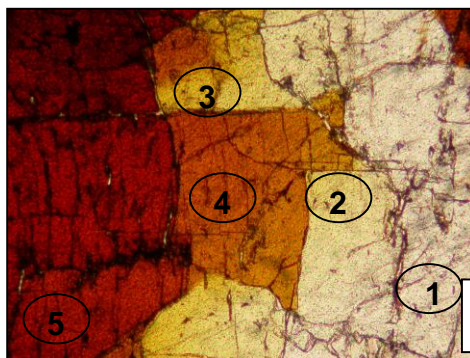


Introduction

- Triphylite [Li(Fe²⁺, Mn²⁺)PO₄] and lithiophilite [Li(Mn²⁺, Fe²⁺)PO₄] occur as primary phosphates in granitic pegmatites. Their crystal structure is identical to that of olivine.
- In pegmatites, lithiophilite progressively oxidizes in sicklerite [Li_{1-x}(Mn²⁺, Fe³⁺)PO₄], and then in purpurite [(Mn³⁺, Fe³⁺)PO₄].
- New chemical analyses and structure refinements were performed on minerals of the lithiophilite-sicklerite series, in order to shed some light on the crystal chemistry of these phosphates.

Microscopic optical characterization

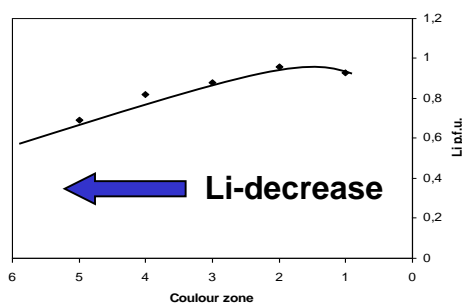


- 1: Colorless
- 2: Light yellow
- 3: Yellow
- 4: Orange
- 5: Red

Sample from the Altai Mountains, China

Chemical data

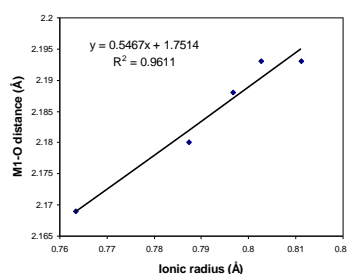
- 1: Li_{0.93}(Fe²⁺_{0.03}Fe³⁺_{0.13}Mn²⁺_{0.80})(PO₄)
- 2: Li_{0.96}(Fe²⁺_{0.08}Fe³⁺_{0.08}Mn²⁺_{0.81})(PO₄)
- 3: Li_{0.88}(Fe³⁺_{0.16}Mn²⁺_{0.80}Mn³⁺_{0.01})(PO₄)
- 4: Li_{0.82}(Fe³⁺_{0.16}Mn²⁺_{0.75}Mn³⁺_{0.06})(PO₄)
- 5: Li_{0.69}(Fe³⁺_{0.16}Mn²⁺_{0.62}Mn³⁺_{0.19})(PO₄)



Structure refinements

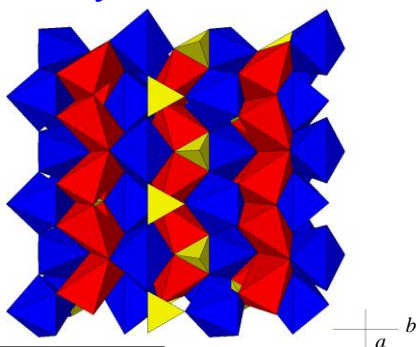
	1	2	3	4	5
R ₁ (%)	2.53	2.36	2.94	2.67	2.19
a (Å)	4.736(1)	4.734(1)	4.740(1)	4.767(1)	4.765(1)
b (Å)	10.432(2)	10.423(2)	10.415(1)	10.403(2)	10.338(1)
c (Å)	6.088(1)	6.094(1)	6.080(1)	6.072(1)	6.060(1)
M(2)	0.99 Li	0.91 Li	0.84 Li	0.81 Li	0.75 Li
M(1)-O	2.193	2.193	2.188	2.180	2.169
M(2)-O	2.163	2.165	2.168	2.186	2.184

Variations of M1-O bond lengths



Decrease of M1-O bond lengths due to the progressive oxidation of iron and manganese

Crystal structure



S.G. *Pmnb*

- M1: Li, □
- M2: Fe²⁺, Mn, Mg

Red octahedra: M1
Blue octahedra: M2

Conclusions

- The chemical analyses indicate a progressive oxidation of lithiophilite to sicklerite, with several intermediate phases. This oxidation is accompanied by a progressive decrease of the Li-content.
- The M1-O bond lengths decrease significantly, due to the progressive oxidation of Fe and Mn.
- The presence of Mn³⁺ is responsible for the strong color of sicklerite.