

An X-ray determinative method for the divalent cation ratio in the triphylite–lithiophilite series

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ABSTRACT. The powder diffractograms of twenty wet chemically analysed samples in the isomorphous triphylite–lithiophilite series and five synthesized members with $Fe/(Fe + Mn) = 1, 0.75, 0.50, 0.25,$ and 0.0 , were recorded. Their unit cell dimensions were accurately refined in order to find a reliable method for semi-quantitative determination of the divalent cation content of these minerals. A multivariate best fit analysis based on Kummell's procedure shows the marked influence of Fe^{2+} and Mg^{2+} on the cell dimensions, as well as that of small amounts of Fe^{3+} substituting for Mn^{2+} , following $LiMn^{2+} \rightarrow \square Fe^{3+}$. The best representation of the correlation between chemical composition and cell parameters is given by the equations:

$$\begin{aligned} a &= 6.1041 - 0.0245 Fe_{tot} - 0.049 Mg^{2+} \\ b &= 10.4511 - 0.0288 Fe_{tot} - 0.082 Mg^{2+} \\ c &= 4.7400 - 0.0130 (Fe^{2+} + Mg^{2+}) - 0.025 Fe^{3+}. \end{aligned}$$

No evidence of non-linearity has been found for the variation of the three cell dimensions with the chemical composition. Assuming the absence of appreciable amounts of Mg^{2+} , the following set of equations is proposed: $Fe_{tot} = 41(6.104 - a)$; $Fe_{tot} = 35(10.451 - b)$; $Fe_{tot} = 77(4.740 - c)$ in which the c dimension gives a relatively poor estimate.

Two sets of determinative graphs were constructed, one based on the cell parameter variation, and the other on the 311, 222, and 142 reflection angular positions, v , the total iron content of these minerals. These two methods, whose reliability is examined, can be used for determination of the divalent cation content, provided the samples contain less than about 0.5 wt. % Na_2O , 0.5 wt. % CaO , and 3 wt. % Fe_2O_3 , and are homogeneous.

In the pegmatites of Varuträsk, Sweden (Quensel, 1957), Viitaniemi, Finland (Volborth, 1954), and Buranga, Rwanda (Fransolet, 1975) several generations of $Li(Fe,Mn)PO_4$ minerals have been distinguished by chemical determination of their Fe/Mn ratios. Lahti (1981) established a few dis-

tinctions among the $Li(Fe,Mn)PO_4$ compounds from the pegmatites of the Eräjärvi area, Finland, by determining this ratio. However, from a general point of view, there is a lack of information about the Fe/Mn ratio in the $Li(Fe,Mn)PO_4$ mother-phases, whereas the mineralogical descriptions of the associated phosphate minerals in a pegmatite are frequently well detailed, especially in terms of their alteration or weathering products.

This fact is unfortunate because triphylite $Li(Fe,Mn)PO_4$ and lithiophilite $Li(Mn,Fe)PO_4$ play a critical role in the genetic and geochemical processes in the pegmatites. Considered as polymorphic minerals by Fersman (1931), they are particularly suitable for the investigation of the Fe and Mn behaviour during the pegmatite evolution as suggested by Ginzbourg (1960) who has claimed to use, among other methods, the Fe/Mn ratio as an indicator of the course of mineral development.

In the isomorphous triphylite–lithiophilite series the variation of the physical properties *vs.* the substitution $Mn^{2+} \rightleftharpoons Fe^{2+}$ has been little studied. Chapman (1943) modified Winchell's first (1933) diagram for the optical properties, showing clearly that an increase of the Fe^{2+} content in $Li(Fe,Mn)PO_4$ minerals involves an increase of the refractive indices, a change of the $2V$ and of the optical orientation. Chapman mentions the role of Mg in this correlation but without specifying it. In the work of Winchell and Winchell (1951) the correlation diagram of Chapman (1943) is simply republished.

On the basis of the crystallographic properties for nine samples of the $Li(Fe,Mn)PO_4$ series, Fransolet (1975) suggested, on the one hand, a variation of the a and b parameters with the atomic content of the $M(2)$ site and, on the other hand, a

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correlation between the d 220 and d 160 values and the Fe/Mn ratios.

By analogy with the correlations established for the isostructural group of the olivines *sensu stricto* (Schwab and Kustner, 1977; Rickel and Weiss, 1978) and pursuing the research of Fransolet (1975), the aim of this work is to propose a physical method for the semi-quantitative determination of the Fe/Mn ratio, in investigating the variation of the cell parameters with the chemical composition of natural members of the triphylite-lithiophilite series.

Analytical methods

Selected specimens. Twenty specimens collected by the first author or received from various collections have been selected for this work. Seven specimens of the list given in Table I were previously analysed; the X-ray measurements have been made on the whole series of specimens.

Chemical composition. The complete wet chemical analyses of thirteen specimens have been carried out on 0.3 g of material carefully purified under the binocular microscope, avoiding contamination by hureaulite, barbosalite, and tavo-

rite, which are frequent alteration products of the Li(Fe,Mn)PO₄ minerals. The X-ray diffraction helped to confirm the absence of these impurities in the purified specimens. Atomic absorption spectrophotometry was used to determine Li, Na, K, Mn, Mg, and Ca. Total Fe and P₂O₅ were colorimetrically dosed. Ferrous iron was determined by Wilson's (1960) method. The results are set out in Table II, in which the numbers of cations are calculated on the basis of 16 oxygens per unit cell.

Synthetic compounds. The cell dimensions of LiFePO₄ and LiMnPO₄, as pure end members, have been previously determined (Geller and Durand, 1960; Pâques-Ledent, 1972) but the measurement techniques are obviously different from those used for this research (see below). In order to apply the same X-ray method for the cell parameter refinement of all the natural and artificial products, five compounds have been synthesized: the end members LiFePO₄ and LiMnPO₄, as well as three intermediate compounds in which Fe/(Fe + Mn) = 0.75, 0.50, and 0.25.

