The structural complexity of phosphates in the Li-Fe$^{2+}$-Fe$^{3+}$ (+ PO$_4$) system

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In the geological context of granitic pegmatites, only two natural phosphates with both lithium and iron are known to date: triphylite [Li(Fe,Mn)PO$_4$] and tavorite [LiFe$^{3+}$+PO$_4$](OH)]. Triphylite is a primary phosphate in pegmatites, which frequently oxidizes in ferrorichlerite [Li$_2$[Fe$^{3+}$,Mn$^{2+}$]PO$_4$] and heterosite [Fe$^{3+}$PO$_4$], according to the substitution mechanism Li$^+$ + Fe$^{2+}$ = [ ] + Fe$^{3+}$. This oxidation process is known as the Quensel-Mason sequence. Since Padhi et al. (1997) reported the reversible electrochemical extraction of lithium from synthetic LiFePO$_4$, triphylite-type phosphates have received a strong attention as candidates for lithium batteries; these phosphates are actually used to produce batteries for many applications, such as electric bicycles, electric boats, electric cars, or for the storage of green energy.

Despite this increasing interest for triphylite-type compounds, only a few synthetic lithium-iron phosphates are reported in the literature, such as LiFe$^{3+}$+(P$_2$O$_7$), Li$_2$Fe$^{3+}$+(PO$_4$)$_3$ and Li$_2$Fe$^{3+}$+(PO$_4$)(HPO$_4$). In order to elucidate the phase relations among lithium-iron phosphates, we consequently decided to investigate the Li-Fe$^{2+}$-Fe$^{3+}$ (+PO$_4$) system hydrothermally between 400 and 700°C, at 1 kbar pressure. Oxygen fugacity was not buffered, and gold capsules (2 mm diameter, 25 mm length) were used in order to keep the initial Fe$^{2+}$/Fe$^{3+}$ ratio constant. The synthesized compounds were identified by X-ray powder diffraction, and electron-microprobe analyses were realized to define their chemical compositions.

These experiments first allowed to determine the stability fields of several phosphate assemblages. In the Li-rich part of the system, triphylite, lithiophosphate [Li$_2$PO$_4$], tavorite, Li$_2$Fe$^{3+}$+(PO$_4$)(HPO$_4$), and Li$_2$Fe$^{3+}$+(PO$_4$), essentially appear. The Fe$^{2+}$-rich part of the system shows an assemblage triphylite + sarkopside [Fe$_3$(PO$_4$)$_2$] + Fe$_7$(PO$_4$)$_6$, whereas the Fe$^{3+}$-rich part of the system shows the presence of Fe$_4$(PO$_4$)$_3$(OH)$_2$ + LiFe(P$_2$O$_7$). In the central part of the system, the assemblage triphylite + Fe$_5$(PO$_4$)$_6$ + Fe$_3$(PO$_4$)$_2$(OH)$_2$ + Li$_3$Fe$_2$(PO$_4$)$_3$ crystallizes. No phosphates with Li and both Fe$^{2+}$ and Fe$^{3+}$ were observed in these experimental conditions.

Three structural investigations on single-crystals obtained at 700°C were performed during this study. Fe$_7$(PO$_4$)$_6$ has been solved in the $P$T space group ($a = 6.357(1)$, $b = 7.976(2)$, $c = 9.319(2)\,\text{Å}$, $\alpha = 105.34(3)$, $\beta = 108.19(3)$, $\gamma = 101.81(3)^\circ$, $R_1 = 0.050$); the structure is similar to that previously reported in the literature (Duan et al., 2004). The structure of Li$_2$PO$_4$ corresponds to that of the polymorph $\gamma$-Li$_2$PO$_4$ ($Pnma$, $a = 10.482(2)$, $b = 6.115(1)$, $c = 4.923(1)\,\text{Å}$, $R_1 = 0.024$), in which the LiO$_4$ and PO$_4$ tetrahedra are not oriented in the same direction. Finally, a black crystal of partially oxidized triphylite has been solved in the $Pnma$ space group ($a = 10.306(4)$, $b = 6.004(2)$, $c = 4.69(1)\,\text{Å}$, $R_1 = 0.041$). 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$^{3+}$ + [ ].

References:
