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Nomenclature of the triphylite group of minerals

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Abstract. In this paper we present a Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA-CNMNC)-accepted scheme for the classification and nomenclature of the triphylite group of minerals. The general formula of those minerals is $M1M2TO_4$, where $M1$ and $M2$ refer to cations in an octahedral coordination: $M1 = \square$, Na, Li; $M2 = Mn^{2+}$, Fe^{2+}, Mg, Fe^{3+}, Mn^{3+}, and T to tetrahedrally coordinated P^{5+} cations. The group contains the Li-bearing phosphates triphylite [$LiFe^{2+}(PO_4)$] and lithiophilite [$LiMn^{2+}(PO_4)$] and their oxidation products heterosite [$Fe^{3+}(PO_4)$] and purpurite [$Mn^{3+}(PO_4)$], as well as the Na-bearing phosphates natrophilite [$NaMn^{2+}(PO_4)$] and karenwebberite [$NaFe^{2+}(PO_4)$]. The Li–Mg-bearing phosphate simferite has been redefined as $LiMg(PO_4)$. Ferrisicklerite and sicklerite correspond to intermediate phases in the triphylite–heterosite and lithiophilite–purpurite solid solutions; consequently, according to the CNMNC dominant-constituent rule, they are discredited. A new mineral oxidation sequence is defined, which considers the different oxidation capacity of iron and manganese, and therefore replaces the traditional Quensel–Mason sequence. The formula calculation procedure for Li-bearing species, based on electron microprobe analyses and single-crystal X-ray diffraction data, is also described.

1 Introduction

The triphylite group includes seven phosphate mineral species, characterized by the well-known olivine-type crystal structure (Brush et al., 1890; Alberti, 1976; Fontan et al., 1976; Hatert, 2012; Hatert et al., 2012; and others). Their general formula is $M1M2TO_4$, where $M1$ and $M2$ refer to cations in an octahedral coordination ($M1 = \square$, Na, Li; $M2 = Mn^{2+}$, Fe^{2+}, Fe^{3+}, Mn^{3+}, Mg), and T corresponds to the tetrahedrally coordinated P^{5+} cation (Losey et al., 2004).

Triphylite, heterosite, sicklerite, ferrisicklerite, lithiophilite, and purpurite are common Li-bearing minerals found in granitic pegmatites. They are connected to each other by heterovalent substitutions following the mechanism $Li^+ + (Fe^{2+}, Mn^{2+}) \leftrightarrow \square + (Fe^{3+}, Mn^{3+})$, leading to the so-called Quensel–Mason oxidation sequence (Schmid-Beurmann et al., 2013; Baijot et al., 2012; Hatert, 2012; Hatert et al., 2012). These phosphates were initially only of mineralogical interest; however, electrochemical studies carried out in the 1990s (Padhi et al., 1997) caused an avalanche-like increase in the number of publications devoted to these compounds, both of natural and synthetic origin. Nowadays, triphylite-like phosphates are considered one of the most effective cathode material for lithium-ion batteries (Fehr et al., 2007; Hatert, 2012; Yakubovich et al., 2020, and references therein).

Sodium-bearing phosphates, natrophilite [$NaMn^{2+}(PO_4)$] (Brush et al., 1890) and the relatively recently approved karenwebberite [$NaFe^{2+}(PO_4)$] (Vignola et al., 2013), are structurally identical to olivine-type Li–(Fe,Mn) phosphates and consequently belong to the triphylite group of minerals, too. Simferite, $Li(Mg,Fe^{3+},Mn^{3+})_2(PO_4)_2$, with an olivine-type crystal structure and half-occupied $M1$ site, is also structurally related to triphylite-type phosphates (Yakubovich et al., 1989).

Ferrisicklerite and sicklerite appear to be intermediate phases of the oxidation of triphylite–lithiophilite into heterosite–purpurite, where ferrous ion is totally or partially oxidized into ferric iron: $Li(Fe^{2+}, Mn^{2+})(PO_4)$ triphylite–lithiophilite → $Li_{1-x}Mn^{2+}_{1-x}Fe^{3+}_x(PO_4)$ sicklerite–ferrisicklerite → $(Fe^{3+}, Mn^{3+})(PO_4)$ heterosite–purpurite. In some cases, it may be difficult to identify these minerals

from their chemical analyses due to the gradual transition from one mineral to another during the oxidation process, difficulties in pure sampling for analysis, and limited analytical capabilities (for example, definition of trivalent manganese is not a routine procedure). Consequently, optical properties are often used to confirm the identification, and most authors consider that lithiophilite and triphylite are colorless, while sicklerite is deep orange, and ferrisicklerite is reddish-brown chocolate or brownish black in the thin section (Fransolet et al., 1986; Hatert et al., 2012; Baijot et al., 2012; Roda-Robles et al., 2014). The local analytical methods only partly solve the situation for these minerals, since the electron probe microanalysis (EPMA) – the most commonly used local method for determining a chemical composition – does not allow us to determine the lithium content and distinguish the valence states of iron and manganese. A direct lithium measurement by the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) method shows a big margin of error (Svetov et al., 2015), while secondary ion mass spectrometry (SIMS) techniques are much more reliable for determining lithium. The higher standard deviations generally pertain to the low or very low Li concentrations (Hatert et al., 2011a). Therefore, researchers continue either to use indirect criteria for mineral definition or to apply different analytical method combinations, which are leading to a more or less acceptable result.

