

## CRYSTAL CHEMISTRY AND GEOTHERMOMETRIC APPLICATIONS OF PRIMARY PEGMATITE PHOSPHATES

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### Introduction

Iron-manganese phosphate minerals are widespread in medium to highly evolved LCT granitic pegmatites, ranging from the beryl-columbite-phosphate subtype to the spodumene subtype. These phosphates play an essential geochemical role in the evolution processes affecting pegmatites, and a good knowledge of their crystal chemistry and of their stability fields is absolutely necessary to better understand the genesis of pegmatites. Among iron-manganese phosphates, several groups are of peculiar interest, since they form primary (magmatic) or high-temperature hydrothermal minerals. These groups are phosphates of the triphylite-lithiophilite [ $\text{Li}(\text{Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$ - $\text{Li}(\text{Mn}^{2+}, \text{Fe}^{2+})\text{PO}_4$ ], karenwebberite-natrophilite [ $\text{Na}(\text{Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$ - $\text{Na}(\text{Mn}^{2+}, \text{Fe}^{2+})\text{PO}_4$ ], and sarcopside-zavaláite series [ $(\text{Fe}^{2+}, \text{Mn}^{2+})_3(\text{PO}_4)_2$ - $(\text{Mn}^{2+}, \text{Fe}^{2+})_3(\text{PO}_4)_2$ ], as well as alluaudite- and wylieite-type phosphates. The crystal-chemical features of these minerals, as well as some experimental data on their stability fields, will be successively presented in this lecture. They demonstrate how a global approach, combining laboratory experiments with petrographic and crystallographic measurements on natural samples, is necessary to decipher all aspects of these complex minerals.

### Primary Li- and Na-bearing phosphates of the triphylite group

In pegmatites, primary phosphates of the triphylite-lithiophilite series 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 [ $(\text{Fe}^{3+}, \text{Mn}^{3+})(\text{PO}_4)$ - $(\text{Mn}^{3+}, \text{Fe}^{3+})(\text{PO}_4)$ ], according to the substitution mechanism  $\text{Li}^+ + \text{Fe}^{2+} \rightarrow [] + \text{Fe}^{3+}$ .

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 (Hatert *et al.* 2011a, 2012), and is characterized by two types of octahedral sites: the *M*(1) octahedra

occupied by Li, and the *M*(2) sites occupied by Fe and Mn. A natural sample from the Altai Mountains, China, was recently investigated by Hatert *et al.* (2012), in order to understand the structural variations occurring during the oxidation of lithiophilite into sicklerite. Five single-crystals, corresponding to intermediate members of the lithiophilite-sicklerite series, were extracted from a thin section and are orthorhombic, space group *Pbnm*, with unit-cell parameters ranging from  $a = 4.736(1)$ ,  $b = 10.432(2)$ ,  $c = 6.088(1)$  Å (lithiophilite) to  $a = 4.765(1)$ ,  $b = 10.338(2)$ ,  $c = 6.060(1)$  Å (sicklerite). The structures show a topology identical to that of olivine-type phosphates, with Li occurring on the *M*(2) site and showing occupancy factors from 0.99 Li atoms per formula unit (*p.f.u.*) (lithiophilite) to 0.75 Li *p.f.u.* (sicklerite). These values are in good agreement with the values measured by SIMS (Secondary Ion Mass Spectrometry), which indicate Li values from 0.96 to 0.69 Li *p.f.u.*

Natrophilite,  $\text{NaMnPO}_4$ , 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. Recently, the Fe-analogue of natrophilite was found at the Malpensata granitic pegmatite, Colico commune, Lecco province, north Italy (Vignola *et al.* 2011). This phosphate,  $\text{Na}(\text{Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$ , has been named karenwebberite in honour of Dr. Karen Louise Webber, Assistant Professor Research at the Mineralogy, Petrology and Pegmatology Research Group, Department of Earth and Environmental Sciences, University of New Orleans, Louisiana, U.S.A. (IMA 2011-015). It forms late stage magmatic exsolution lamellae up to 100µm thick, hosted in graftonite and associated with Na-bearing ferrisicklerite and with an heterosite-like phase (Fig. 1a). Karenwebberite is orthorhombic, space group *Pbnm*,  $a = 4.882(1)$ Å,  $b = 10.387(2)$ Å,  $c = 6.091(1)$ Å,  $V = 308.9(1)$ Å<sup>3</sup>, and  $Z = 4$ . The mineral shows the olivine structure, with *M*(1) occupied by Na and *M*(2) occupied by Fe and Mn.