LiFePO₄ was obtained from a mixture FeC₂O₄·2H₂O + ½Li₂CO₃ + (NH₄)₂HPO₄, progressively heated up to 800°C in a nitrogen stream as suggested by Pâques-Ledent (1972). The synthesis of LiMnPO₄ was conducted following the indirect procedure described by Thilo (1941). By reheating at 800°C in a nitrogen stream, suitable mixtures of the end members gave the three intermediate phases (see A, B, and C in Table II).

Measurement of the cell dimensions. Each natural or synthesized sample was run twice on a diffractometer equipped with a monochromator (Fe-K α , scanning speed ¼°2 θ /min and chart driving speed 5 mm/min.). For the second run the powder was remounted with an admixture of Pb(NO₃)₂ as internal standard. The amount of material used was 20–30 mg, taken from the sample purified for the wet chemical analysis. All peaks were measured as close to the top as was reasonable and 2 θ values were then corrected using the calculated Fe-K α ₁ values for Pb(NO₃)₂ (a = 7.8568 Å, JCPDS card 6-0151).

The least-squares refinement of the cell dimensions was made employing the Fortran program of Cox (1967) with an input of twenty-two uniquely indexed peaks following the structural data published by Geller and Durand (1960). The d (240) value corresponding to a very weak peak, not visible on every diffraction powder pattern, did not serve for calculation, nor did the doublets d (112) (022) and d (321) (042), occurring at around 54°2 θ and 67°2 θ respectively. The calculated cell dimensions are given in Table II. The mostly very small computer-calculated standard errors of the para-

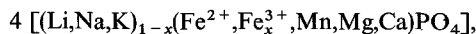
Table I. List of specimens

P1	: Mg-rich triphylite, Angarf-Sud, Zenaga Plain, Morocco (Fransolet, 1974).
P23	: Kobokobo, Kivu, Zaïre (Fransolet, 1975); R.G.M. 6233, Musée royal d'Afrique centrale, Tervuren.
P24	: Mangualde, Portugal (Fransolet, 1975); specimen MP-19 donated by J. Mantiène.
P26	: Buranga, Rwanda (Fransolet, 1980); Applied Geology Lab., Coll. 1371.
P27	: Buranga, Rwanda (Fransolet, 1975); Applied Geology Lab., Coll. 1384
P54	: Nyiramuganza (Rongi II), Rwanda; specimen NM-9.
P62	: ditto; specimen NM-3.
P91	: Pénitence, Arize Massif, Ariège, France (Fontan <i>et al.</i> , 1970); donated by F. Fontan.
P92	: Palermo Not, North Groton, New Hampshire, U.S.A.; donated by P. Keiler.
P94	: Townsite, Black Hills, South Dakota, U.S.A.; donated by P.B. Moore.
P95	: Hagendorf-Sud, Bavaria, Germany.
P96	: Buck Claim, Bernik Lake, Manitoba, Canada; specimen BCNW.
P97	: Dan Patch, near Keystone, South Dakota, U.S.A.; specimen DP-11.
P98	: Tanco, Bernic Lake, Manitoba, Canada; specimen TRT-B, zone 5.
P99	: Tanco, Bernic Lake, Manitoba, Canada; specimen TRT-A, zone 4. P96, P97, P98 and P99: donated by P. Cerny.
P100	: Serra Branca, Paraíba, Brazil.
P101	: Branchville, Connecticut, U.S.A.; Institut of Mineralogy, Univ. Liège, Coll. 15264.
P102	: Rwanza Mine, Kabira, Uganda.
P103	: Kitokye, Uganda.
P105	: Nyakishozus Mine, Kabira, Uganda. P102, P103 and P105: donated by O. Von Knorring.

meters (Table II), the number of indexed peaks for the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ minerals, and the calibration of six $\text{Pb}(\text{NO}_3)_2$ peaks distributed throughout the whole pattern lead to relatively high precision and reliability.

Discussion and interpretation of the results

In the isomorphous triphylite-lithiophilite series, Li lies on the $M(1)$ octahedral site of the olivine-type structure and the divalent transition metal cations Fe-Mn reside in $M(2)$ (Geller and Durand, 1960; Finger and Rapp, 1970). For the determination of the structural formulae, Fe^{3+} , Mg^{2+} , and Ca^{2+} are also considered to occupy the $M(2)$ site, whereas the small amounts of Na^+ are located on $M(1)$ as deduced from the conclusions of Moore (1972) who solved the structure of natrophilite NaMnPO_4 . Following these considerations and if we assume a unit cell content of



the analyses calculated to 16 oxygen should give 4 PO_4^{3-} and $4(\text{Fe}_{\text{tot}} + \text{Mn} + \text{Mg} + \text{Ca})$. In fact, these figures (Tables II) are quite closely reproduced; the biggest departures are P105 with 4.034 PO_4^{3-} , and P23 with 4.150 for the cations on the $M(2)$ site.

Upon receiving our original manuscript in which the statistical analysis was carried out by the conventional regression technique, Dr. M. H. Hey suggested use of the procedure he developed (Hey, 1969) for obtaining best-fits for multivariate correlations. The procedure is summarized in the Appendix, and we can conclude that the best currently available representation of the relation between chemical composition and cell dimensions for the triphylite-lithiophilite series is given by equations:

$$a = 6.1041 - 0.0245 (0.0023) \text{Fe}_{\text{tot}} - 0.049 (0.016) \text{Mg}^{2+} \quad (1)$$

$$b = 10.4511 - 0.0288 (0.0040) \text{Fe}_{\text{tot}} - 0.082 (0.029) \text{Mg}^{2+} \quad (2)$$

$$c = 4.7400 - 0.0130 (0.0026) (\text{Fe}^{2+} + \text{Mg}) - 0.025 (0.030) \text{Fe}^{3+} \quad (3)$$

The figures in parentheses are, in each case, the standard errors (or standard deviations) of the coefficients.

The negative influence of Fe^{3+} on c must be pointed out but cannot receive a satisfactory explanation. When ferrisicklerites are considered, in which the oxydation process of Fe^{2+} is virtually complete, as well as the subsequent leaching of Li^+ , Fransolet (1975) and Fontan *et al.* (1976) have observed a shrinkage of the a and b cell parameters, but an increase of c . As the ferric iron contents are

generally low in the chemical analyses (Table II), except for sample P62 which is free of impurities and in which the 1.59% Fe_2O_3 is likely to be due to a low oxidation phenomenon, it seems justified to suggest that more than 3 wt. % Fe_2O_3 actually present in the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ cell could alter for the worse the good agreement of correlation here observed.

Since the equations above are best-fit lines, following the method of C. H. Kummell (Hey, 1969), and not regressions, they are equally valid for assessing the composition given the physical data, so we can properly write, assuming absence of appreciable amounts of Mg^{2+} :

$$\text{Fe}_{\text{tot}} = 41(6.104 - a) \quad (4)$$

(standard error of the coefficient, 4)

$$\text{Fe}_{\text{tot}} = 35(10.451 - b) \quad (5)$$

(standard error of the coefficient, 5)

$$\text{Fe}_{\text{tot}} = 77(4.740 - c) \quad (6)$$

(standard error of the coefficient, 20)

Obviously, the c dimension gives a relatively poor estimate, though useful as a check. We may reasonably accept an accuracy of about 0.025 in the mean of the total iron content derived from a and from b assuming MgO is less than 0.5 wt. %. If MgO is more than 0.5 wt. % the accuracy of the Fe estimate would fall off rather rapidly.

Reliability of the method

Complete and accurate on both the chemical and the crystallographic properties for the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ minerals are relatively rare in the literature. In order to test the reliability of the semi-quantitative method suggested here, three published results have been selected: two cases with no Mg reported in the analysis, and one case of a Mg-bearing triphylite.

Finger and Rapp (1970) have refined the crystal structure of the triphylite from Dan Patch Mine, Keystone, South Dakota, with 3.04 Fe^{2+} in the cell, chemically determined. Using their accurate cell measurements on a single crystal, the values for the Fe content derived from the three relations (4) (5) (6) are 3.10, 3.24, and 2.84: the mean value 3.06 (0.20) is in very good agreement.

The virtually pure lithiophilite from the Foote Mine, Kings Mountain, North Carolina, is plotted on the graph (fig. 1) using the data obtained by Thomssen and Anthony (1977); the a and b cell parameters are notably low. This is a puzzling case. These authors were not able to determine Li and if we take Li_2O by difference from 100% in their two analyses, we get Li_2O 7.3 and 8.8%, distinctly low for LiMnPO_4 . This, combined with the striking sherry colour, unusual for lithiophilite, suggests

Table 11. Chemical Compositions and Crystallographical Properties

	LiFePO ₄	P 1*	P 92	P 91	A	P 97	P 95	P 23*	P 103	P 102
P ₂ O ₅	44.99	45.62	45.01	45.50	45.05	45.46	45.29	44.45	45.11	45.20
FeO	45.54	35.42	33.78	32.22	34.21	33.05	32.13	32.19	29.23	25.46
Fe ₂ O ₃	-	0.62	n.d.	n.d.	-	n.d.	n.d.	0.40	n.d.	0.29
MnO	-	4.64	9.67	10.15	11.26	11.10	13.11	13.36	15.94	19.32
MgO	-	3.71	1.65	1.69	-	0.39	0.07	0.28	0.14	0.29
CaO	-	0.12	0.02	0.34	-	0.05	0.01	0.27	0.07	0.04
Li ₂ O	9.47	9.41	9.24	9.14	9.48	9.42	9.33	8.85	9.27	8.87
K ₂ O	-	-	0.01	0.01	-	n.d.	n.d.	-	n.d.	n.d.
Na ₂ O	-	0.23	0.03	0.03	-	0.02	0.02	0.05	0.02	0.05
H ₂ O	-	0.31	n.d.	n.d.	-	-	-	0.00	-	-
insol.	-	-	-	0.55	-	-	-	0.08	-	-
total	100.00	100.08	99.41	99.58	100.00	99.49	99.96	99.93	99.74	99.52
P ⁵⁺	4.000	3.971	3.990	4.025	4.000	4.029	4.017	3.979	4.010	4.028
Fe ²⁺	4.000	3.046	2.958	2.815	3.000	2.893	2.815	2.847	2.567	2.241
Fe ³⁺	-	0.048	-	-	-	-	-	0.032	-	0.023
Mn ²⁺	-	0.404	0.857	0.898	1.000	0.984	1.163	1.196	1.417	1.722
Mg ²⁺	-	0.569	0.258	0.263	-	0.061	0.011	0.044	0.022	0.045
Ca ²⁺	-	0.013	0.002	0.038	-	0.006	0.001	0.031	0.008	0.005
	4.000	4.080	4.075	4.073	4.000	3.944	3.990	4.150	4.014	4.036
Li ⁺	4.000	3.892	3.892	3.841	4.000	3.966	3.931	3.764	3.915	3.755
K ⁺	-	-	0.001	0.001	-	-	-	-	-	-
Na ⁺	-	0.046	0.006	0.006	-	0.004	0.004	0.010	0.004	0.010
	4.000	3.938	3.899	3.848	4.000	3.970	3.935	3.774	3.919	3.765
x	1.000	0.899	0.790	0.774	0.750	0.750	0.708	0.707	0.646	0.570
\bar{a} (Å)	6.006(1)	6.002(2)	6.022(2)	6.023(2)	6.029(2)	6.029(2)	6.035(2)	6.034(2)	6.040(2)	6.044(2)
\bar{b} (Å)	10.332(2)	10.316(3)	10.349(3)	10.350(2)	10.361(2)	10.362(3)	10.370(3)	10.369(3)	10.377(3)	10.382(3)
\bar{c} (Å)	4.689(1)	4.695(2)	4.703(1)	4.704(1)	4.705(1)	4.707(1)	4.708(2)	4.707(1)	4.708(1)	4.713(1)
\bar{V} (Å ³)	290.97(17)	290.70(29)	293.10(24)	293.24(21)	293.90(22)	294.00(25)	294.64(30)	294.50(24)	295.08(25)	295.74(24)
2 θ 311	64.64	64.54	64.37	64.38	64.25	64.28	64.20	64.26	64.18	64.08
2 θ 222	67.65	67.56	67.39	67.38	67.34	67.33	67.27	67.30	67.25	67.17
2 θ 142	70.95	70.90	70.76	70.75	70.70	70.68	70.66	70.65	70.61	70.55