In this paper we present a CNMNC-approved nomenclature scheme for the triphylite group, in which end-member mineral formulae are defined (Miyawaki et al., 2022). Simferite is redefined as $LiMgPO_4$, and ferrisicklerite and sicklerite are discredited, since they constitute intermediate members in solid solutions. We also discuss the interpretation of chemical analyses in these complex minerals affected by variable valence states during their oxidation processes.

2   Previous data on the triphylite group of phosphates

Minerals of the triphylite group (Table 1) crystallize in the space group *Pbnm* (Finger and Rapp, 1969; Eventoff et al., 1972; Moore, 1972; Alberti, 1976; Losey et al., 2004; Fehr et al., 2007; Hatert et al., 2012; Vignola et al., 2013; Schmid-Beurmann et al., 2013) and show the olivine crystal structure characterized by two chains of edge-sharing octahedra parallel to the *c* axis. The first chain is constituted by the $M1$ octahedra occupied by Li, Na, or vacancies, while the second chain is formed by the $M2$ sites occupied by Fe, Mn, and Mg (Fig. 1). The occupancy of the $M1$ position varies from 0 to 1 in Li-bearing species, and it approaches 1 in Na-bearing species. The structural formula of triphylite-type phosphates is $M1M2TO_4$, where T corresponds to P^{5+} in tetrahedral coordination (Losey et al., 2004). The cation ordering between $M1$ and $M2$, first defined for natrophilite (Moore, 1972), is the main crystal–chemical difference between triphylite-type
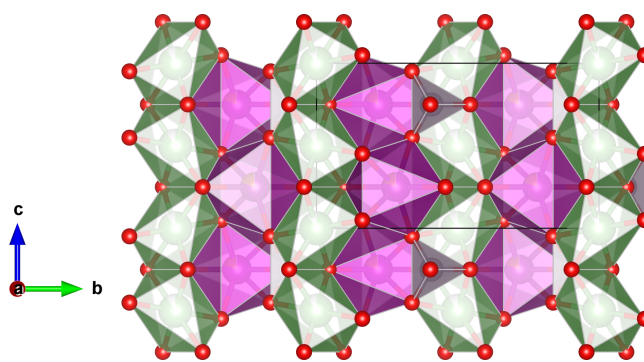
Figure 1. The crystal structure of lithiophilite, projected perpendicular to the *a* axis (Hatert et al., 2012). The $M1$ octahedra containing Li are green, the $M2$ octahedra containing Fe and Mn are purple, and the PO_4 tetrahedra are light grey.

phosphates and silicates of the forsterite–fayalite series, in which Fe and Mg are disordered over the two sites.

Oxidation of Fe^{2+} to Fe^{3+} and of Mn^{2+} to Mn^{3+} produces Li vacancies at the $M1$ sites, which are necessary to maintain charge balance. The alignment of $M1$ octahedra along the *c* axis explains why the [001] direction becomes an easy and fast pathway for Li/Na leaching during oxidation or absorption when conditions lead to the reduction in Fe and Mn. This is the principle widely in used Li-ion batteries based on olivine-type phosphates (Rakovan, 2005; Yakubovich et al., 2020).

The main chemical, crystallographic, and optical data for triphylite-group minerals are summarized in Table 1. These data are those of the first-described occurrence of the species, as well as supplementary references for which complete structural and/or chemical datasets were available. Heterosite is the oldest mineral of the group (Alluaud, 1826), but in the present case, the name of the more common species triphylite (Fuchs, 1834) was given for the group, in contradiction with the precedence rule (Mills et al., 2009). Heterosite was followed by the discoveries of triphylite $LiFe^{2+}(PO_4)$ (Fuchs, 1834), lithiophilite $LiMn^{2+}(PO_4)$ (Brush and Dana, 1878), and purpurite $\square Mn^{3+}(PO_4)$ – another completely leached and oxidized phase (Graton and Schaller, 1905) – and then by the intermediate products, sicklerite (Schaller, 1912), and ferrisicklerite (Quensel, 1937).

As mentioned above, the accurate determination of minerals in the Quensel–Mason sequence is delicate due to the difficulties in the determination of Fe and Mn valence states and of the lithium contents. Methods based on unit-cell parameter variations do not solve the problem because these parameters are affected by several variables simultaneously, e.g., the Fe/(Fe + Mn) ratio; the presence of Mg, Fe^{3+}, and other impurities (Na, Ca, etc.); and the sample homogeneity (Fransolet et al., 1984) (Table 1). Moreover, for natural purpurite, crystallographic data are absent, since the sam-

Table 1. Chemical composition, cell dimensions (space group *Pbnm*, $Z = 4$), and optical data for triphylite-group minerals. RI stands for refractive index.

