SYNTHETIC LITHIOPHORITE : ELECTRON MICROSCOPY AND X-RAY DIFFRACTION

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I. INTRODUCTION

Considerable confusion has been dominating the classification of manganese-oxygen compounds until very recently. The first useful approach was that of de Wolff (8) and Laudy (26) which has initiated several investigations of ourselves (2, 11, 12, 13, 14, 27, 29). The relations between γ-MnO$_2$ (mineral: nsutite), ramsdellite MnO$_2$ (no Greek sign attributed), β-MnO$_2$ (mineral: pyrolusite or polianite), α-MnOOH (mineral: groutite), and γ-MnOOH (mineral: manganite) could thereby be cleared up. The basic structural principle in this group of mineral species are single or double chains of edge sharing octahedra, and intergrowth of these chains. The octahedrally coordinated Mn^{4+} ions may also be partly reduced to Mn^{3+} which gives an unlimited number of phases between, e.g., γ-MnO$_2$ and α-MnOOH.

There are three other groups of poorly crystallized manganese-oxygen compounds left which are distinctly different from the above mentioned group. One is the "δ-MnO$_2$" (mineral: birnessite) ; on closer inspection this turned out to be a more complicated compound of analytical composition Na$_1$Mn$_{14}$O$_{27}$.9H$_2$O, Mn$_7$O$_{13}$.5H$_2$O, and Mn$_7$O$_{12}$.6H$_2$O, depending on the oxidation state of the Mn and on whether or not there are Na$^+$ ions present in the lattice (15, 16, 17, 18, 19, 30). It has previously been named "7 Å manganite" (for bibliography see in references 17, 18 and 30) ; but this is somewhat misleading as there is the mineral species γ-MnOOH named manganite, of entirely different composition and structure. "δ-MnO$_2$" is misleading either, as the compounds of this group do not belong to the manganese dioxides at all and do not have the composition MnO$_2$. We have chosen the chemical names sodium manganese(II,III) man-

ganate(IV), manganese(III) manganate(IV), and manganese(II) manganate (IV), respectively *.

A second group has first been found in manganese nodules of the oceans by Buser and Grütter (3, 4, 6, 21, 22, 23). It has been synthesized eight years earlier by Feitknecht and Marti and has been named "10 Å manganite» (9, 28). To avoid, again, confusion with manganite (γ-MnOOH), we shall drop this unappropriate name and use the accepted mineral name buserite (after the late Professor W. Buser) for this group. We shall show in another article that the buserite group is a group of hydrates of the above mentioned manganates(IV), differing from these mainly by the layer separation.

A third group is the hollandite-cryptomelane group, to which has (incorrectly) been attributed the formula "α-MnO$_2$"; actually this is a group of non-stoichiometric inclusion compounds of the variable analytical composition $Me_{2-x}Mn_8O_{16}$ ($Me = K^+$, Ba^{2+}, Zn^{2+}, etc.).

While mainly concerned with the buserite group, our interest has been directed to the lithium aluminium manganese(II) manganate(IV) (mineral: lithiophorite), $LiAl_2Mn_3O_9.3H_2O$, of which the structure is known from single crystal X-ray data (31). This compound consists of a layer lattice with 10 Å layer separation (1). Since the X-ray powder pattern of the buserite group may also be explained as consisting of a layer lattice with 10 Å layer separation, our interest turned to the synthesis and variability of lithiophorite. The aim was to clarify the difference between the buserite group on the one hand and the hollandite-cryptomelane group on the other hand, and also to show whether there is a true or only a formal relationship between lithiophorite and the buserite group. In other words, the question should be answered: is buserite a group of microcrystalline and non-stoichiometric varieties of lithiophorite with Li^+ ions replaced by Na^+ and Al^{3+} by $Mn^{2+,3+}$ or not.

In order to answer this question, lithiophorite was synthesized and investigated in the first place, starting from different cation mixtures. Secondly, we tried to synthesize non-stoichiometric, cation-substituted lithiophorite. It seemed appropriate to us to use primarily the electron microscope, electron diffraction, and X-ray diffraction as tools.