	P 100	P 94	P 24*	B	P 96	P 62*	P 54*	P 105	P 27*	P 26*
P ₂ O ₅	45.00	43.91	44.60	45.12	44.64	45.30	45.46	45.19	43.87	44.33
FeO	24.84	23.05	22.87	22.84	19.82	20.18	19.55	19.34	16.80	14.94
Fe ₂ O ₃	n.d.	n.d.	0.49	-	n.d.	1.59	0.64	n.d.	0.80	-
MnO	20.40	19.75	21.96	22.55	22.62	23.32	24.53	25.62	27.90	30.74
MgO	0.01	0.30	0.02	-	0.84	0.32	0.23	0.15	0.08	0.06
CaO	0.03	0.08	0.07	-	0.43	0.05	0.03	0.02	0.07	0.10
Li ₂ O	9.37	9.00	9.22	9.49	9.09	9.10	9.45	8.92	8.66	9.00
K ₂ O	n.d.	0.01	-	-	n.d.	n.d.	0.01	0.01	-	-
Na ₂ O	0.04	0.04	0.05	-	0.03	0.14	0.03	0.05	0.05	0.04
H ₂ O	-	-	-	-	-	-	-	-	0.91	0.14
insol.	-	3.72	0.40	-	-	-	-	-	0.72	0.63
total	99.69	99.86	99.68	100.00	97.47	100.00	99.93	99.30	99.86	99.98
P ⁵⁺	4.004	4.029	3.991	4.000	4.025	4.004	4.012	4.034	3.986	3.985
Fe ²⁺	2.184	2.089	2.022	2.000	1.765	1.762	1.704	1.705	1.508	1.327
Fe ³⁺	-	-	0.039	-	0.123	0.050	0.050	-	0.065	-
Mn ²⁺	1.816	1.813	1.966	2.000	2.040	2.061	2.165	2.287	2.535	2.764
Mg ²⁺	0.002	0.048	0.005	-	0.133	0.050	0.036	0.024	0.013	0.009
Ca ²⁺	0.003	0.009	0.008	-	0.049	0.006	0.003	0.002	0.008	0.011
	4.005	3.959	4.038	4.000	3.987	4.004	3.958	4.018	4.129	4.111
Li ⁺	3.961	3.924	3.920	4.000	3.894	3.821	3.963	3.783	3.738	3.844
K ⁺	-	-	-	-	-	-	0.001	-	-	-
Na ⁺	0.008	0.008	0.010	-	0.006	0.028	0.006	0.010	0.010	0.008
	3.969	3.932	3.930	4.000	3.900	3.849	3.970	3.794	3.748	3.852
x	0.546	0.541	0.507	0.500	0.482	0.468	0.446	0.431	0.375	0.326
\bar{a} (Å)	6.052(2)	6.046(2)	6.054(1)	6.060(2)	6.050(2)	6.055(2)	6.059(2)	6.059(1)	6.068(2)	6.071(2)
\bar{b} (Å)	10.391(3)	10.386(3)	10.389(2)	10.402(2)	10.386(2)	10.393(3)	10.403(3)	10.397(2)	10.407(3)	10.411(3)
\bar{c} (Å)	4.715(2)	4.715(2)	4.714(1)	4.722(1)	4.716(1)	4.720(1)	4.720(2)	4.717(1)	4.722(2)	4.725(2)
\bar{V} (Å ³)	296.51(30)	296.07(30)	296.49(17)	296.66(22)	296.35(25)	297.03(25)	297.51(31)	297.15(30)	298.19(31)	298.65(31)
2 θ 311	64.07	64.08	63.99	63.90	64.02	63.99	63.94	63.95	63.91	63.79
2 θ 222	67.16	67.16	67.12	67.02	67.14	67.08	67.04	67.08	66.99	66.95
2 θ 142	70.51	70.51	70.46	70.37	70.51	70.46	70.41	70.41	70.36	70.32

Table II (cont.)