Mineral	Empirical formula	Crystallography a, Å; b, Å; c, Å	V, Å³	Optical data (RI values, color, pleochroism)	Reference
Heterosite	[a]$\square(Fe^{3+}_{0.60}Mn^{3+}_{0.31})_{0.91}(P_{1.05}O_4)$	No data			Alluaud (1826)
	$\square(Fe^{3+}_{0.65}Mn^{3+}_{0.35})_{1.00}(PO_4)$	4.765(5) 9.79(1) 5.83(1)	271.70(2)	No data	Eventoff et al. (1972)
	$\square(Fe^{3+}_{0.62}Mn^{3+}_{0.38})_{1.00}(PO_4)$	No data		Pleochroic in deep purple and brownish	Langer et al. (2007)
Triphylite	[a]$(Li_{0.82}Na_{0.05}K_{0.01})_{0.88}(Fe^{2+}_{0.67}Mg_{0.27}Mn^{2+}_{0.06})_{1.00}(P_{0.95}Al_{0.09}Si_{0.01})_{1.05}(O_{3.81}(OH)_{0.09})_{4.00}$	No data		[b]$\alpha = 1.675$, $\beta = 1.684$, $\gamma = 1.685$, $2V = 25°$	Chapman (1943)
	$Li_{0.93}(Fe^{2+}_{0.73}Mn^{2+}_{0.21}Mg_{0.06}Fe^{3+}_{0.01})_{1.01}P_{1.00}O_4$	4.7010(4) 10.335(1) 6.0163(6)	292.30(5)	Colorless	Schmid-Beurmann et al. (2013)
	$Li_{0.95}(Fe_{0.59}Mn_{0.41}Ca_{0.03}Mg_{0.02})_{1.05}PO_4$	No data		$\alpha = 1.670$, $\beta = 1.670$, $\gamma = 1.678$	Shannon et al. (2002)
Lithiophilite	[a]$(Li_{0.91}Na_{0.01})_{0.92}(Mn^{2+}_{0.91}Fe^{2+}_{0.09})_{1.00}P_{0.99}(O_{3.86}(OH)_{0.14})_{4.00}$	No data		Pleochroic in deep pink, pale greenish yellow, and faint pink	Brush and Dana (1878)
	$Li_{0.96}(Mn^{2+}_{0.81}Fe^{2+}_{0.09}Fe^{3+}_{0.08})_{0.98}PO_4$	4.736(1) 10.432(2) 6.088(1)	300.78	Light yellow	Hatert et al. (2012)
Purpurite	[a]$(\square_{0.96}Na_{0.04})_{1.00}(Mn^{3+}_{0.52}Fe^{3+}_{0.28}Ca_{0.04})_{0.84}P_{0.93}(O_{3.18}(OH)_{0.82})_{4.00}$	No data		Pleochroic in deep scarlet, rose red, and purple	Graton and Shaller (1905)
Purpurite (syn)	$(Mn_{0.8}Fe_{0.2})_{1.0}PO_4$	4.7770(1) 9.6629(2) 5.8841(1)	271.608	No data	Yamada et al. (2006)
Simferite	$Li_{0.5}(Mg_{0.5}Fe^{3+}_{0.3}Mn^{3+}_{0.2})PO_4$	4.7468(7) 10.101(2) 5.8992(7)	282.851	$n_p = 1.690$–1.704, $n_m = 1.702$–1.716, $n_g = 1.712$–1.726	Yakubovich et al. (1989)
Natrophilite	[a]$(Na_{0.95}Li_{0.02})_{0.97}(Mn^{2+}_{0.93}Fe^{2+}_{0.07})_{1.00}P_{0.99}(O_{3.92}(OH)_{0.08})_{4.00}$	No data			Brush et al. (1890)
	$Na(Mn^{2+}_{0.93}Fe^{2+}_{0.07})_{1.00}(PO_4)$	4.987(2) 10.523(5) 6.312(3)	331.242	No data	Moore (1972)
Karenwebberite	$(Na_{0.82}\square_{0.18})_{1.00}(Fe^{2+}_{0.62}Mn^{2+}_{0.23}Fe^{3+}_{0.15}Mg_{0.01})_{1.01}(PO_4)$	4.882(1) 10.387(2) 6.091(1)	308.9(1)	$\alpha = 1.701(2)$, $\beta = 1.708(2)$, $\gamma = 1.717(2)$, $2V(\text{meas.}) = 87(4)°$/ pleochroic in pale and dark green	Vignola et al. (2013)

Table 1. Continued.

Mineral	Empirical formula	Crystallography a, Å; b, Å; c, Å	V, Å³	Optical data (RI values, color, pleochroism)	Reference
Discredited species					
Sicklerite	$(\square_{0.34-0.71}Li_{0.29-0.66})_{1.00}(Mn_{0.80-0.84}Fe^{3+}_{0.15-0.17})_{0.95-1.01}(PO_4)_{1-1.02}$	4.750(5) 10.082(9) 6.03(2)	288.8(5)	$\alpha = 1.710-1.720$, $\beta = 1.730-1.738$, $\gamma > 1.738$, 2V > 60°/brown-yellow/ pleochroic in pale and deep yellow	Shigley and Brown (1985)
	[a] $(\square_{0.59}Li_{0.41})_{1.00}(Mn^{2+}_{0.77}Fe^{3+}_{0.23}Mn^{3+}_{0.04}Ca_{0.01})_{1.05}P_{0.98}(O_{3.69}(OH)_{0.31})_{4.00}$	No data		Pleochroic in yellow and brown	Schaller (1912)
	$(Li_{0.69}\square_{0.31})_{1.00}(Mn^{2+}_{0.62}Mn^{3+}_{0.19}Fe^{3+}_{0.16})_{0.97}PO_4$	4.765(1) 10.338(1) 6.060(1)	298.52	Deep orange	Hatert et al. (2012)
Ferrisicklerite	[a] $(\square_{0.57}Li_{0.39}Na_{0.04})_{1.00}(Fe^{3+}_{0.53}Mn^{2+}_{0.42}Ca_{0.04}Fe^{2+}_{0.01})_{1.00}P_{0.99}(O_{3.91}(OH)_{0.09})_{4.00}$	No data		The medium indices of refraction is well over 1.78/deep reddish brown/ almost unpleochroic	Quensel (1937)
	$(\square_{0.53}Li_{0.43}Na_{0.02}Ca_{0.02})_{1.00}(Fe^{3+}_{0.65}Mn^{2+}_{0.36}Mg_{0.04}Fe^{2+}_{0.01})_{1.06}PO_4(OH)_{0.27}$	4.799(3) 10.037(6) 5.918(3)	285.05(2)	$n_g = 1.820$, $n_m = 1.805$, $n_p = 1.790$; 2V – negative and very large/pleochroic in gold yellow and orange yellow	Alberti (1976), Fontan et al. (1976)