II. EXPERIMENTAL

1. *Preparations*

In a *first series* of experiments 1 g of mixtures of γ-Al(OH)$_3$ "Baker's Analyzed" (gibbsite=hydrargillite), $Mn_7O_{13}.5H_2O$, and LiOH.H$_2$O "Merck" in varying proportions was enclosed in a folded gold foil (0,2 mm thick) and heated in an auto-

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* The IUPAC rules for nomenclature unfortunately do not give decisive indications. They however suggest that endings such as "-ite" should be dropped. For oxide hydroxides they recommend the ending "-ate" where applicable (zincate, aluminate); but otherwise such compounds should be written out as "oxide hydroxide". This would, in the present case, cause considerable confusion with the manganese (III) oxide hydroxides (MnOOH), and we have therefore chosen the above nomenclature.

Synthetic lithiophorite

clave with 200 ml H_2O for 48 h at 300 °C and approximately 90-130 atm. The product was thoroughly washed with deionized water * and dried at 50 °C. $Mn_7O_{13}.5H_2O$ was prepared according to reference (19).

The starting materials are listed in Table 1.

TABLE 1. — *Starting compositions for the synthesis of unsubstituted lithiophorite (series 1).*

Preparation No.	Molar ratio of cations			Remarks
	Mn	Al	Li	
1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.12, 1.13, 1.14, 1.15, 1.20, 1.21	30	20	10	Stoichiometric ratio
1.8	36	20	10	Mn excess 20 %
1.19	30	26	7	Al excess 30 %, Li deficiency 30 %
1.17	30	24	8	Al excess 20 %, Li deficiency 20 %
1.18	30	22	9	Al excess 10 %, Li deficiency 10 %
1.22	30	18	11	Al deficiency 10 %, Li excess 10 %
1.10, 1.11	27	20	10	Mn deficiency 10 %
1.9, 1.16	24	20	10	Mn deficiency 20 %

In a *second series* of experiments 1 g of a mixture of γ-Al(OH)$_3$ "Baker's Analyzed" (gibbsite=hydrargillite), $Mn_7O_{13}.5H_2O$, LiOH.H_2O "Merck", and NaOH p. a. "Merck" was treated in an autoclave in the manner mentioned above for 48 h at 300 °C and 90-130 atm with 200 ml H_2O. In some instances, γ-MnO$_2$ was used in place of $Mn_7O_{13}.5H_2O$. γ-MnO$_2$ was prepared as follows:

450 g (NH$_4$)$_2$S$_2$O$_8$ p. a. "Merck" were added in small portions to a solution of 200 g MnSO$_4$.H_2O p. a. "Merck" in 4 L H_2O at 97 °C.

The brownish black precipitate was washed anion-free with deionized water and dried at 60 °C for 190 h.

The starting materials are listed in Table 2.

In a *third series* of experiments 1 g of a mixture of γ-Al(OH)$_3$ "Baker's Analyzed" (gibbsite=hydrargillite), $Mn_7O_{13}.5H_2O$ (in some instances γ-MnO$_2$), LiOH.H_2O "Merck", and ε-Zn(OH)$_2$, in varying proportions was treated in an autoclave in the same manner for 48 h at 300 °C with 200 ml H_2O. The ε-Zn(OH)$_2$ was prepared as follows: 2260 ml 0,2 N Zn(NO$_3$)$_2$ solution were precipitated in a 3 L beaker with 100,0 ml concentrated NaOH solution (carbonate free) which were added in one go under heavy stirring. The gelatinous precipitation that

* Preparations No. 1.1 to 1.7 proved to have excess Li$^+$. The washing process was therefore considerably intensified from No. 1.8 onwards.

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TABLE 2. — *Starting compositions for Na-substituted lithiophorite (series 2)*

Preparation No.	Molar ratio of cations			
	Mn	Al	Li	Na
2.3, 2.19	30	20	8	2
2.20	30	20	7	3
2.4, 2.9	30	20	5	5
2.5, 2.18	30	20	3	7
2.6	30	20	2	8
2.21	30	20	1	9
2.8	30	20	0,4	9,6
2.22	30	20	0	10

forms at first redissolved under stirring. After 4-10 min a well sedimenting precipitate appeared. It was isolated on a glass frit, thoroughly washed with deionized water and dried at room temperature over KOH in a desiccator. It consists of monodisperse, crystalline ε-$Zn(OH)_2$ in the form of distorted bipyramids (20).

