the Postmasburg ores in 1943. It was originally distinguished by means of chemical tests but after its ore-microscopical properties and etch reactions had been determined it could be readily identified by means of these properties. In the past I have found it either as very fine-grained material, or as small flakes, very sparingly disseminated through a sitaparite ore (see Fig. 1). Recently, however, a few specimens of coarsely crystalline lithiophorite were obtained from the farm Gloucester near Postmasburg. These are exceptionally well suited for study and some of the physical, ore-microscopical and chemical properties of the mineral have accordingly been determined. The results obtained are given in this paper.

The specimens are coarse-grained and black; as received they were partly coated with brown ferruginous clay which could be washed off. On fresh surfaces they present a glistening appearance due to the reflection of light from many cleavage planes and in part they are lined with crystals which project into vugs (see Fig. 2). The samples are composed predominantly of lithiophorite, the other minerals present being braunite, sitaparite, psilomelane, and a trace of hematite. It is believed that, in common with the Postmasburg manganese ores generally, they were deposited by solutions which were either wholly, or in part, of magmatic origin. The specimens are described more fully in a subsequent section.

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* Since I submitted this manuscript for publication it has come to my notice that Dr. J. W. Gruner identified lithiophorite in the Postmasburg manganese ores a few years ago. See *Am. Mineral.*, **28**, 174 (1943), also **28**, 615 (1943).

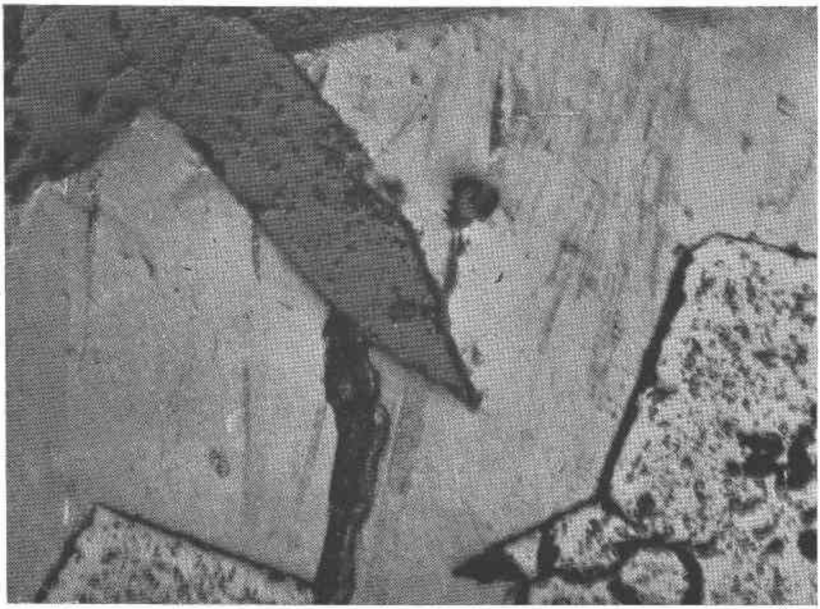

FIG. 1. Polished section showing lithiophorite with dark-coloured diaspore and sitaparite (mineral with square outlines). ×170.

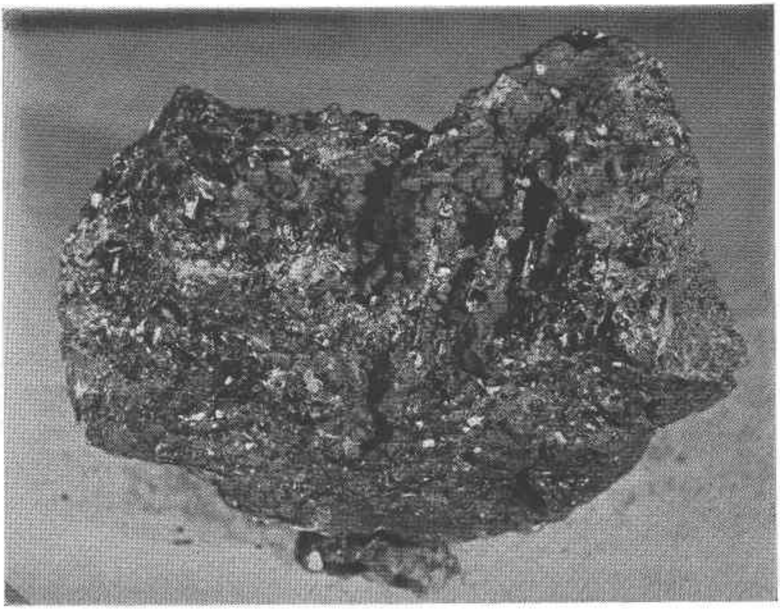

FIG. 2. Specimen of coarsely crystalline lithiophorite. Note crystals; and films of braunite encrusted with lithiophorite. About $\frac{2}{3}$ natural size.

