

THE CRYSTAL CHEMISTRY OF OLIVINE-TYPE PHOSPHATES

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INTRODUCTION

Iron-manganese phosphates are common accessory minerals occurring in granitic pegmatites, in metamorphic rocks, and in meteorites. In rare elements pegmatites, primary phosphates of the triphylite-lithiophilite series $[\text{Li}(\text{Fe}^{2+}, \text{Mn}^{2+})(\text{PO}_4)\text{-Li}(\text{Mn}^{2+}, \text{Fe}^{2+})(\text{PO}_4)]$ form masses that can reach several meters in diameter, enclosed in silicates. During the oxidation processes affecting the pegmatites, these olivine-type phosphates progressively transform to ferrisicklerite-sicklerite $[\text{Li}_{1-x}(\text{Fe}^{3+}, \text{Mn}^{2+})(\text{PO}_4)\text{-Li}_{1+x}(\text{Mn}^{2+}, \text{Fe}^{3+})(\text{PO}_4)]$ and to heterosite-purpurite $[(\text{Fe}^{3+}, \text{Mn}^{3+})(\text{PO}_4)\text{-}(\text{Mn}^{3+}, \text{Fe}^{3+})(\text{PO}_4)]$, according to the substitution mechanism $\text{Li}^+ + \text{Fe}^{2+} \rightarrow + \text{Fe}^{3+}$. This oxidation sequence was first observed by Quensel (1937), and then confirmed by Mason (1941).

The crystal structure of minerals of the triphylite-lithiophilite series (triphylite: $a = 4.690$, $b = 10.286$, $c = 5.987$ Å, $Pbnm$) has been investigated from synthetic samples and natural minerals (Finger & Rapp 1969, Losey *et al.* 2004), and is characterized by two chains of edge-sharing octahedra parallel to the c axis. The first chain is constituted by the $M(1)$ octahedra occupied by Li, while the second chain is formed by the $M(2)$ sites occupied by Fe and Mn. The chains are connected in the b direction by sharing edges of their octahedral sites, and the resulting planes are connected in the a direction by the PO_4 tetrahedra. Natrophilite, NaMnPO_4 , is another pegmatite phosphate with the olivine structure, in which the $M(1)$ site is occupied by Na while the $M(2)$ site contains the smaller divalent cations (Moore 1972).

Since the electrochemical investigation of $\text{LiFe}(\text{PO}_4)$ by Padhi *et al.* (1997), an increasing number of papers devoted to olivine-type phosphates were published. The exceptional performance of triphylite as cathode material for Li-ion batteries has initiated an increasing interest for these phosphates, which are now produced industrially and used in batteries for many applications such as electric cars, electric bicycles, or for the storage of green energy.

This paper presents new structural and chemical data on natural olivine-type phosphates, data that will help us to shed some light on the crystal chemistry of this complex group of minerals.

ANALYTICAL METHODS

Electron-microprobe analyses were performed with a Cameca SX-50 instrument located in Bochum, Germany (analyst H.-J. Bernhardt), which operated in the wavelength-dispersion mode with an accelerating voltage of 15 kV and a beam current of 15 nA. The standards used were grafftonite from Kabira (for Fe, Mn, P), pyrope (Mg, Al, Si), ZnO (Zn), andradite (Ca), jadeite (Na), and a K-glass (K).

The Li_2O contents were determined with a Cameca IMS 4f ion microprobe (SIMS) installed at CNR-IGG, Pavia (Italy). We used a 12.5-kV accelerated $^{16}\text{O}^-$ primary-ion beam with a current intensity in the range 0.8–4 nA, corresponding to a beam diameter of 3–6 mm. The samples were polished, washed in an ultrasonic tank with ethanol, and Pt coated (400 Å thickness) before analysis. Secondary-ion signals of the following isotopes $^6\text{Li}^+$, $^{31}\text{P}^+$ and $^{57}\text{Fe}^+$ were detected at the electron multiplier. Acquisition times were 3 seconds for Li and P (each), and 6 seconds for Fe over 3 cycles. Analyses were done under *steady-state* sputtering conditions after 360-second sputtering using ~75–125 eV secondary ions. The choice of medium-to-high-energy (*energy filtering*) secondary ions as analytical ones is particularly useful to reduce matrix effects affecting light-element ionization and improve the reproducibility of analysis. We used as reference material for SIMS Li-analyses triphylite from the Buranga pegmatite, Rwanda; more details concerning the SIMS analytical procedure are given by Hatert *et al.* (2010).

The crystal structures of the samples were refined from data obtained by single-crystal X-ray diffraction techniques, with an Oxford Diffraction Gemini PX Ultra 4-circle diffractometer using the MoK_α radiation (50 kV, 40 mA).

TABLE 1. Chemical compositions of the olivine-type phosphates investigated in this study.