Karenwebberite is also a polymorph of maričite,  $\text{NaFePO}_4$  ( $a = 6.861(1)$ ,  $b = 8.987(1)$ ,  $c = 5.045(1)$  Å, *Pmnb*), which shows a crystal structure distinct

around 325°C (P = 100 bars). Hydrothermal investigations performed on alluaudite-type phosphates at 1 kbar (Harter *et al.* 2006 and 2011b) also produced several maricite-type phosphates with various Fe/(Fe+Mn) ratios; these results indicate a transition temperature of about 500–550°C between karenewebberite and maricite. Consequently, karenewebberite certainly crystallized below 550°C in the Malpensata dyke.

from that of olivine. This polymorphic relationship is of particular interest, since the transformation between olivine-type and maricite-type phosphates is temperature-dependant, as shown experimentally by Corlett and Armbruster (1979). These authors confirmed that olivine-type  $\text{Na(Fe,Mn)PO}_4$  phosphates are low-temperature polymorphs of maricite-type phosphates, and that the transition between the two polymorphs of  $\text{NaMnPO}_4$  occurs

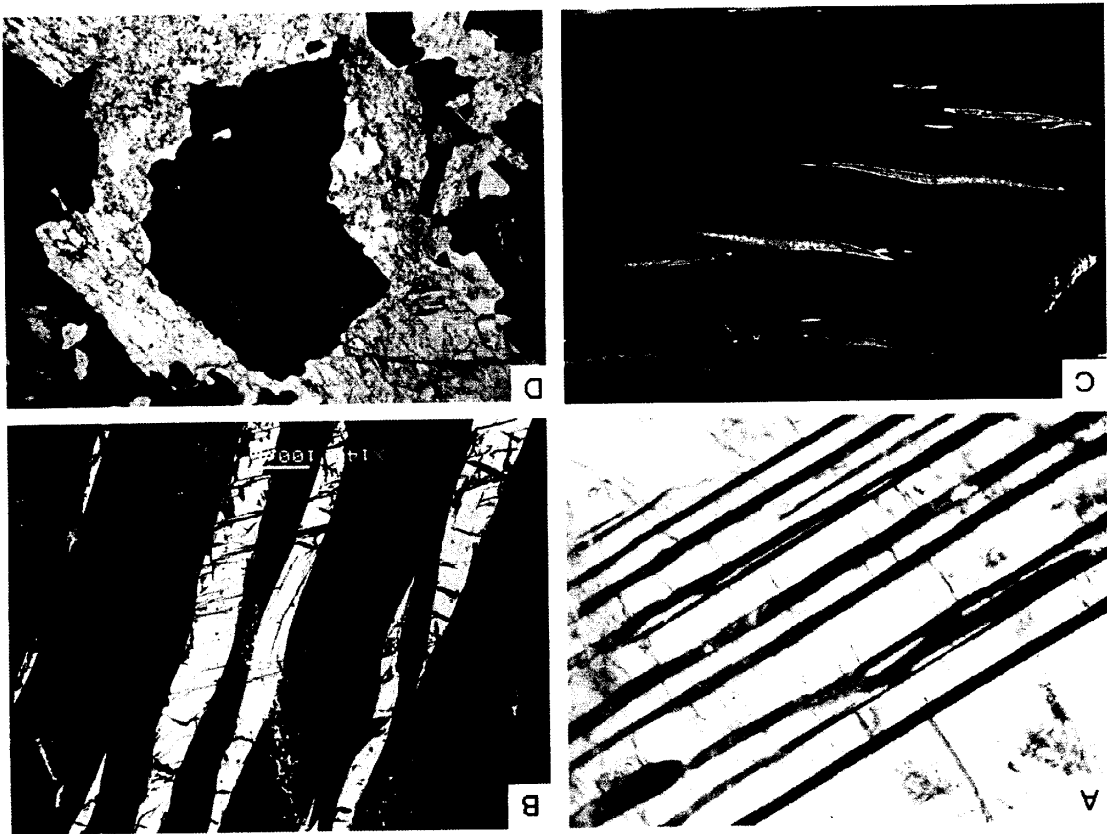


Fig. 1: A) Exsolution lamellae of karenewebberite (light brown), oxidized into Na-bearing ferrisicklerite (dark brown) and included in graptone. Malpensata pegmatite, Colico, Italy (plane polarized light; the length of the photograph is 1.5 mm). B) Triphylite (dark grey) including lamellae of sarcopside (white), Canada pegmatite, Spain (sample SS-3, BSE image). C) Lamellae of zavaite included in lithiophyllite, La Empeada pegmatite, San Luis, Argentina (crossed polars; the length of the photograph is 2.5 mm). D) Rim of qingheite-( $\text{Fe}^{2+}$ ) (brown) surrounding frondelite (red) in a quartz-albite matrix. Sebastião Cristino, Minas Gerais, Brazil (plane polarized light, sample SC-34).