The metal ion ratios used for the starting materials are listed in Table 3.

TABLE 3. — *Starting compositions for Zn-substituted lithiophorite (series 3)*

Preparation No.	Molar ratio of cations			
	Mn	Al	Zn	Li
3.13	30	17	3	10
3.11	30	14	6	10
3.12	30	13	7	10
3.23	30	11	9	10
3.14	30	10	10	10
3.24	30	8	12	10
3.15	30	6	14	10
3.16	30	3	17	10
3.17	30	0	20	10

2. *Analytical*

Where products were pure with respect to X-ray diffraction, quantitative analyses were done with following procedures: Na and Li were determined by Atomic Absorption Analysis directly in a solution of 600 mg substance

in boiling conc. HCl (38 %) that was diluted to 1 L. — Al had to be separated from this solution by the acetate method (7) and was then determined gravimetrically. — In the filtrate of this procedure Mn could be titrated with EDTA at pH 10 after reduction with $NH_2OH.HCl$. — The valence of Mn was determined by a modified iodometric-EDTA method (10). The result is given as the "formal oxidation degree" ranging from 1 to 2: divalent Mn gives 1, trivalent Mn yields $\frac{3}{2}$, and tetravalent Mn gives 2. Mixed valence Mn compounds will yield values in between. The formal oxidation degree actually is the ratio:

$$\frac{\text{Total number of positive charges}}{\text{Twice total Mn ions}}$$

Zn was not determined quantitatively for reasons to be discussed in section IV.

3. *X-ray diffraction*

Starting materials as well as products were finely ground and prepared on a sample holder using a Scotch tape and Bedacryl I.C.I. They were X-rayed with $FeK_{1.2}$ radiation using a Guinier camera with focusing quartz monochromator. The exposure time was approximately 8 to 16 h (mostly 10 h). For precise d spacings an internal standard was used: KCl proved unsatisfactory because of too few reflections in the higher d range, while $KAl(SO_4)_2.12H_2O$ gives too many coincidences. After some trials TlCl was used but later replaced by $\alpha\text{-}SiO_2$.

4. *Electron microscopy*

For the investigation of our samples in a Hitachi HU-11 and a Siemens Elmiskop I microscope, specimens were prepared according to current techniques, mainly directly in suspension on a carbon substrate. Surface replicas were also used, with Cr shadowing at 45° incident angle. Selected area electron diffraction (using evaporated TlCl as reference) served to identify single crystals.

III. RESULTS

1. *Synthetic unsubstituted lithiophorite*

1.1. **X-ray diffraction and morpology**

The only pure products (pure with respect to X-ray diffraction and electron microscopic morphology) were those of stoichiometric starting composition, as shown by Pl. I, fig. *a*. A run with 20 % Mn excess happened to yield almost pure lithiophorite (No. 1.8), out was not reproducible. On the other hand, some preparations with identical stoichiometric starting

composition did not yield pure lithiophorite. Figures *b* and *c*, Pl. I, show electron micrographs of typical lithiophorite crystals.

Whenever the starting composition departed significantly from stoichiometry, additional phases turned up. Al excess led to the appearance of γ-AlOOH, whereas other contaminations could not be identified and were not traced any further. Synthetic Lithiophorite consists of plate shaped crystals, of about 500-2,000 Å thickness and of about 10,000 Å diameter.

1.2 Electron diffraction

Though most of the samples consisted of characteristically twinned crystals, thus making the evaluation tedious, 38 diffraction patterns of untwinned crystals could be photographed and evaluated. A typical example is shown in fig. *a*, Plate II. All diffractions, regardless of their history, gave *essentially identical spacings* and trigonal symmetry, at least within the limits of experimental accuracy.
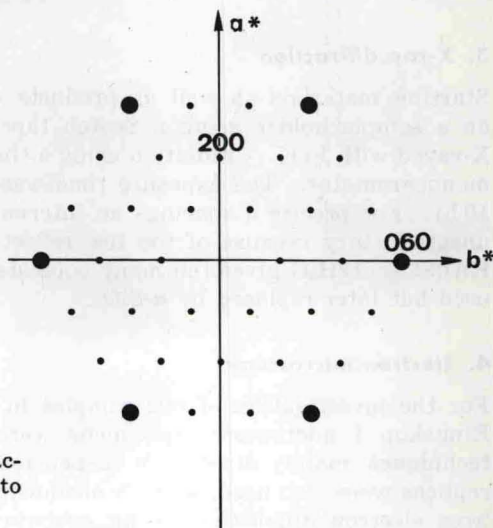