[a] Calculated on the basis of O = 4. [b] "The indices of refraction and optic angle were determined for sodium light" (Chapman, 1943).

ple considered purpurite by Björling and Westgren (1938) indeed corresponds to heterosite (Table 1).

Triphylite, heterosite, sicklerite, ferrisicklerite, lithiophilite, and purpurite are the most common and well-studied members of the group, and their investigations aimed to elucidate the formation conditions and the mechanism of topotactic reactions leading to this suite of phosphate minerals and therefore contributed to the reconstruction of the physico-chemical conditions of phosphate mineral formation in granitic pegmatite. The other phosphates of the group are very rare minerals, which are described below.

Simferite shows the olivine-type crystal structure, with the $M1$ site being half occupied by Li and the $M2$ site dominantly occupied by Mg (Yakubovich et al., 1989). Magnesium-rich triphylite samples were also described from a quartz–albite pegmatite at Newport, New Hampshire (Chapman, 1943) (Table 1). Natrophilite is almost as old as lithiophilite (Brush et al., 1890), but it is still an extremely rare mineral. There is a reason to assume that natrophilite is a product of the Na-metasomatic exchange reaction with lithiophilite so that natrophilite may occur only in Mn-rich geological environments. Natrophilite was the first olivine-type phosphate with a confirmed ordered cationic distribution over the two M sites (Moore, 1972). Finally, karenwebberite can be regarded as the Fe equivalent of natrophilite or as the Na equivalent of triphylite (Table 1). In progressive oxidation conditions, karenwebberite is affected by the substitution mechanism $Na^+ + Fe^{2+} \rightarrow \square + Fe^{3+}$, leading to heterosite.

In *Fleischer's Glossary of Mineral Species* (2008), in addition to the minerals listed in Table 1, marićite ($NaFePO_4$; $a = 6.861(1)$, $b = 8.987(1)$, $c = 5.045(1)$, $Pmnb$) and buchwaldite ($NaCaPO_4$; $a = 5.17(3)$, $b = 9.26(5)$, $c = 6.74(3)$, $Pmn2_1$) are also included in the triphylite group, since they show the same general formula $M1M2PO_4$. However, these minerals have a topology distinct from that of olivine (Struman et al., 1977; Le Page and Donnay, 1977). Marićite is also the high-temperature dimorph of karenwebberite, and the transition between the two polymorphs of $NaFe^{2+}(PO_4)$ occurs around $325\,°C$ ($P = 100$ bars) (Vignola et al., 2013). A similar high-temperature synthetic polymorph with a marićite-like structure is known for natrophilite (Hatert et al., 2006, 2011a) and can be obtained by heating a synthetic analog of natrophilite (Jana et al., 2020).

3   Nomenclature problem

The formulae of the nine species included in the triphylite group are given in Table 2, with the formulae occurring in the IMA-CNMNC before this nomenclature revision (December 2022), and the new end-member formula is also given.

Examination of the mineral formulae previously occurring in the CNMNC list shows several inconsistencies:

1. The same formula is reported for sicklerite and lithiophilite – $LiMn^{2+}(PO_4)$.

2. The formulae of ferrisicklerite, $Li_{1-x}(Fe^{3+},Mn^{2+})(PO_4)$, and of simferite, $Li(Mg,Fe^{3+},Mn^{3+})_2(PO_4)_2$, are not end-member formulae.

3. The formula of simferite is expressed on the basis of two (PO_4) groups per formula unit, while the formulae of other members of the group are expressed on the basis of one (PO_4) group per formula unit.

4. Dual names are sometimes used in the literature for some of these minerals, i.e., "lithiophilite–sicklerite" (Hatert et al., 2011b).

5. Major uncertainties exist in mineral identification. This is explained, for example, by Roda-Robles et al. (2014): "a wide range of Li content, which could be related to different degrees of leaching of Li from the primary triphylite, giving intermediate values between triphylite and ferrisicklerite". These difficulties are caused by the contradictions between the traditional definition of ferrisicklerite and sicklerite as separate species (IMA List of Minerals, December 2022) or series (Fontan et al., 1976) containing a comparable content of divalent and trivalent components in the $M2$ site and the IMA rules for mineral species determination based on crystal–chemical principles. It is noteworthy that the problem of nomenclature of olivine-type phosphates in general and the question of distinction between lithiophilite and sicklerite, in particular, have already been raised (Hatert et al., 2012).