## PHYSICAL PROPERTIES OF THE LITHIOPHORITE

The colour is iron black with a bluish tinge. Streak is greenish black. Specific gravity $=3.37$ ($\pm 0.02$). This value was obtained by immersing small grains of the mineral in Clerici's solution, diluting until neither floating nor sinking occurred and measuring the specific gravity of the liquid. Cleavage in one direction, micaceous. Laminae somewhat flexible and sectile. Hardness $=2\frac{1}{2}$ to 3. This varies with the crystallographic direction and is least on the cleavage face.

The crystal faces are usually curved and slightly corroded. They are thus unsuitable for goniometric measurement. On the cleavage surfaces the outlines of the crystals are hexagonal and rude measurements indicate that the angles approximate 60°. Such surfaces generally show striations, probably due to twinning, which divide the hexagons into six sectors. It is considered likely that the mineral is hexagonal or pseudo-hexagonal.

## ORE-MICROSCOPICAL PROPERTIES

The colour in polished section varies from light grey to dark brownish grey, the pleochroism being exceptionally strong. In the brightest direction the reflectivity is about equal to that of braunite, i.e. about 18%, while in the darkest direction it is probably less than half of this figure. The anisotropic effects are extreme and the polarisation colours light grey to dark brown and bluish grey. Sections parallel to the cleavage face have the highest reflectivity and show no pleochroism or anisotropism. Lithiophorite is relatively little affected by the etch reagents ordinarily employed to distinguish between the manganese oxides. HCl (conc.) has no effect and the action of $H_2O_2+H_2SO_4$ [equal parts of $H_2SO_4(1:1)$ and $H_2O_2$ (5%)], $SnCl_2$ (sat. soln. in conc. HCl) and HF (comml. conc.) are negative, or very feeble if the reagent is left on for one minute. On prolonging the time of the reaction, the effect of HF and $H_2O_2+H_2SO_4$ becomes more marked.

## CHEMISTRY

A chemical analysis of lithiophorite was carried out by Dr. C. F. J. van der Walt of the Division of Chemical Services. The sample analysed was prepared by selecting small, clean cleavage flakes and is considered to have been of excellent purity.

According to qualitative chemical tests, cobalt and nickel are either absent or present only in traces.

In calculating the formula of lithiophorite, $SiO_2$ and $Fe_2O_3$ have been neglected. The amount of the former constituent is very small and, as was concluded in the case of the analysis given in Table 2, the $Fe_2O_3$ probably represents admixed impurity.

Table 1. Analysis of Lithiophorite from Gloucester

| | % | Mol. rat. | At. rat. | | | Alternative At. ratios | | |
|---|---|---|---|---|---|---|---|---|
| MnO | 48.15 | 0.6787 | $Mn^{III}$ | 0.231 | 1.02 | $Mn^{II}$ | 0.116 | 1.02 |
| O | 9.01 | 0.5631 | $Mn^{IV}$ | 0.447 | 1.97 | $Mn^{IV}$ | 0.563 | 4.94 |
| $Al_2O_3$ | 23.84 | 0.2339 | Al | 0.468 | 2.06 | Al | 0.468 | 4.11 |
| $Fe_2O_3$ | 0.96 | 0.0060 | — | — | — | — | — | — |
| $Li_2O$ | 3.30 | 0.1104 | Li | 0.221 | 0.97 | Li | 0.221 | 1.94 |
| $H_2O+$ | 13.15 | 0.7298 | $H_2O$ | 0.730 | 3.22 | $H_2O$ | 0.730 | 6.40 |
| $H_2O-$ | 1.45 | — | — | — | — | — | — | — |
| $SiO_2$ | 0.30 | — | — | — | — | — | — | — |
| CaO | Tr. | — | — | — | — | — | — | — |
| $Na_2O$<br>$K_2O$ | Nil | — | — | — | — | — | — | — |
| | 100.16 | | | | | | | |

Analyst: C. F. J. van der Walt.