FIGURE 1. Indexed electron diffraction of lithiophorite, corresponding to fig. *a* on Pl. II.

Figure 1 represents an idealized version of such a pattern and illustrates the d spacings as listed in Table 4. The coordinates used in Figure 1 are orthogonal notwithstanding the trigonal (pseudo)-symmetry; the true unit cell actually is monoclinic as will be mentioned later.

TABLE 4. — *Spacings of electron diffractions of synthetic lithiophorite.*

Spacing	Measured	Literature (32)
d_{020}	4,3₄ Å	4,4₁ Å
d_{200}	2,5₃ Å	2,5₀ Å

1.3 Unit cell : ordering of Li^+ and Al^{3+}

The unit cell of lithiophorite was recalculated from the indexed powder pattern of a stoichiometric preparation (Table 5). Several reflection could not be indexed using Wadsley's value for b_0. As these reflections were consistent in all preparations and also consistent with additional reflections in the electron diffractions, they have to be considered as super-lattice reflections. Using b_0 three times that of Wadsley's resulted in a satisfactory indexing. On the other hand about 4 reflections (listed in

TABLE 5. — *X-ray powder pattern of synthetic stoichiometric lithiophorite.*

Reflection No.	Intensity (visual 1-10)	d (Å) Measured	d (Å) Calculated	hkl
1	8	9,52	9,46	001
2	1	8,11		
3	2	6,99	impurity	
4	1	6,13		
5	10	4,74	4,73	002
6	3	4,36	4,35	020
7	2	4,32	4,20	$\bar{1}11$
8	1	4,17	4,16	012
9	1	4,10	4,10	101
10	3	3,16	3,15	003
11	3	2,534	2,527	$\bar{2}01$
12	1	2,513	2,506 / 2,481 / 2,491	130 / $\bar{1}31$ / 200
13	2	2,437	2,427	$\bar{2}11$
14	2	2,418	2,425	$\bar{1}23$
15	9	2,377	2,395 / 2,368	$\bar{2}02$ / 131
16	2	2,307	2,306 / 2,305	$\bar{1}32$ / 201
17	2	2,165	2,160	$\bar{2}03$
18	2	2,120	2,133	132
19	1	2,059	2,058 / 2,052	$\bar{1}33$ / 202
20	1	1,973	impurity	
21	7	1,887	1,892 / 1,878	005 / 133
22	3	1,583	1,583	$\bar{1}35$

Table 5 as Nos. 2, 3, 4 and 20) cannot be lithiophorite reflections, as they vary in intensity or may even be absent in some preparations. We thus attribute these reflections to traces of admixtures; e.g. No. 4 obviously is the most intensive reflection (020) of γ-AlOOH, with d = 6,11 Å.

The unit cell satisfying the values of Table 5 is only slightly different from Wadsley's cell (31), except that the b_0 is three times that of Wadsley's. The powder data are consistent with the electron diffractions of single crystals. These, however, differ from single crystal X-ray data by superstructure reflections. Such additional reflections have also been observed on natural material with electron diffraction by Wilson et al. (32). Table 6 lists the dimensions of the unit cell.

TABLE 6. — *Unit cell dimensions of synthetic stoichiometric lithiophorite.*

	This paper	Wadsley (31)
a_0	5,06 Å ± 0,01	5,06 Å ± 0,01
b_0	8,70 Å ± 0,01	2,91 Å ± 0,01
c_0	9,61 Å ± 0,01	9,55 Å ± 0,01
β	100°7' ± 20'	100°30' ± 20'

While Wadsley (31) had to leave unanswered the question as to whether or not the Li^+ and Al^{3+} ions were ordered, our electron diffraction indicate unambiguously that the b_0 of Wadsley's unit cell must be multiplied by three; the Li^+ and Al^{3+} ions, thus, are ordered.