	P 99	C	P 101	P 98	LiMnPO ₄
P ₂ O ₅	45.26	45.20	45.18	45.26	45.25
FeO	13.09	11.43	9.11	8.79	-
Fe ₂ O ₃	0.19	-	0.19	n.d.	-
MnO	30.45	33.87	36.17	36.37	45.23
MgO	0.28	-	n.d.	0.02	-
CaO	0.62	-	0.09	0.47	-
Li ₂ O	9.24	9.50	9.42	9.43	9.52
K ₂ O	0.04	-	n.d.	n.d.	-
Na ₂ O	0.05	-	0.03	0.02	-
H ₂ O	n.d.	-	n.d.	n.d.	-
insol.	0.93	-	-	-	-
total	100.13	100.06	100.19	100.36	100.00
p ⁵⁺	4.021	4.000	3.996	3.995	4.000
Fe ²⁺	1.149	1.000	0.796	0.766	-
Fe ³⁺	0.013	-	0.015	-	-
Mn ²⁺	2.706	3.000	3.200	3.211	4.000
Mg ²⁺	0.044	-	-	0.003	-
Ca ²⁺	0.070	-	0.010	0.053	-
	3.982	4.000	4.021	4.033	4.000
Li ⁺	3.900	4.000	3.958	3.955	4.000
K ⁺	0.005	-	-	-	-
Na ⁺	0.006	-	0.006	0.004	-
	3.911	4.000	3.964	3.959	4.000
x	0.306	0.250	0.199	0.195	0.000
a (Å)	6.073(2)	6.081(1)	6.082(2)	6.085(2)	6.105(1)
b (Å)	10.407(2)	10.421(1)	10.423(3)	10.431(2)	10.453(2)
c (Å)	4.725(1)	4.732(1)	4.730(2)	4.731(2)	4.748(1)
V (Å ³)	298.63(21)	299.87(12)	299.85(31)	300.29(28)	303.01(17)
2θ ₃₁₁	63.79	63.71	63.68	63.64	63.44
2θ ₂₂₂	66.95	66.83	66.82	66.80	66.60
2θ ₁₄₂	70.32	70.20	70.22	70.18	69.98

x : previously analysed samples

A : Li(Fe_{0.75}Mn_{0.25})PO₄

B : Li(Fe_{0.5}Mn_{0.5})PO₄

C : Li(Fe_{0.25}Mn_{0.75})PO₄

n.d.: not detected

x : (Fe²⁺ + Mg)/(Fe²⁺ + Mg + Mn) ratio

The 2θ positions are given for the FeK_{α1} radiation.

Mn³⁺ replacing some LiMn²⁺. Mn³⁺ could well have a similar effect to Fe³⁺, reducing the cell dimensions.

For the triphylite from Tohmajärvi, Finland (Kallio and Alviola, 1975), the calculation of the cell content for 16 oxygen gives Fe_{tot} = 2.60; Mn²⁺ = 1.08; Mg²⁺ = 0.43 (Σ = 4.11). However, these authors did not refine the cell dimensions of this material. From our suggested relations (4) (5) (6), the values for the Fe content are 3.24, 3.54, and 2.70 respectively. In this case the Mg content (2.72 wt % MgO) is much higher than the prerequisite of < 0.5% mentioned above and the derived values are unsatisfactory. If, instead, we use the equations (1) (2), representing the best fit of the relation between the chemical composition and the cell parameters, we find for the Tohmajärvi triphylite Fe_{tot} = 2.56 and Mg²⁺ = 0.33, in good agreement

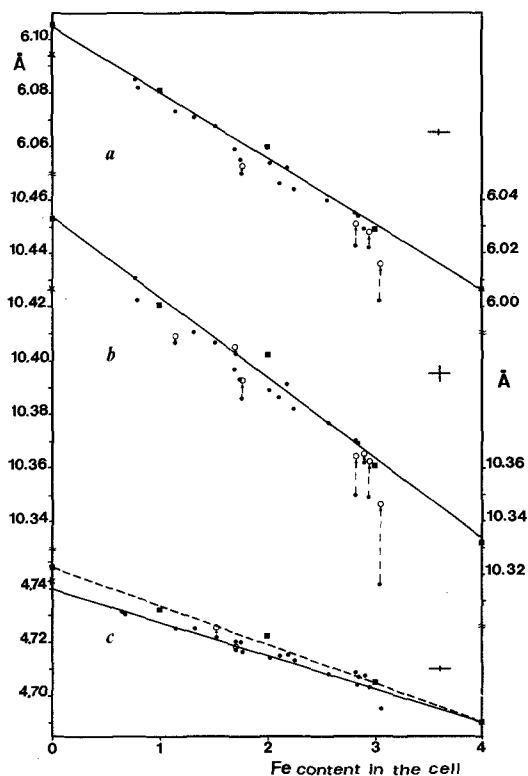


FIG. 1. Unit cell dimensions plotted against the total Fe content. The dashed line (variation of the *c* dimension) is calculated for the synthetic products, indicated by solid squares. The star represents the pure lithiophilite from Foot Mine (Thomssen and Anthony, 1977). For the relations between *a* and *b*, and the Fe content, the open circles and the arrows indicate the effect of the adjustment of their values for the Mg cell content. For the *c* variation the symbols indicate, in two cases, the adjustment for the Fe³⁺ cell content. The estimated errors are also checked.

with the chemical results of Kallio and Alviola (1975).

Chapman (1943), in an investigation of the variation of the optical properties for the triphylite-lithiophilite minerals, found a marked influence of Mg²⁺. Our calculations similarly show a marked influence of Mg²⁺ on the cell dimensions. For more convenient understanding of this influence, the chemical data on the Li(Fe,Mn)PO₄ series provided by the literature, and our analytical results as well (Table II), have been plotted in a Fe-Mn-Mg ternary diagram (fig. 2). Although the Fe³⁺ contents are generally negligible, the Fe values are given as total iron because the analytical error in the Fe²⁺: Fe³⁺ ratio could be significant in the older wet chemical analyses. From this diagram the Mg