Sample	Mineral	Locality	Composition
PK-17	Triphylite	Hagendorf-Süd, Germany	$\text{Li}_{0.99}(\text{Fe}^{2+}_{0.73}\text{Fe}^{3+}_{0.05}\text{Mn}^{2+}_{0.19}\text{Mg}_{0.01})\text{PO}_4$
PK-20	Triphylite	Engelbrechts Claim, Brandberg, Namibia	$\text{Li}_{1.06}(\text{Fe}^{2+}_{0.65}\text{Mn}^{2+}_{0.34})\text{PO}_4$
K9-5-6 (colourless)	Lithiophilite	Koktokay #3 pegmatite, Altai, China	$\text{Li}_{0.93}(\text{Fe}^{2+}_{0.03}\text{Fe}^{3+}_{0.13}\text{Mn}^{2+}_{0.80})\text{PO}_4$
K9-5-6 (light yellow)	Lithiophilite-sicklerite	Koktokay #3 pegmatite, Altai, China	$\text{Li}_{0.96}(\text{Fe}^{2+}_{0.08}\text{Fe}^{3+}_{0.08}\text{Mn}^{2+}_{0.81})\text{PO}_4$
K9-5-6 (yellow)	Lithiophilite-sicklerite	Koktokay #3 pegmatite, Altai, China	$\text{Li}_{0.88}(\text{Fe}^{3+}_{0.16}\text{Mn}^{2+}_{0.80}\text{Mn}^{3+}_{0.01})\text{PO}_4$
K9-5-6 (orange)	Lithiophilite-sicklerite	Koktokay #3 pegmatite, Altai, China	$\text{Li}_{0.82}(\text{Fe}^{3+}_{0.16}\text{Mn}^{2+}_{0.75}\text{Mn}^{3+}_{0.06})\text{PO}_4$
K9-5-6 (deep orange)	Sicklerite	Koktokay #3 pegmatite, Altai, China	$\text{Li}_{0.69}(\text{Fe}^{3+}_{0.16}\text{Mn}^{2+}_{0.62}\text{Mn}^{3+}_{0.19})\text{PO}_4$
AB-2-2	Ferrisicklerite	Cañada pegmatite, Spain	$\text{Li}_{0.17}(\text{Fe}^{3+}_{0.75}\text{Mn}^{2+}_{0.08}\text{Mn}^{3+}_{0.10}\text{Mg}_{0.06})\text{PO}_4$
AB-X1-2-ME-3	Ferrisicklerite	Cañada pegmatite, Spain	$\text{Li}_{0.19}(\text{Fe}^{3+}_{0.57}\text{Mn}^{3+}_{0.19}\text{Mg}_{0.24})\text{PO}_4$
AB-X1-2-TB-5	Ferrisicklerite	Cañada pegmatite, Spain	$\text{Li}_{0.23}(\text{Fe}^{3+}_{0.67}\text{Mn}^{2+}_{0.14}\text{Mn}^{3+}_{0.10}\text{Mg}_{0.07})\text{PO}_4$
PK-1	Ferrisicklerite	McDonalds Claim, Brandberg, Namibia	$\text{Li}_{0.15}(\text{Fe}^{3+}_{0.67}\text{Mn}^{2+}_{0.13}\text{Mn}^{3+}_{0.12}\text{Mg}_{0.07})\text{PO}_4$
PK-18	Ferrisicklerite	Strathmore tin mine, Namibia	$\text{Li}_{0.18}(\text{Fe}^{3+}_{0.73}\text{Mn}^{2+}_{0.11}\text{Mn}^{3+}_{0.10}\text{Mg}_{0.06})\text{PO}_4$
PK-3	Heterosite	Ariakas, Usakos, Namibia	$(\text{Fe}^{3+}_{0.64}\text{Mn}^{2+}_{0.05}\text{Mn}^{3+}_{0.31}\text{Mg}_{0.01})\text{PO}_4$
PK-15	Heterosite	Sandamap, Usakos, Namibia	$\text{Li}_{0.02}(\text{Fe}^{3+}_{0.70}\text{Mn}^{3+}_{0.25}\text{Mg}_{0.03})\text{PO}_4$

CHEMICAL COMPOSITION

SIMS analyses of six natural triphylite samples show lithium contents from 9.51 to 9.88 wt. % Li_2O , while the analyses of four lithiophilites show higher Li_2O contents ranging from 10.23 to 11.15 wt. %. These compositions correspond to 0.99-1.04 Li atoms per formula unit (*a.p.f.u.*) in triphylites, and 1.07-1.15 Li *a.p.f.u.* in lithiophilites. The significant Li enrichment of lithiophilites indicates that Li can also occur in the *M*(2) site of the olivine structure. Eleven ferrisicklerite samples show Li_2O -contents from 1.65 to 2.84 wt. % (= 0.17 to 0.29 *a.p.f.u.*), and three heterosite samples contain 0.16 to 0.21 wt. % Li_2O (= 0.02 *a.p.f.u.*). The presence of significant amounts of Li in heterosites was unexpected, and the low Li content of ferrisicklerites indicates that trivalent manganese also occurs in this mineral. The formula of Li-poor ferrisicklerite corresponds to $\text{Li}_{0.17}(\text{Fe}^{3+}_{0.75}\text{Mn}^{3+}_{0.10}\text{Mn}^{2+}_{0.08}\text{Mg}_{0.06})(\text{PO}_4)$ (Table 1).