1.4 Analysis

The analytical results, listed in Table 7, confirm the formula

$$[Mn_3^{4+}Mn^{2+}O_{12}]^- \cdot [Al_4Li_2(OH)_{12}]^+$$
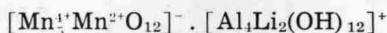
which is more appropriate than the often quoted $(Al,Li)MnO_2(OH)_2$ as it gives the correct ratio of cations and valence states and moreover indicates the two different layers stacked on each other (1).

The three products 1.4, 1.5 and 1.14 were analyzed; they were pure with respect to X-rays and electron microscopical investigation.

TABLE 7. — *Analysis of synthetic stoichiometric lithiophorite.*

Preparation No.	Molar ratio		
	Li	Mn	Al
1.4	14	30,3	20,0
1.5	12	29,7	21,0
1.14	8	30,3	20,2
Theor.	10,000	30,000	20,000

1.5 Valence of manganese

We initially have planned an attempt to determine the manganese valence (indicated by the formal oxidation degree) as a function of Mn excess or deficiency. As, however, any distinctive departure from stoichiometry produced phase mixtures, this would be meaningless. It was determined, though, for the pure sample 1.15 and also for preparation 1.9 with an initial Mn deficiency of 20 Mol-%. Since in No. 1.9 the additional phase was γ-AlOOH, all Mn was in the lithiophorite phase, and the valence ratio can thus be given (cf. Table 8).

The considerable excess of Li^+ in Nos. 1.4 and 1.5 must be put down as a consequence of unsufficient washing. No. 1.14 has been washed thoroughly while Nos. 1.4 and 1.5 have been washed distinctly less. The variations in Al^{3+} content reflect that already under stoichiometric starting conditions part of the initial $Al(OH)_3$ may segregate as γ-AlOOH and does then no longer take part in the reaction. X-ray patterns often show very faintly the (020) reflection of this phase. This will be yet more pronounced in series 2 and 3.

TABLE 8. — *Formal oxidation degree of Mn in synthetic lithiophorite.*

Preparation No.	Starting composition	By-product	Oxidation degree
1.15	Stoichiometric	—	1,81
1.9	20 % Mn deficiency	γ-AlOOH	1,86
Theoretical	Stoichiometric, calc.	—	1,83

The variations of the formal oxidation degree being within an expected statistical range of $\pm 0,03$, we conclude that the Mn valence is unaffected by variations of the initial material.

2. Na-substituted lithiophorite

2.1 X-ray diffraction and morphology

Figures *a* and *b* of Plate IV show the X-ray powder patterns of the preparations in this series. There appear some minor differences, originating in the Mn compound used as starting material. These were not followed further.

The overall result is that additional reflections turn up when Na^+ ions are introduced. Lithiophorite does not form at all, when Li^+ is entirely replaced by Na^+. Li^+ ions, hence, are *essential* constituents of that structure that can not be substituted.

Figure *b* of Plate II shows a fairly representative sample (preparation No. 2.9). A needle shaped phase turned up, e.g., in preparation No. 2.8 (Pl. II, figs. *c* and *d*). Its morphology and X-ray pattern have some resemblance to those of the cryptomelane-hollandite group.

Several preparations, e.g. No. 2.22. contained rafts of needles (Pl. III, figs. *e* and *f*).

Some of the more predominant X-ray lines which do not belong to lithiophorite could be attributed again to γ-AlOOH (mineral name: boehmite). In one case, i.e. preparation No. 2.5, we isolated the γ-AlOOH by dissolving the sample in hot HCl (38 %). The white residue was filtered off after dilution with H_2O, thoroughly washed with deionized water, dried, and investigated by X-rays and electron microscopy. Its powder pattern is shown in fig. a, Pl. III.