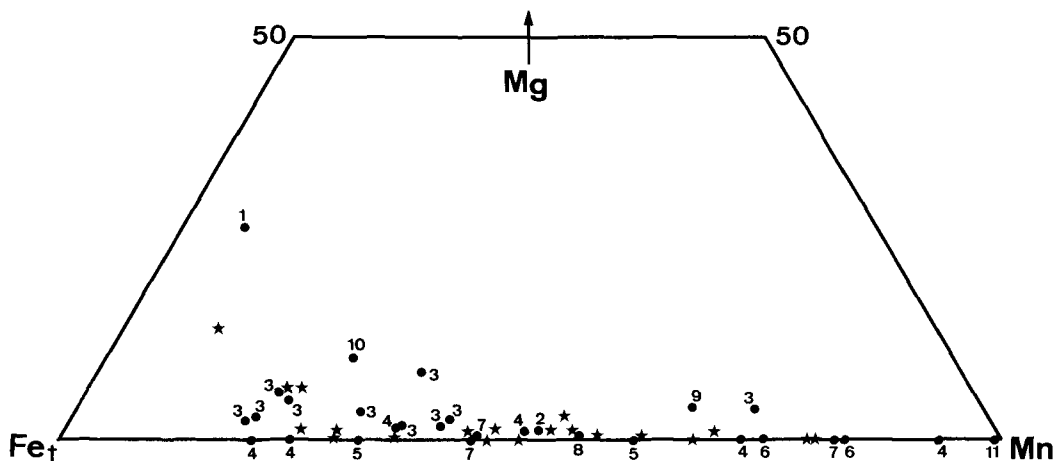


FIG. 2. Compositions of triphylite-lithiophilite series minerals on the ternary Fe-Mn-Mg diagram. Stars represent the chemical compositions recorded in this study. Dots with a number refer to chemical compositions given in the literature: 1. Chapman (1943); 2. Jesus (1933); 3. Mason (1941); 4. Palache *et al.* (1951); 5. Thoreau and Safiannikoff (1957); 6. Volborth (1954); 7. Quensel (1957); 8. Murdoch (1955); 9. Murdoch (1958); 10. Kallio and Alviola (1975); 11. Thomssen and Anthony (1977).

contents generally tend to decrease as the Fe/Mn ratios decrease; the triphylites are therefore generally richer in Mg than the lithiophilites. It means, on the one hand, that the Mg contents in these minerals could serve as a relevant geochemical indicator for the investigation of different types of triphylite-bearing pegmatites, and on the other hand, that the crystallographic parameters of the Fe-rich compounds in the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ series are more likely to be affected by the influence of Mg than the Mn-rich ones. Although we have no evidence for a departure from linearity, the very low *a* and *b* values of the three Mg-rich triphylite specimens, particularly P1 from Angarf-Sud pegmatite, Morocco (Fransolet, 1974), is a puzzling point. However, this fact may also be merely an underestimate of the effect of Mg: without more data on natural Mg-rich triphylites this aspect of the problem cannot be solved with reasonable accuracy at the present time.

From these considerations we finally propose using the mean of equations (4) (5) and (6) to calculate the Fe content in the minerals of the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ series in which the Mg content is normally lower than 0.070 atom in the cell, i.e. in lithiophilites with an Fe/(Fe+Mn) ratio varying from 0.5 to 0.0. Triphylites with this ratio between 1.0 and 0.5 are frequently richer in Mg than the lithiophilites (fig. 2) and the combined use of the equations (1) (2) and (4) (5) (6) is advisable and can eventually display the presence of Mg by comparing the derived values from these equations.

Selected reflections variation

Although accurate cell dimensions should yield a good estimate for the total iron content, this data collecting and computing process is time-consuming. For this reason we have attempted a more simple method, based on selected diffraction lines.

All the $2d(hkl)$ values decrease systematically when the Fe^{2+} contents increase. A graph for the determination of the Fe content based on the variation in 2θ Fe- $K\alpha_1$ angle of 311, 222, and 142 reflections (given in Table II) is presented in fig. 3. It shows a rather small scatter of individual plots.

The best-fit lines after C. H. Kummel's procedure (Hey, 1969) are:

$$2\theta_{311} = 63^\circ 438 + 0.2835 (\text{Fe}_{\text{tot}} + \text{Mg})$$

$$2\theta_{222} = 66^\circ 609 + 0.2485 (\text{Fe}_{\text{tot}} + \text{Mg})$$

$$2\theta_{142} = 69^\circ 996 + 0.2368 (\text{Fe}_{\text{tot}} + \text{Mg})$$

where (Fe+Mg) is calculated on a basis of $\text{Fe} + \text{Mg} + \text{Mn} + \text{Ca} = 4$ on the *M*(2) sites. The coefficients are subject to a large standard deviation (about 0.13) but lead to quite reasonable calculated 2θ , or vice versa to reasonable calculated (Fe+Mg). The data for P1 were not used in the calculations because that specimen is abnormally rich in Mg, which, as we have already seen, affects the cell dimensions, and hence the 2θ , more than Fe replacing Mn. If we exclude specimens B and P96, also showing a very poor fit, the standard deviation of the residuals is 0.065, corresponding to a standard

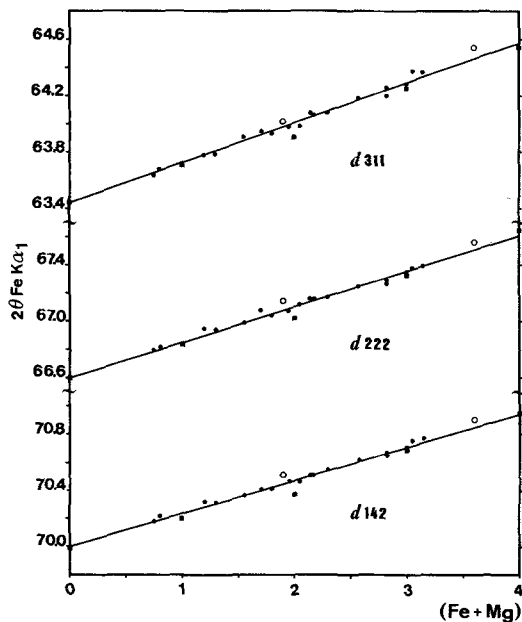


FIG. 3. Measured values of the 2θ FeK α_1 angles for the 311, 222, and 142 reflections plotted against the (Fe_{tot} + Mg) content, calculated on the basis of Fe + Mg + Mn + Ca = 4. The solid squares refer to synthetic compounds and the open circles correspond to P1 and P96, excluded for the calculation of Kummell's line.

deviation of error of 0.02° in the 2θ values. So we can safely use the mean of the (Fe + Mg) values calculated from the above equations and assert that for a triphylite-lithiophilite series member containing little or no Mg, the probable error in (Fe + Mg) per four cations is about 0.05 if 2θ was measured to 0.01° .