**Phosphates of the sarcopside group and their exsolution textures**

Lamellar triphylite + sarcopside  $[\text{Fe,Mn}_3(\text{PO}_4)_2]$  associations are well known in numerous rare-element granitic pegmatites (Fig. 1b). These intergrowths are traditionally interpreted as exsolution textures, and Moore (1972) suggests the existence of a complete  $\text{Li(Fe,Mn)(PO}_4\text{)-}$   $(\text{Fe,Mn}_3(\text{PO}_4)_2)$  solid solution at high temperature. According to this hypothesis, exsolutions of

unique phase. Harter *et al.* (2007) performed hydrothermal experiments between 400 and 700°C (1 kbar), in order to determine the stability field of the triphylite + sarcopside assemblage. These experiments indicate that the triphylite + sarcopside assemblage is a primary assemblage in granitic pegmatites, since

sarcopside into triphylite, or of triphylite into sarcopside, would appear during cooling, depending on the composition of the parent high-temperature

it has been reproduced hydrothermally at 500 and 700°C (1 kbar). The electron-microprobe and SIMS analyses of these synthetic phosphates show that the Li content of triphylites significantly increases with temperature, from 0.72 *a.p.f.u.* at 400°C, to 0.037 *a.p.f.u.* at 700°C, for the  $\text{LiFe}_{2.5}(\text{PO}_4)_2$  starting composition. By comparison with the analytical data collected on natural assemblages, these experimental results provide a relatively accurate determination of the temperature at which the exsolutions crystallized.

Zavalíaite, ideally  $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})_3(\text{PO}_4)_2$ , is a new phosphate mineral species from the La Empleada granitic pegmatite, San Luis province, Argentina (Hatert *et al.* 2013), which forms exsolution lamellae occurring within lithiophilite (Fig. 1c). Zavalíaite is the  $\text{Mn}^{2+}$ -rich equivalent of sarcopside and of chopinite  $[(\text{Mg}, \text{Fe})_3(\text{PO}_4)_2]$ , and belongs to the sarcopside group of minerals. Its single-crystal unit-cell parameters are  $a = 6.088(1)$ ,  $b = 4.814(1)$ ,  $c = 10.484(2)$  Å,  $\beta = 89.42(3)^\circ$ ,  $V = 307.2(1)$  Å<sup>3</sup>, space group  $P2_1/c$ . The mineral is named in honour of María Florencia de Fátima Márquez Zavalía (or Márquez-Zavalía (1955-)), researcher and Head of the Department of Mineralogy Petrography and Geochemistry, IANIGLA, CCT Mendoza, CONICET, Argentina, for her contribution to the knowledge of Argentinean mineralogy.

The genesis of zavalíaite lamellae is compared to the genetical processes responsible for the formation of sarcopside lamellae observed in triphylite. Exsolutions of zavalíaite appeared during the cooling of primary, Li-poor lithiophilite; consequently, this mineral can be considered as a primary phosphate, which crystallized under pegmatitic conditions similar to those of lithiophilite formation. Starting from the proportions of zavalíaite in the exsolution textures (less than 10% zavalíaite), and using the experimental triphylite-sarcopside geothermometer described by Hatert *et al.* (2007, 2009), a temperature of ca. 300°C can be estimated for the crystallisation of zavalíaite exsolutions. This temperature is in good agreement with those occurring in such lithiophilite-rich evolved pegmatites.

#### **Alluaudite- and wylieite-type phosphates: the transition between primary minerals and Na-metasomatic phases**

The alluaudite group of minerals consists of Na-Mn-Fe-bearing phosphates which are known to occur in Li-rich granitic pegmatites. Due to their

flexible crystal structure, which is able to accommodate  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in variable amounts, alluaudites are very stable and crystallize from the first stages of pegmatite evolution to the latest oxidation processes. These minerals exhibit chemical compositions ranging from  $\text{Na}_2\text{Mn}(\text{Fe}^{2+}\text{Fe}^{3+})(\text{PO}_4)_3$  to  $\text{NaMnFe}^{3+}_2(\text{PO}_4)_3$ , with  $\text{Mn}^{2+}$  or some  $\text{Ca}^{2+}$  replacing  $\text{Na}^+$ ,  $\text{Fe}^{2+}$  replacing  $\text{Mn}^{2+}$ , and some  $\text{Mg}^{2+}$  or  $\text{Mn}^{2+}$  replacing iron. The alluaudite structure was described on a natural sample from the Buranga pegmatite, Rwanda. The mineral is monoclinic, space group  $C2/c$ , and the structural formula corresponds to  $X(2)X(1)M(1)M(2)_2(\text{PO}_4)_3$ , with four formula units per unit cell. The structure consists of kinked chains of edge-sharing octahedra stacked parallel to  $\{101\}$ . These chains are formed by a succession of  $M(2)$  octahedral pairs linked by highly distorted  $M(1)$  octahedra. Equivalent chains are connected in the  $b$  direction by the  $P(1)$  and  $P(2)$  phosphate tetrahedra to form sheets oriented perpendicular to  $[010]$ . These interconnected sheets produce channels parallel to the  $c$  axis, channels which contain the  $X$  sites.