The analysis presents the difficulty that only the total amount of the available oxygen can be determined. There is no means of determining chemically the amount of manganese of any particular valence present. Two arrangements of the analysis are therefore possible, one in which the manganese is 3- and 4-valent, and the other in which it is 2- and 4-valent, viz:

$$Li\,Mn^{III}\,Mn_2^{IV}\,Al_2O_9\cdot 3H_2O$$
$$Li_2\,Mn^{II}\,Mn_5^{IV}\,Al_4O_{18}\cdot 6H_2O.$$

Below, the analysis of lithophorite from Bishop, Postmasburg, is given. This was made in 1943 on material described in a subsequent section.

Table 2. Analysis of Lithiophorite from Bishop

| | % | Mol. rat. | At. rat. | | | Alternative At. ratios | | |
|---|---|---|---|---|---|---|---|---|
| MnO | 44.9 | 0.6330 | $Mn^{III}$ | 0.253 | 1.20 | $Mn^{II}$ | 0.127 | 1.27 |
| O | 8.1 | 0.5063 | $Mn^{IV}$ | 0.380 | 1.81 | $Mn^{IV}$ | 0.506 | 5.06 |
| $Al_2O_3$ | 22.0 | 0.2158 | Al | 0.432 | 2.06 | Al | 0.432 | 4.32 |
| $Fe_2O_3$ | 10.5 | 0.0657 | $Fe^{III}$ | 0.131 | — | — | — | — |
| $Li_2O$ | 2.7 | 0.0904 | Li | 0.181 | 0.86 | Li | 0.181 | 1.81 |
| $H_2O+$ | 11.7 | 0.6494 | $H_2O$ | 0.649 | 3.09 | $H_2O$ | 0.649 | 6.49 |
| $SiO_2$ | 0.1 | | | | | | | |
| | 100.0 | | | | | | | |

Analyst: C. F. J. van der Walt.

If the $Fe_2O_3$ is considered as part of the lithiophorite molecule, the above analysis leads to the formula: $Li_2(Mn''', Fe''')_4Mn_4^{iv}Al_4O_{21} \cdot 7H_2O$, which differs considerably from that of the fairly pure material from Gloucester.

It is thus concluded that the $Fe_2O_3$ is probably present as an impurity. Disregarding the $Fe_2O_3$, the analysis gives the formula: $Li\,Mn^{III}Mn_2^{IV}Al_2O_9 \cdot 3H_2O$. This is the formula deduced for the Gloucester material, but the agreement with the analysis is less close.

## Description of the Specimens

As stated previously, the specimens are coarsely crystalline, the diameters of the individual grains of lithiophorite varying from a few millimetres to about a centimetre. In part they are rudely botryoidal and show protruding crystals. Braunite,partly altered to psilomelane, is found in the cores of the botryoidal masses and from a macroscopic examination it appears as if the lithiophorite was in large part deposited on the braunite in cavities. In a few of the cavities thin films of braunite (usually encrusted with lithiophorite) may be observed. These apparently originated as veins in some rock which was later dissolved, leaving behind the braunite. Subsequently lithiophorite was deposited on the films (see Fig. 2). Braunite predominates in one specimen and the lithiophorite forms lenticles and irregular patches in the ore.

The grain size of the braunite is much smaller than that of the lithiophorite (0.01–0.1 mm.). In polished section it can be seen that the boundaries between the two minerals are either irregular and fretted or the braunite is idiomorphic towards the lithiophorite. In part these boundaries are obscured by the development of psilomelane as an alteration product. The braunite often occurs as veinlets and if sitaparite is present it again veins the braunite. Hematite occurs very sparingly as small scattered grains chiefly in the sitaparite. The order of crystallisation of the main minerals comprising the specimens appears to be as follows:—

(1) Braunite, (2) sitaparite, (3) lithiophorite.

Part of the braunite however, like the psilomelane, may have been formed through the alteration of earlier minerals and this braunite would therefore be younger than the lithiophorite. Between the periods of deposition of the sitaparite and the lithiophorite there was evidently a period of solution.

The lithiophorite from Bishop, the analysis of which is given in Table 2, has a purplish-black colour and is extremely fine-grained (grain size for the most part is less than a hundredth of a millimetre). It occurs as layers, a few millimetres thick, in a laminated psilomelane-hematite ore. The sample submitted for analysis was judged to be fairly pure, the only impurity observed in polished section being a very small amount of hematite. The amount of this, however, could not be estimated.

## REFERENCES

1. Ramsdell, L. S., An $x$-ray study of psilomelane and wad: *Am. Mineral.*, **17,** 143–149 (1932).
2. Fleischer, M., and Richmond, W. E., The manganese oxide minerals: (A Preliminary Report) *Econ. Geol.*, **38,** 269–286 (1943).