With reagent grade $\text{Pb}(\text{NO}_3)_2$ as an internal standard these other three parameters for the total iron estimate in the triphylite-lithiophilite series can be easily measured on powder diffractograms scanned in the 2θ range 60° – 75° 2θ using the Fe-K α_1 radiation and the other operating conditions mentioned above.

Conclusions

Because of the relative abundance and the significance of the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ minerals in the pegmatitic process, we suggest, in this study, a semi-quantitative method for the determination of the divalent cation contents in these minerals, based on their crystallographic properties.

By plotting all the available chemical data on a Fe–Mn–Mg ternary diagram (fig. 2) the Mg

content in these minerals clearly decreases when the Fe/Mn ratios decrease and could serve as a geochemical indicator for the investigation of different types of triphylite-bearing pegmatites.

A multivariate correlation between the chemical composition and the cell dimensions of twenty-five samples, including five synthetic compounds, of the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ series shows the influence of Fe^{2+} , Mg^{2+} , Fe^{3+} substituting for Mn^{2+} on the M(2) site on the *a*, *b*, and *c* cell parameters. The best representation of this relation is given by the equations (1) (2) (3) but, when the MgO wt. % is lower than 0.5, the equations (4) (5) (6) can be used very satisfactorily. It must be pointed out that the *c*-dimension gives a relatively poor estimate, though useful as a simple check.

As the cell parameter refinement requires both an accurate measurement of twenty-two indexing reflections on slowly scanned powder diffractograms and a computing process, a simpler technique for the (Fe + Mg) content estimate, based on the variations in 2θ Fe-K α_1 of three peaks (*d* 131, *d* 222, and *d* 142) is also proposed.

Unusual phases of the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ series cannot be reliably investigated by the relationships and graphs given in this study. Reasonable upper limits in wt. % suggested are Na_2O (0.5%), CaO (0.5%), and Fe_2O_3 (3%) contents. These limits do not constitute constraining prerequisites in most cases.

It must be stressed, however, that this semi-quantitative method could provide completely erroneous information about the Fe/Mn ratio in cases on non-homogeneous materials. Zoning phenomena have never been described in $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ crystals, but they could be expected when occurring in very fractionated pegmatites. As an optical check is presently useless, the best way to avoid such discrepancies is to X-ray several times very small amounts of material from different parts of the same specimen.

It seems highly desirable that this investigation be extended to the oxidized ferrisicklerite-sicklerite $\text{Li}_{1-x}(\text{Fe}_x^{3+}, \text{Mn}_{1-x}^{2+})\text{PO}_4$ and heterosite-purpurite $(\text{Fe}_x^{3+}, \text{Mn}_{1-x}^{2+})\text{PO}_4$ series. Fransolet (1975) recorded that the cell dimensions of the ferrisicklerites *sensu lato* increase when the Mn^{2+} content increases, while the substitution of Mn^{3+} for Fe^{3+} in the heterosites induces a contraction of the *b* parameter. As the $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ minerals can be systematically oxidized in some pegmatites, and, as the oxidation process, accompanied by Li-leaching, preserves the olivine-type structure and probably the initial Fe/Mn ratio, the determination of this ratio, even in the oxidized minerals, could give some information for the succession of the formerly crystallized $\text{Li}(\text{Fe},\text{Mn})\text{PO}_4$ compounds.

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REFERENCES

- Chapman, C. A. (1943) *Am. Mineral.* **28**, 90-8.
 Cox, A. A. (1967) *A Program for Least-squares Refinement of Unit Cell Dimensions*. The City University London, Dept. of Physics, Crystallogr. Lab.
 Fersman, A. (1931) *Les pegmatites granitiques, leur importance scientifique et pratique*. Acad. Sci. USSR, 3 vol., 675 pp., Univ. de Louvain (French translation 1951).
 Finger, L. W., and Rapp, G. R. (1970) *Carnegie Inst. Washington, Yearb.* **68**, 290-2.
 Fontan, F., Gramont, P. de, Monchoux, P., and Tollon, F. (1970) *Sur quelques phosphates des pegmatites lithinifères de l'Arize (Ariège)*. C.R. 94e Congrès Nat. Soc. Savantes, Pau 1969, Sect. Sci. ii, 131-4.
 —Huvelin, P., Orliac, M., and Permingeat, F. (1976) *Bull. Soc. fr. Minéral. Cristallogr.* **99**, 274-86.
 Fransolet, A. M. (1974) *Notes Serv. géol. Maroc*, **35**, 137-43.
 —(1975) *Étude minéralogique et pétrologique des phosphates de pegmatites granitiques*. Thèse de doctorat inédite. Univ. de Liège, Belgique.
 —(1980) *Mineral. Mag.* **43**, 1015-23.
 Geller, S., and Durand, J. L. (1960) *Acta Crystallogr.* **13**, 325-31.
 Ginzbourg, A. I. (1960) *Specific Geochemical Features of the Pegmatitic Process*. Intern. Geol. Congr., Rep. 21th Sess., Norden, part xvii, sect. 17, 111-21.
 Hey, M. H. (1969) *Mineral. Mag.* **37**, 83-9.
 —(1973) *Ibid.* **39**, 4-24.
 Jesus, A. M. de (1933) *Com. Serv. Geol. Portugal*, **19**, 65-210.
 Kallio, P., and Alviola, R. (1975). *Fortschr. Mineral.* **52**, Spec. Issue, IMA-papers, 9th Meeting, Berlin 1974, 279-83.
 Lahti, S. I. (1981) *Geol. Surv. Finland, Bull.* **314**, 82 pp.
 Mason, B. (1941) *Geol. Fören. Förh.* **63**, 117-75.
 Moore, P. B. (1972) *Am. Mineral.* **57**, 1333-44.
 Murdoch, J. (1955) *Ibid.* **40**, 50-63.
 —(1958) *Ibid.* **43**, 1148-56.