In order to shed some light on the chemical and structural modifications induced by the oxidation processes affecting lithiophilite, we investigated a natural sample from the Altai Mountains, China, in which a progressive transition from lithiophilite to sicklerite is observed. Under the polarizing microscope, lithiophilite is colorless, whereas sicklerite shows a deep orange color. Several grains also show intermediate

colors, suggesting a progressive transition from lithiophilite to sicklerite. This progressive transition is confirmed by the SIMS analyses, which indicate Li values from 0.96 to 0.69 Li *a.p.f.u.* (Table 1).

STRUCTURAL DATA

The crystal structures of 14 natural olivine-type phosphates were refined to an R_1 factor from 2.19 to 8.24 %, and the unit-cell parameters of these minerals are given in Table 2. The structures show an ordered cationic distribution, with Li located on the *M*(1) site, and with the divalent cations Fe, Mn, and Mg located on *M*(2). The refined site occupancy factors of Li on *M*(1) are in the ranges 0.93-0.95 for triphylites, 0.22-0.59 for ferrisicklerites, and 0-0.09 for heterosites. In the sample from the Altai (China), the occupancy factors on *M*(1) range from 0.99 Li *p.f.u.* (lithiophilite) to 0.75 Li *p.f.u.* (sicklerite). These values are in good agreement with the values measured by SIMS.

In the crystal structure of heterosite, Eventoff & Martin (1972) noticed that the *M*(1) site was empty, and that the complete oxidation of iron and manganese induced a Jahn-Teller distortion of the $\text{M}(2)\text{O}_6$ octahedron, characterized by two short bonds (1.912-1.914 Å) and four long bonds (2.030-2.163 Å). This observation is confirmed by our data, which show distortion coefficients (Bond length distortion,

TABLE 2. Cryst

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TABLE 2. Crystal data for the olivine-type phosphates investigated in this study.

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)	R _i (%)
PK-17	4.704(1)	10.365(1)	6.025(1)	293.7(1)	4.07
PK-20	4.711(1)	10.369(1)	6.038(7)	294.9(1)	3.56
K9-5-6 (colourless)	4.736(1)	10.432(2)	6.088(1)	300.8(1)	2.53
K9-5-6 (light yellow)	4.734(1)	10.423(2)	6.094(1)	300.7(1)	2.36
K9-5-6 (yellow)	4.740(1)	10.415(1)	6.080(1)	300.1(1)	2.94
K9-5-6 (orange)	4.767(1)	10.403(2)	6.072(1)	301.1(1)	2.67
K9-5-6 (deep orange)	4.765(1)	10.338(1)	6.060(1)	298.5(1)	2.19
AB-2-2	4.787(2)	9.954(3)	5.875(2)	280.0(2)	5.87
AB-X1-2-ME-3	4.776(3)	10.035(3)	5.883(3)	282.0(3)	8.24
AB-X1-2-TB-5	4.797(3)	9.978(5)	5.881(3)	281.5(3)	6.92
PK-1	4.795(1)	9.979(2)	5.890(1)	281.8(1)	4.01
PK-18	4.795(2)	9.959(6)	5.892(3)	281.3(3)	4.92
PK-3	4.776(3)	9.732(3)	5.826(3)	270.8(2)	6.32
PK-15	4.777(2)	9.776(3)	5.817(2)	271.7(2)	5.76

BLD) between 2.69 and 3.54 % for triphylites and ferrisicklerites, and between 4.46 and 5.01 % for heterosites.

Fransolet *et al.* (1984) investigated twenty natural and five synthetic olivine-type phosphates of the triphylite-lithiophilite series by X-ray powder diffraction, and established correlations between the unit-cell parameters and the chemical composition. We also attempted to correlate the unit-cell parameters of natural and synthetic Li-bearing olivine-type phosphates with the mean ionic radius of the cations occurring on the M(2) site. These correlations are excellent and generally follow Vegard's law, except for the *c* parameter which has been fitted with a second order polynomial curve. The correlations can be used to predict the unit-cell parameters of olivine-type phosphates, but also to estimate the Fe/(Fe+Mn) ratio within the triphylite-lithiophilite solid solution. Starting from the unit-cell parameters published by Fransolet *et al.* (1984) and by Losey *et al.* (2004) on natural minerals of the triphylite group, we estimated Fe/(Fe+Mn) ratios which fit fairly to those obtained by chemical analysis, except when the Mg content of the phosphates is higher than 0.016 atoms per formula unit (*a.p.f.u.*). Indeed, an increase of the Mg content induces a significant overestimation of the Fe/(Fe+Mn) ratio, which is characterized by an error reaching 35% for a Mg content of 0.23 *a.p.f.u.*

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