We believe that these mineral species should be determined only on the basis of their fundamental characteristics, namely their chemical composition and crystal structure, and that they should be characterized by unique end-member formulae. For that reason, we submitted a proposal to the CNMNC, which was accepted in October 2022 (Miyawaki et al., 2022).

4   The new classification scheme

The heterovalent substitution mechanism $Li^+ + (Fe^{2+},Mn^{2+}) \leftrightarrow \square + (Fe^{3+},Mn^{3+})$ connects the minerals in the triphylite–heterosite (Fe mineral species) and in the lithiophilite–purpurite series (Mn mineral species). Moreover, homovalent substitutions $Fe^{2+} \leftrightarrow Mn^{2+}$ in the triphylite–lithiophilite series and $Fe^{3+} \leftrightarrow Mn^{3+}$ in the heterosite–purpurite series are also present. Consequently, the four cations Fe^{2+}, Mn^{2+}, Fe^{3+}, and Mn^{3+} occur in the $M2$ site of these phosphates.

Due to the difference in oxidation potential of iron and manganese (Schmid-Beurmann et al., 2013), we can assume

Table 2. Formulae of minerals belonging to the triphylite group.

Mineral	IMA List of Minerals, December 2022	New end-member formulae
Triphylite	$LiFe^{2+}(PO_4)$	$LiFe^{2+}(PO_4)$
Lithiophilite	$LiMn^{2+}(PO_4)$	$LiMn^{2+}(PO_4)$
Heterosite	$Fe^{3+}(PO_4)$	$Fe^{3+}(PO_4)$
Purpurite	$Mn^{3+}(PO_4)$	$Mn^{3+}(PO_4)$
Sicklerite	$LiMn^{2+}(PO_4)$	Discredited
Ferrisicklerite	$Li_{1-x}(Fe^{3+},Mn^{2+})(PO_4)$	Discredited
Simferite	$Li(Mg,Fe^{3+},Mn^{3+})_2(PO_4)_2$	$LiMg(PO_4)$
Karenwebberite	$NaFe^{2+}(PO_4)$	$NaFe^{2+}(PO_4)$
Natrophilite	$NaMn^{2+}(PO_4)$	$NaMn^{2+}(PO_4)$

that the manganese oxidation will start after the complete transformation of Fe^{2+} into Fe^{3+}. As a consequence, in the $M2$ site, only the following cation combinations are possible: (1) Fe^{2+}, Mn^{2+}; (2) Fe^{2+}, Mn^{2+}, Fe^{3+}; (3) Mn^{2+}, Fe^{3+}; (4) Mn^{2+}, Fe^{3+}, Mn^{3+}; and (5) Fe^{3+}, Mn^{3+}. Ternary diagrams Fe^{2+}–Mn^{2+}–Fe^{3+} and Mn^{2+}–Fe^{3+}–Mn^{3+} can therefore be used to represent the isomorphic substitutions in the $M2$ site (Fig. 2a). Triangles show a common Mn^{2+}–Fe^{3+} edge and can be combined along this line (Fig. 2b, c).

The "dominant-valency rule" for defining minerals in solid solution series with heterovalent substitutions can be applied here (Fig. 3b in Hatert and Burke, 2008). Boundaries between mineral species should ideally be defined as shown in Fig. 2d. In this case, we do not consider "ferrisicklerite" and "sicklerite" as valid mineral species, since they were defined on the basis of their optical features: both of them appear as brownish phases forming between triphylite and heterosite and between lithiophilite and purpurite, respectively. Since these phases are intermediate members of solid solutions, it is impossible to establish valid end-member formulae for them, and, consequently, they cannot be maintained as valid mineral species. *We have consequently suggested discrediting both ferrisicklerite and sicklerite; this discreditation was approved by the IMA-CNMNC (Miyawaki et al., 2022).*
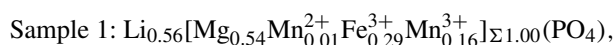
Triphylite, lithiophilite, heterosite, and purpurite are the end-members of solid solution series, and their compositions correspond to the Fe^{2+}, Mn^{2+}, Fe^{3+}, and Mn^{3+} vertices of the diagrams, respectively. In the case of magnesium-bearing species, the diagram can be completed by the Fe^{3+}–Mn^{3+}–Mg triangle (Fig. 3). According to Yakubovich et al. (1989), the composition of simferite is $Li(MgFe_{0.6}^{3+}Mn_{0.4}^{3+})_2(PO_4)_2$, which is graphically represented by the point exactly between heterosite and the hypothetical end-member $LiMg(PO_4)$ (Fig. 3). This composition, however, was obtained from crystal structural data and cannot be considered the empirical chemical composition of the species.