2.2 **Electron diffraction**

The lithiophorite platelets could be identified by selected area electron diffractions similar to those mentioned before. Typical spacing were 4,32 Å $(=d_{020})$ and 2,52 Å $(=d_{200})$ (cf. Table 4). The rafts of needles already mentioned (Pl. III, figs. e and f), which presumably take up the Na^+ ions, show a distinctive electron diffraction with characteristic streaking perpendicular to the needle axis (Pl. III, fig. d). The d spacings found were $2,82\pm0,07$ Å (direction of needle axis) and $2,29\pm0,04$ Å (perpendicular to needle axis) (average of 14 and 10 measurements, respectively). The first of these two spacings obviously represents an octahedral Mn-Mn distance. Both Mn^{3+} and Mn^{4+} compounds have a preference for distances in this range, as is shown in Table 9.

TABLE 9. — *Distances of octahedrally coordinated Mn^{4+} and Mn^{3+} ions.*

Phase	Mineral name	Distance	Spacing (Å)
$Ba_{2-x}Mn_8O_{16}$	Hollandite	$\dfrac{b_0}{2}$ (monoclinic) or c_0 (tetragonal)	2,88
$Mn_7O_{13}.5H_2O$	Birnessite	a_0 (pseudohexag.)	2,845
$ZnMn_3O_7.3H_2O$	Chalcophanite	a_0 (pseudohexag.)	2,84
$Na_4Mn_{14}O_{27}.9H_2O$	Na-Birnessite	$\dfrac{a_0}{3}$	2,847
γ-MnOOH	Manganite	$\dfrac{c_0}{2}$	2,85
Mn_5O_8	—	$\dfrac{b_0}{2}$	2,86
α-MnOOH	Groutite	c_0	2,852
γ-MnO$_2$	Nsutite	c_0	2,849
β-MnO$_2$	Pyrolusite	c_0	2,87

γ-AlOOH has usually been too thick to be penetrated by 100 keV electrons. Some selected area diffractions could, however, be obtained. An example is shown in fig. c, Pl. III. The spacings found were $a_0 = 3,71\pm0,03$ Å (Literature: 3,700 Å (24)) and $c_0 = 2,86\pm0,02$ Å (Literature: 2,868Å (24)). It is interesting to note in this connection, that the c_0 dimension of the

γ-AlOOH structure is also one of octahedrally coordinated Al^{3+} ions and is furthermore virtually identical with comparable Mn-Mn distances of trivalent and tetravalent Mn, regardless of the ion radius of Al^{3+} which differs distinctly from that of trivalent Mn.

2.3 Analyses

As we had some doubts as to the purity of the preparations although this did not show in all X-ray powder patterns (but in the electron microscope morphology), no analytical investigations could be done.

3. Zn-substituted synthetic lithiophorite

On Plate IV, fig. c, the powder patterns of series 3 are shown. The first preparation actually isolated was No. 3.11 which showed sharp reflections of ZnO that has not undergone any reaction. As from there, the $Mn^{3+,4+}$ ions were introduced in the form of the more reactive manganese(III) manganate(IV) $Mn_7O_{13}.5H_2O$. The replacement of ZnO by ε-Zn(OH)$_2$ was also tried but had no significant effect (cf. Nos. 3.23 and 3.24).

With rising amount of introduced Zn^{2+}, this ion tends to segregate as ZnO (Nos. 3.15-3.17 and 3.23-3.24). There are some further reflections which were identified in No. 3.17 by comparison with the JCPDS file (25) as well as with our own reference films. This is summarized in fig. d of Pl. IV. Apart from ZnO there is also $ZnMn_2O_4$ (mineral: hetaerolite). Some weak reflections remain unexplained. A major component of preparation No. 3.17 seems to be a member of the hollandite-cryptomelane group, presumably with Zn^{2+} ions in the channel of this inclusion compound. An approximate formula of that phase would be $Zn_{2-x}Mn_8O_{16}$. Lithiophorite could not be found at all, and electron micrographs are therefore not shown, for the sake of brevity. Electron diffractions and chemical analyses were not conclusive either and are also omitted. It was, in particular, impossible to determine accurately the limit of Zn^{2+} ions that can be introduced into the lattice, as there appeared phase mixtures in the mentioned erratic manner.

