

## Oral Contributions

[M518-02] Structural Variations of Olivine-type Phosphates: a good Example of how Minerals can inspire the Development of new Materials. Frédéric Hatert, Fabrice Dal Bo, Maxime Bajot.

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Phosphates of the triphylite-lithiophilite series  $[Li_{1-x}Fe^{2+}PO_3]_{1-x}[MnPO_3]_x$  occur in the geological context of granitic pegmatites, where they form masses that can reach several meters in diameter. During the oxidation processes affecting the pegmatites, these olivine-type phosphates progressively transform to ferrisicklerite-sicklerite  $[Li_{1-x}(Fe^{3+}, Mn^{2+})(PO_3)_{1-x}(Mn^{2+}, Fe^{3+})(PO_3)_x]$  and to heterosite-purpurite  $[(Fe^{3+}, Mn^{2+})(PO_3)_2(Mn^{2+}, Fe^{3+})PO_3]$ , according to the substitution mechanism  $Li^{2+} + Fe^{2+} \rightarrow [ ] + Fe^{3+}$ . This oxidation mechanism was described by mineralogists in the 1940's, based on petrographic observations of phosphates under the polarizing microscope and on chemical data [1,2]. In 1997, Padhi *et al.* [3] demonstrated the efficiency of triphylite-type phosphates as cathode material for Li-ion batteries. Such  $LiFePO_3$ -based batteries are actually produced industrially, and are used as power sources for electric cars, laptops, or mobile phones. The crystal structure of minerals of the triphylite-lithiophilite series (triphylite:  $a = 4.690$ ,  $b = 10.286$ ,  $c = 5.987$  Å,  $Pbnm$ ) 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.* [4], 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). 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. Recently, the Fe-analogue of natrophilite was found at the Malpensata granitic pegmatite, Colico commune, Lecco province, north Italy [5]. This phosphate,  $Na(Fe^{2+}, Mn^{2+})PO_3$ , 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. In order to elucidate the phase relations among lithium-iron phosphates, we decided to investigate the  $Li-Fe^{2+}-Fe^{3+} (+PO_3)$  system hydrothermally between 400 and 700°C, at 1 kbar pressure. These experiments first allowed to determine the stability fields of several phosphate assemblages. A black crystal of partially oxidized triphylite has been synthesized during these experiments, and its crystal structure has been solved in the  $Pnma$  space group ( $a = 10.306(4)$ ,  $b = 6.004(2)$ ,  $c = 4.69(1)$  Å,  $R1 = 0.041$ ). The structural data, electron-microprobe analysis, as well as the colour of this phosphate, indicate that this triphylite-type compound contains both  $Fe^{2+}$  and  $Fe^{3+}$ ; the insertion of  $Fe^{3+}$  in the structure is achieved through the substitution mechanism  $3Fe^{2+} = 2Fe^{3+} + [ ] [6]$ .

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