Hatert *et al.* (2006) explored the geothermometric potential of the  $\text{Na}_2(\text{Mn}_{1-x}\text{Fe}^{2+}_x)_2\text{Fe}^{3+}(\text{PO}_4)_3$  solid-solution series ( $x = 0$  to 1), which represents the compositions of natural weakly oxidized alluaudites; they performed hydrothermal experiments between 400 and 800°C, at 1 kbar. Under an oxygen fugacity controlled by the Ni/NiO buffer, single-phase alluaudites crystallize at 400 and 500°C, whereas the association alluaudite + mariçite appears between 500 and 700°C. The limit between these two fields corresponds to the maximum temperature that can be reached by alluaudites in granitic pegmatites, because mariçite has never been observed in these geological environments. Because alluaudites are very sensitive to variations of oxygen fugacity, the field of hagendorfite,  $\text{Na}_2\text{MnFe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ , has been positioned in the  $f(\text{O}_2)$ - $T$  diagram, and provides a tool that can be used to estimate the oxygen fugacity conditions which prevailed in granitic pegmatites during the crystallization of this phosphate.

Hydrothermal experiments were also performed by Hatert & Fransolet (2006) in the Na- $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  (+ $\text{PO}_4$ ) ternary system, between 400 and 700°C, at 1 kbar. Alluaudite-type phosphates were observed between 400 and 700°C, and occupy the central part of the Na- $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  diagram. Electron-microprobe

analyses indicate that the compositional field of alluaudites covers ca. 10 % of the diagram surface at 400°C, but only ca. 2-3 % at 500 and 600°C. The results of these experiments are applicable to Fe-rich alluaudites, as for example ferrohagendorfite from Angarf-sud, Morocco, which exhibits an ideal chemical composition  $\text{Na}_2\text{Fe}^{2+}_2\text{Fe}^{3+}(\text{PO}_4)_3$ . Alluaudite-type compounds with similar compositions were obtained between 400 and 700°C in the hydrothermal experiments, thus confirming again the existence of primary alluaudites in granitic pegmatites.

In order to constrain the conditions of temperature and oxygen fugacity which occurred in pegmatites, we also decided to reproduce experimentally several associations of pegmatite phosphates. Primary alluaudite + triphylite assemblages were reported in the Hagendorf-Süd (Germany), Buranga, and Kibingo (Rwanda) pegmatites, and the hydrothermal experiments ( $P = 1$  kbar,  $T = 400$ - $800^\circ\text{C}$ ) lead to the crystallisation of alluaudite + triphylite at 400 and 500°C, and of alluaudite + triphylite + mariçite at 600 and 700°C (Hatert *et al.* 2011b). In these experiments, significant amounts of Na were observed in synthetic triphylites; the Na content of triphylites consequently constitutes a geothermometric tool that can be used to constrain the temperature conditions in which the alluaudite + triphylite assemblages crystallized in pegmatites.

Qingheite-( $\text{Fe}^{2+}$ ), ideally  $\text{Na}_2\text{Fe}^{2+}\text{MgAl}(\text{PO}_4)_3$ , is a new mineral species recently described in the Sebastião Cristino pegmatite, Minas Gerais, Brazil (Hatert *et al.* 2010). It occurs as rims around frondelite grains, included in a matrix of quartz and albite (Fig. 1d). The mineral exhibits a wyllieite-type structure, topologically identical to that of alluaudite, with single-crystal unit-cell parameters  $a = 11.910(2)$ ,  $b = 12.383(3)$ ,  $c = 6.372(1)$  Å,  $\beta = 114.43(3)^\circ$ ,  $V = 855.6(3)$  Å<sup>3</sup>, space group  $P2_1/n$ . Since frondelite from Sebastião Cristino is an oxidation product of primary triphylite, rims of qingheite-( $\text{Fe}^{2+}$ ) can be interpreted as the result of a reaction between this primary Mg-bearing triphylite (source of Fe, Mn, Mg, P) and albite from the matrix (source of Na, Al). This reaction certainly took place at the albitization stage, during which high amounts of Na were available. The oxidation processes affecting the pegmatite subsequently oxidized triphylite in ferrisicklerite and then in frondelite, and

provoked an oxidation of qingheite-( $\text{Fe}^{2+}$ ) following the substitution mechanism  $\text{Na}^+ + \text{Fe}^{2+} = \square + \text{Fe}^{3+}$ . This oxidation is responsible for the presence of vacancies and  $\text{Fe}^{3+}$  in qingheite-( $\text{Fe}^{2+}$ ).

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