IV. DISCUSSION

All results give firm evidence that the lithiophorite structure can not substitute its lattice constituents by substantial amounts of Na^+ or other ions. Nor is the composition of lithiophorite itself widely variable. Zn^{2+} ions can apparently be accommodated up to some percent. We would name this "doping" rather than "substitution". Quite obviously any amount of Na^+ ions worthwile mentioning gives rise to the formation of another phase, or other phases, than lithiophorite. Likewise any substantial amounts of Zn^{2+} ions favour the formation of $Zn_{2-x}Mn_8O_{16}$ on the one hand and the spinel lattice $ZnMn_2O_4$ on the other hand. Both are variable in considerable range and are much more likely to accommodate non-stoichiometric amounts of any ions. ZnO may be left if the starting mixture has

not been intimately mixed, or when the reaction allowed segregation. As opposed to the spinel lattice or the cryptomelane-hollandite lattice, the lithiophorite lattice basically exists only under conditions of stoichiometry.

This answers our initial question. Lithiophorite may incorporate foreign ions, but there is *no connection at all* to the buserite group. The latter can also incorporate various cations as will be shown in another article, but the range of variability is much wider and thus forms a group of its own. It has only some *formal structural similarities* to the lithiophorite lattice, namely the Mn-Mn distance within the plane of the platelets, and the 10 Å reflection and its higher orders which may be attributed to a layer separation of a hypothetical layer lattice. Our results thus open the path to an investigation of the buserite group amongst the manganates(IV), of which a full account will be given in another article.

Acknowledgements

SUMMARY

In the course of investigations on Mn compounds, authors synthesize $LiAl_2Mn_3O_9.3H_2O$ (lithiophorite). Preparations starting from stoichiometric composition as well as excess or deficiency of Li, Al, or Mn were synthesized. Results show that lithiophorite cannot be varied considerably in composition. The unit cell determined was monoclinic with $a_o = 5.06$ A, $b_o = 8.70$ A, $c_o = 9.61$ A, $\beta = 100°7'$. b_0 is three times that of Wadsley's. Analyses are consistent with the structural formula $[Mn^{4+}Mn^{2+}O_{12}]^-.[Al_4Li_2(OH)_{12}]^+$ indicating the composition of the two layers stacked on each other. Small amounts of Zn^{2+} can be incorporated into the lattice of lithiophorite, but no Na^+. The conclusion is that lithiophorite has a fairly rigid lattice and that it differs fundamentally from the buserite group. The only similarities of buserite are the basal reflection at 10 A and its higher orders, and the Mn-Mn distance within the platelet plane.

RÉSUMÉ

Dans le cadre d'une série de travaux sur les oxydes et oxydehydroxydes du manganèse, les auteurs essayent de synthétiser $LiAl_2Mn_3O_9.3H_2O$ (lithiophorite). La synthèse de la lithiophorite stoechiométrique et du même composé avec excès ou déficit de Li, Al ou Mn a montré que cette phase n'est que très modestement variable. Sa maille élémentaire est monoclinique et a les caractéristiques suivantes : $a_o = 5.06$ A, $b_o = 8.70$ A, $c_o = 9.61$ A, $\beta = 100°7'$. Le b_o est trois fois plus grand que celui de la maille de Wadsley. Les analyses donnent la formule $[Mn^{4+}Mn^{2+}O_{12}]^-.[Al_4Li_2(OH)_{12}]^+$ qui correspond plus précisément aux deux couches séparées du composé entercalaire. Zn^{2+} peut être introduit en faible quan-

tité dans le réseau de la lithiophorite, mais la substitution des ions Li^+ par des ions Na^+ est impossible.

On peut conclure que la composition de la phase lithiophorite est très peu variable et que cette phase diffère donc de manière fondamentale du groupe de la buserite. Les seules similitudes de la buserite sont : la réflexion basale à 10 A ainsi que celle du deuxième et troisième ordre, et la distance Mn-Mn dans le plan des cristaux lamellaires.

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Plate I

Fig. a. — X-ray powder patterns of lithiophorite preparations of **series 1**. The patterns are numbered according to Table 1.

Fig. b. — Synthetic lithiophoric. Direct preparation; ×25,000.

Fig. c. — Synthetic lithiophorite. Carbon replica, Cr shadowed; ×25,000.

Synthetic lithiophorite