Bayrakov et al. (2005) re-analyzed simferite samples by electron microprobe, obtaining two analyses in which they considered the theoretical content of 1 Li pfu, lead-
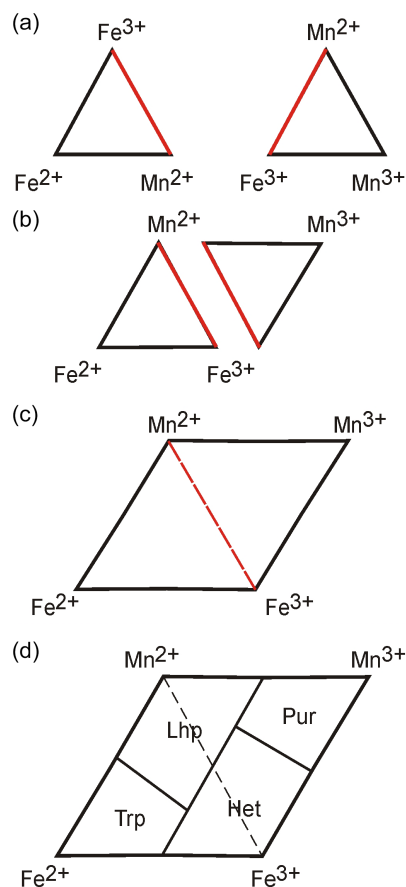
Figure 2. Diagrams for the representation of chemical compositions of (Fe,Mn)-olivine-type phosphates. Abbreviations: Trp – triphylite, Lhp – lithiophilite, Pur – purpurite, and Het – heterosite.

ing to 5.45 wt. % and 5.35 wt. % Li_2O. They also measured lithium independently by an unknown technique, leading to 6.12 wt. % Li_2O (Ercit et al., 2006). By using this measured lithium content, we can calculate the two following empirical formulae for simferite:

Sample 1: $Li_{0.56}[Mg_{0.54}Mn_{0.01}^{2+}Fe_{0.29}^{3+}Mn_{0.16}^{3+}]_{\Sigma 1.00}(PO_4)$,
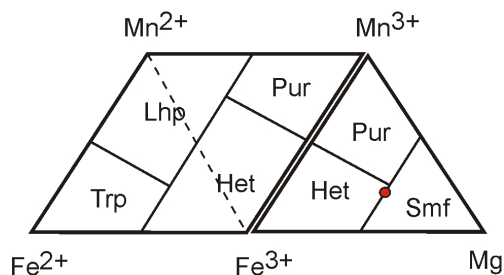
Figure 3. Diagram for the representation of chemical compositions of Mn, Fe, and Mg mineral species. Abbreviations: Trp – triphylite, Lhp – lithiophilite, Pur – purpurite, Het – heterosite, and Smf – simferite.

Sample 2: $Li_{0.57}[Mg_{0.43}Mn^{2+}_{0.12}Fe^{3+}_{0.30}Mn^{3+}_{0.14}]_{\Sigma 0.99}(PO_4)$.

These two recalculated analyses indicate that significant amounts of Mg^{2+} occur on the $M2$ site and that lithium is higher than 0.5 Li pfu on the $M1$ site. According to the dominant-valency rule (Hatert and Burke, 2008), the end-member formula of simferite should show Li dominant on $M1$ and divalent cations dominant on $M2$, among which Mg is the most abundant element.

We consequently revised the end-member formula of sim-ferite (Table 2) to LiMg(PO4) in order to be consistent with the nomenclature of the triphylite group in which end-member formulae are expressed with one (PO4) group per formula unit.

It is important to note that the compound $LiMg(PO_4)$ exists as a synthetic product and has been extensively investigated, since it is used as an efficient phosphor (Gai et al., 2013; Marczewska et al., 2016; Kulig et al., 2017).

The new CNMNC-approved end-member formulae of minerals of the triphylite group are given in Table 2 (Miyawaki et al., 2022).

5 Mineral sequence during oxidation

According to traditional views, a change in mineral species during oxidation (Quensel–Mason sequence) occurs in the triphylite $\rightarrow$ ferrisicklerite $\rightarrow$ heterosite and lithiophilite $\rightarrow$ sicklerite $\rightarrow$ purpurite series; this corresponds to a displacement along horizontal arrows in Fig. 4a during simultaneous oxidation of iron and manganese.