- Palache, C., Berman, H., and Frondel, C. (1951) *Dana's System of Mineralogy*, **2**, 7th edn., John Wiley and Sons, Inc., New York, 1124 pp.
 Pâques-Ledent, M.-T. (1972) *Corrélations entre le type structural et le spectre vibrationnel des composés ABXO₄*. Thèse de doctorat inédite. Univ. de Liège, Belgique.
 Quensel, P. (1957) *Ark. Mineral. Geol.* **2**, 9-125.
 Rickel, C., and Weiss, A. (1978) *Z. Naturforsch.* **33b**, 731-6.
 Schwab, R. B., and Kustner, D. (1977) *Neues Jahrb. Mineral. Mh.* 205-15.
 Thilo, E. (1941) *Naturwissenschaften*, **29**, 239.
 Thomssen, R. W., and Anthony, J. W. (1977) *Mineral. Rec.* **8**, 95-7.
 Thoreau, J., and Safiannikoff, A. (1957) *Bull. Acad. roy. Belgique, Cl. Sci., série 5*, **43**, 324-7.
 Volborth, A. (1954) *Ann. Acad. Sci. Fennicae*, ser. A, iii, Geol. Geogr. no. 39, 91 pp.
 Wilson, A. D. (1960) *The Analyst*, **85**, 823-7.
 Winchell, A. N. (1933). *Elements of Optical Mineralogy*, **2**, 3rd edn., John Wiley and Sons, Inc., New York, 459 pp.
 —and Winchell, H. (1951) *Ibid.* **2**, 4th edn., 551 pp.

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APPENDIX

In a multivariate best-fit analysis, we know that the several sets of observations will not exactly fit the relation derived, but we seek a relation in which the estimated probable errors in the several variables are given equal weight, instead of assuming, as in regression analysis, that the error is wholly in the 'dependent variable'. Therefore, we need estimates (which need only be approximate) of the probable standard errors of all the variables. So far as the physical variables are concerned, these are usually available; for the errors in the chemistry, two approaches are possible. First, we can, following Washington, Hillebrand, and others (cf. Hey, 1973), assume that in a good analysis the error in a major constituent is likely to be around 1% of the amount present, and in a minor constituent (e.g. Ca) about 0.02 to 0.03%. Alternatively, we can look at the mean departure of the cation sum in *M*(2) from 4, which is 0.0432, and share this between the cations in proportion to their average amounts; this leads to estimated probable errors of about 0.022 in Fe_{tot}, 0.020 in Mn and 0.001 in Mg, in reasonable agreement with the first method; for Ca, the second method suggests too great accuracy, and an error of 0.002 (per four cations), in agreement with the first method, seems better.

For the cell dimensions, we have standard deviations of error *a* 0.002, *b* 0.003, *c* 0.001 Å. These figures look as if the errors in Fe and Mn were far greater than in *a*, *b*, or *c*, but the error in Fe is only 0.5% of its range, while the error in *a* is about 2% of its range; and it is this relative error that matters.

Ferric iron could enter the Li(Fe,Mn)PO₄ structure in two ways: either by the replacement 3Fe²⁺ → 2Fe³⁺, leaving a vacancy in the *M*(2) site, or by a replacement LiFe²⁺ → Fe³⁺, with a vacancy in the *M*(1) site; an

inspection of those analyses in which Fe^{3+} was determined shows a match between Fe^{3+} and $4-(\text{Li} + \text{Na} + \text{K})$, well within the probable experimental error, except for analyses P23 and P27, and in these two cases, particularly in P27 with 0.91 wt. % H_2O , impurities could have escaped attention during purification. We have therefore assumed that where Fe^{3+} was not determined it was present in an amount equal to $4-(\text{Li} + \text{Na} + \text{K})$. The best-fit line obtained for all twenty-five sets of data on this assumption is almost the same as that derived for the fourteen sets of data for which Fe^{3+} was determined or known to be absent (the synthetics), and is very similar to that for the five synthetics only. It is:

$$\begin{aligned} a &= 6.1050 - 0.0245 (0.0023) \text{Fe}^{2+} \\ &\quad - 0.0282 (0.0258) \text{Fe}^{3+} - 0.0488 (0.0164) \text{Mg}^{2+} \\ b &= 10.4511 - 0.0288 (0.0040) \text{Fe}^{2+} \\ &\quad - 0.0309 (0.0454) \text{Fe}^{3+} - 0.0820 (0.0289) \text{Mg}^{2+} \end{aligned}$$

$$\begin{aligned} c &= 4.7400 - 0.0130 (0.0026) \text{Fe}^{2+} \\ &\quad - 0.0245 (0.0299) \text{Fe}^{3+} - 0.0132 (0.0190) \text{Mg}^{2+}. \end{aligned}$$

The coefficients refer, of course, to that cation replacing Mn^{2+} , and in the case of Fe^{3+} to the replacement of LiMn^{2+} by Fe^{3+} .

For both a and b it is evident that the effect of Fe^{3+} cannot be differentiated from that of Fe^{2+} , but Mg^{2+} has a decidedly greater effect than Fe^{2+} ; on fig. 1 an arrow indicates the effects of an adjustment of a or b for the Mg^{2+} , and clearly improves the fit notably, though P1 still falls below the line. There is no evidence of any departure from linearity.

For c , Mg^{2+} clearly has the same effect as Fe^{2+} within the limits of error, but the effect of Fe^{3+} appears to be greater than that of Fe^{2+} , though the standard deviation of its coefficient is uncomfortably great; further data on material with more Fe^{3+} are desirable.