A structural study of natural olivine-type phosphates

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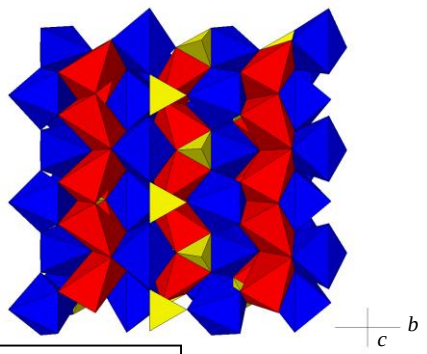
Introduction

- Triphylite [$Li(Fe^{2+},Mn^{2+})PO_4$] and lithiophilite [$Li(Mn^{2+}, Fe^{2+})PO_4$] occur as primary phosphates in granitic pegmatites. Their crystal structure is identical to that of olivine.
- In pegmatites, these phosphates progressively oxidize in ferrisicklerite-sicklerite [$Li_{1-x}(Fe^{3+},Mn^{2+})PO_4$-$Li_{1-x}(Mn^{2+},Fe^{3+})PO_4$], and then in heterosite-purpurite [$(Fe^{3+},Mn^{3+})PO_4$-$(Mn^{3+},Fe^{3+})PO_4$].
- New chemical analyses and structure refinements were performed, in order to shed some light on the complex crystal chemistry of these phosphates.

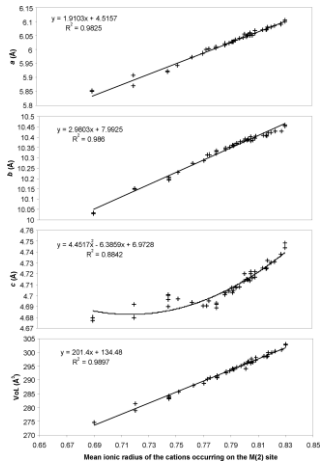
Crystal structure



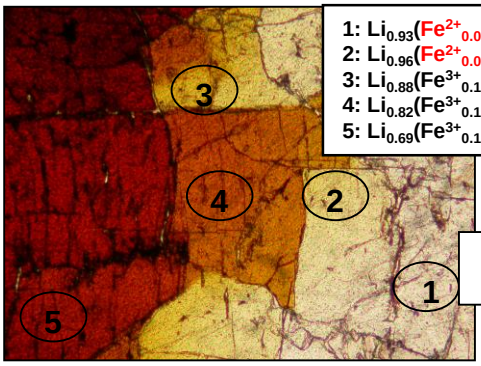
S.G. *Pmnb*
- M(1): Li, []
- M(2): Fe^{2+}, Mn, Mg

Red octahedra: M(1)
Blue octahedra: M(2)

Unit-cell parameters



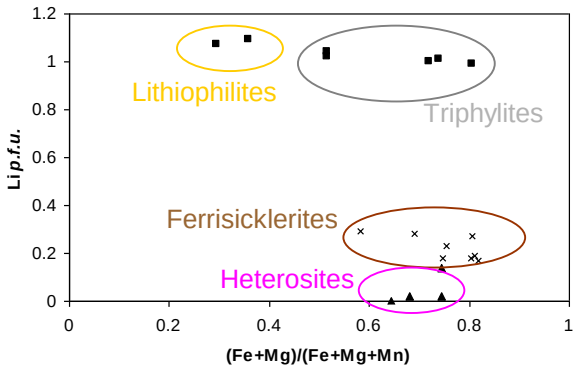
The lithiophilite-sicklerite transition



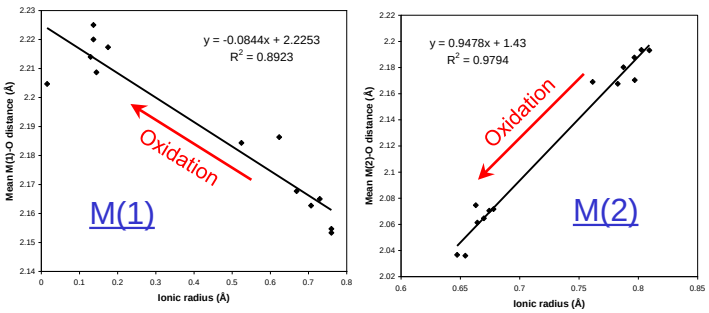
1: $Li_{0.93}(Fe^{2+}_{0.03}Fe^{3+}_{0.13}Mn^{2+}_{0.80})(PO_4)$
2: $Li_{0.96}(Fe^{2+}_{0.08}Fe^{3+}_{0.08}Mn^{2+}_{0.81})(PO_4)$
3: $Li_{0.88}(Fe^{3+}_{0.16}Mn^{2+}_{0.80}Mn^{3+}_{0.01})(PO_4)$
4: $Li_{0.82}(Fe^{3+}_{0.16}Mn^{2+}_{0.75}Mn^{3+}_{0.06})(PO_4)$
5: $Li_{0.69}(Fe^{3+}_{0.16}Mn^{2+}_{0.62}Mn^{3+}_{0.19})(PO_4)$

Sample from the Altaï Mountains, China

Chemical data (SIMS +EMPA)



Variations of M-O bond lengths



Conclusions

- The chemical analyses indicate a progressive oxidation from lithiophilite to sicklerite, with several intermediate phases.
- The Li contents of ferrisicklerites and heterosites are very close to each other.
- The oxidation from triphylites to heterosites provokes a decrease of the M(2)-O bond lengths, as well as an increase of the M(1)-O bond lengths.
- The unit-cell parameters are correlated with the ionic radius of the cations occurring on M(2), and can consequently be used to estimate the Fe^{2+}/Mn^{2+} ratio on this site.

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