By considering the boundaries between mineral species, defined in accordance with the dominant-constituent and dominant-valency rules, we can observe that such a displacement of mineral compositions in certain areas of intermediate Fe–Mn compositions leads to a transition of triphylite under partial oxidation first into lithiophilite and then into heterosite (Fig. 4b). The accurate sequence is $Fe^{2+}_{0.6}Mn^{2+}_{0.4}$ (triphylite) $\rightarrow Mn^{2+}_{0.4}Fe^{2+}_{0.3}Fe^{3+}_{0.3}$ (lithiophilite) $\rightarrow Fe^{3+}_{0.6}Mn^{2+}_{0.4}$ (heterosite). Triphylite may directly oxidize into heterosite when the manganese content in it is lower than 25 %. We can
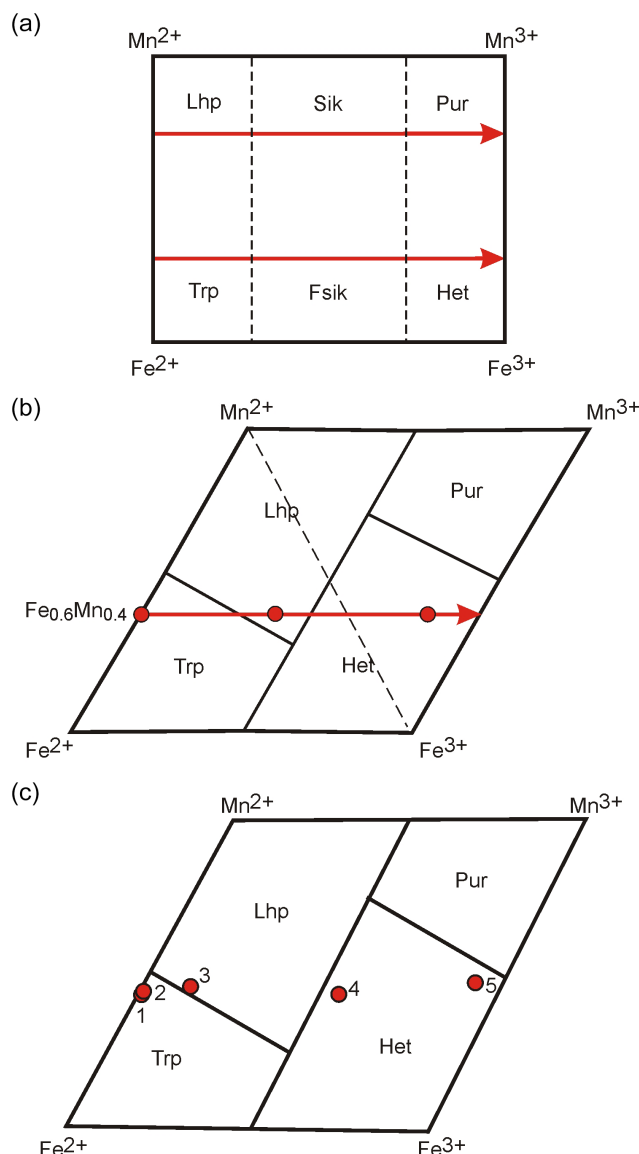
Figure 4. Change in mineral species during oxidation of various original compositions. **(a)** Traditional view on the change in mineral species in the Quensel–Mason sequence. Elements located in vertices of the rectangle emphasize the view on simultaneous oxidation of iron and manganese. **(b)** Change in the original triphylite under partial oxidation to lithiophilite and complete oxidation to heterosite in the diagram Fe^{2+}–Mn^{2+}–Mn^{3+}–Fe^{3+} where boundaries between minerals species are in accordance with the IMA rules. A shift in the line Mn^{2+}–Mn^{3+} in relation to the line Fe^{2+}-Fe^{3+} points out that iron oxidizes before manganese. **(c)** Triphylite series from Varuträsk (Quensel, 1937) at the diagram. Data are presented in the Supplement. Points: 1 – fresh blue triphylite; 2 – wine-yellow triphylite; 3 – somewhat oxidized triphylite; 4 – ferrisicklerite, with outer ring surrounding the fresh triphylite; and 5 – heterosite.
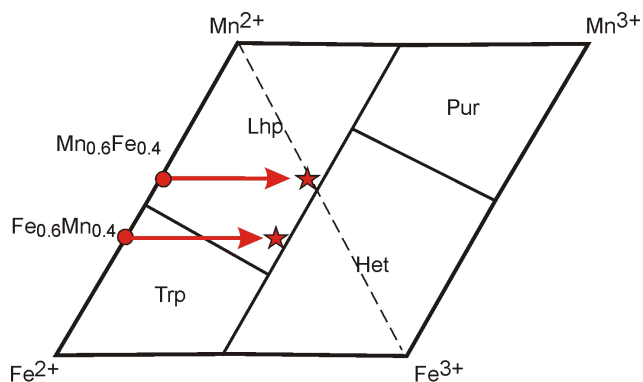
Figure 5. Example of mineral species change under oxidation of minerals with a different ratio of iron and manganese in the diagram: Fe^{2+}-Mn^{2+}-Mn^{3+}-Fe^{3+}.

also show this feature by choosing as an example the chemical composition of triphylite analyzed by Quensel (1937) (see analysis of triphylite 3 in the Supplement and point 3 in Fig. 4c), which enters the lithiophilite field during oxidation.

The reason for this unexpected behavior is the different oxidation capacity (oxidation potential) of manganese and iron. During the oxidation of minerals of the triphylite–lithiophilite series with any ratio of components, iron oxidizes first. Consequently, in products of oxidation of minerals with different values of $Fe/(Fe + Mn)$, i.e., with different contents of total iron (= initially different mineral species), the amount of Fe^{3+} can finally be similar. Then, newly formed phases will be related to one mineral species (Fig. 5). Thus, mineral phases with values $Fe/(Fe + Mn) > 0.5$ cannot always be considered to represent iron end-members (triphylite–ferrisicklerite–heterosite), and those with values $Fe/(Fe + Mn) < 0.5$ are not always manganese end-members (lithiophilite–sicklerite–purpurite).

Consequently, the problem can only be solved by discarding the traditional views on succession of mineral species during oxidation. In other words, it is necessary to separate the concepts of the origin of the mineral and the boundaries of the species, and it should be recognized that the paragenetic relations between minerals cannot be connected in any way with an unambiguously defined formula for the species. Resolution of this rigid contradiction is rather distressing but essential.

The contradictory history goes back to the past when authors devoted little attention to the fact that despite being crystal chemically similar, manganese and iron have significantly different oxidation potentials. Indeed, if manganese and iron would oxidize more or less simultaneously, the problem with formulae would be non-existent; i.e., a cation prevailing in an original mineral in the divalent form would also prevail in its successor in the trivalent form. For that reason, the simple Quensel–Mason sequence was created and

is still often used in publications. Starting from Fontan et al. (1976), differences in the behavior of iron and manganese were taken into account, and along with this comprehension, the confusion with formulae appeared. It is not obvious when a composition is mainly ferric or mainly manganoan; however, it is intractable for intermediate compositions.

6   Calculation of empirical formulae

As shown in Sect. 2, it is difficult to identify the triphylite-group minerals based on common available methods for chemical composition. It is clear that wet chemical methods using substance quantities are not suitable, taking into account the material heterogeneity due to, among other things, the well-known process of triphylite and lithiophilite oxidation. It is also evident that the most commonly used local microprobe analysis (EPMA) does not provide necessary data for the calculation in the case of Li-containing minerals. However, it is sufficient to additionally define lithium using one of the methods and make assumptions that iron oxidizes first; i.e., Mn^{3+} is introduced in the formula only when Fe^{2+} is completely absent.

Microprobe analyses provide data on the contents of Fe_{total} and Mn_{total} without dividing them into +2 and +3 valency states and provide no data on the lithium content. As a result, if we do not consider Mg, Na, and other minor elements, we obtain five unknown variables, i.e., Li, Fe^{2+}, Mn^{2+}, Fe^{3+}, and Mn^{3+}, two pairs of which are connected by equations

$$Fe^{2+} + Fe^{3+} = Fe_{total}, \tag{1}$$

$$Mn^{2+} + Mn^{3+} = Mn_{total}. \tag{2}$$

We obtain one of the unknown variables – Li content – by measuring it directly or, if such opportunity is absent, from single-crystal X-ray diffraction (SCXRD) data:

$$Li \text{ apfu} = \text{occupancy } M1 - (Na + K), \text{ apfu}. \tag{3}$$

The total content of trivalent cations $R^{3+} = (Fe^{3+} + Mn^{3+})$ in the $M2$ site is taken to be equal to

$$R^{3+} = 1 - \text{occupancy } M1 \text{ or}$$

$$R^{3+} = 1 - (Li + Na + K), \text{ apfu}. \tag{4}$$

Based on these relations and assuming condition (5) of gradual rather than simultaneous oxidation of the elements, we get an amount of Fe^{2+}, Mn^{2+}, Fe^{3+}, and Mn^{3+}. The gradual oxidations mean that iron oxidizes first and completely. Manganese starts oxidizing only when all iron have transitioned into the oxidizing (Fe^{3+}) state (see Sect. 4).

For convenience the calculation procedure for Li-containing minerals is given in Algorithm 1.

The examples of the calculation according to proposed procedures are presented in Table 3.

Algorithm 1. Calculation algorithm for Li-bearing phosphates.

1	calculation of cation numbers for Fe_{total} and Mn_{total}
2	calculation of total content of trivalent cations as
	$R^{3+} = 1 -$ occupancy $M1$ (from SCXRD data) or
	$R^{3+} = 1 - (Li+Na+K)$, apfu (from chemical data)

	If $R^{3+}<Fe_{total}$	If $R^{3+}>Fe_{total}$
3	$R^{3+} = Fe^{3+}$	$R^{3+} = Fe_{total} + Mn^{3+}$
4	$Fe^{2+} = Fe_{total} - Fe^{3+}$	$Mn^{3+} = R^{3+} - Fe_{total}$
5	$Mn^{3+} = 0$	$Fe^{2+} = 0$
		$Fe^{3+} = Fe_{total}$
6	$Mn^{2+} = Mn_{total}$	$Mn^{2+} = Mn_{total} - Mn^{3+}$

Table 3. Calculation of trivalent cations and lithium contents according to proposed algorithm.

Mineral	Ferrisicklerite Tri-87		Synth. ferrisicklerite Tri-77	
P_2O_5	46.00		44.9	
SiO_2	0.25		0.24	
Fe_2O_3	35.80[a]	35.94[b]	36.7[a]	34.57[b]
FeO	2.42[a]	2.34[b]	2.87[a]	4.57[b]
MgO	1.60		1.61	
MnO	9.80		11.1	
Na_2O	0.10		0	
K_2O	0.30		0.11	
Li_2O	2.90[c]			4.73[b]
Total	99.17	99.23[b]	97.53	101.83[b]
Occupancy M1			0.32	
apfu on the basis	O = 4	P + Si = 1	P + Si = 1	
P	1.01	0.99	0.99	
Si	0.01	0.01	0.01	
Fe^{3+}	0.65	0.69	0.72	
Fe^{2+}	0.05	0.05	0.06	
Mg	0.06	0.06	0.06	
Mn	0.22	0.21	0.25	
Na	0.01	0.00	0.00	
K	0.01	0.01	0.00	
Li	0.30	0.30	0.32[b]	
Calculation according to proposed algorithm				
$R^{3+} = 1 - (Li + Na + K)$		0.69	$R^{3+} = 1 -$ occupancy $M1$	0.68
R^{3+} vs. Fe tot		0.69 < 0.74		0.68 < 0.78
Fe^{3+}		0.69		0.68
Fe^{2+}		0.05		0.10
Mn^{3+}		0		0

Ferrisicklerite Tri-87 and synth. ferrisicklerite Tri-77 from Schmid-Beurmann et al. (2013). These compositions correspond to heterosite according to proposed classification. [a] Determined by Mössbauer spectroscopy. [b] Calculated according to proposed algorithm. [c] Determined by SIMS.

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