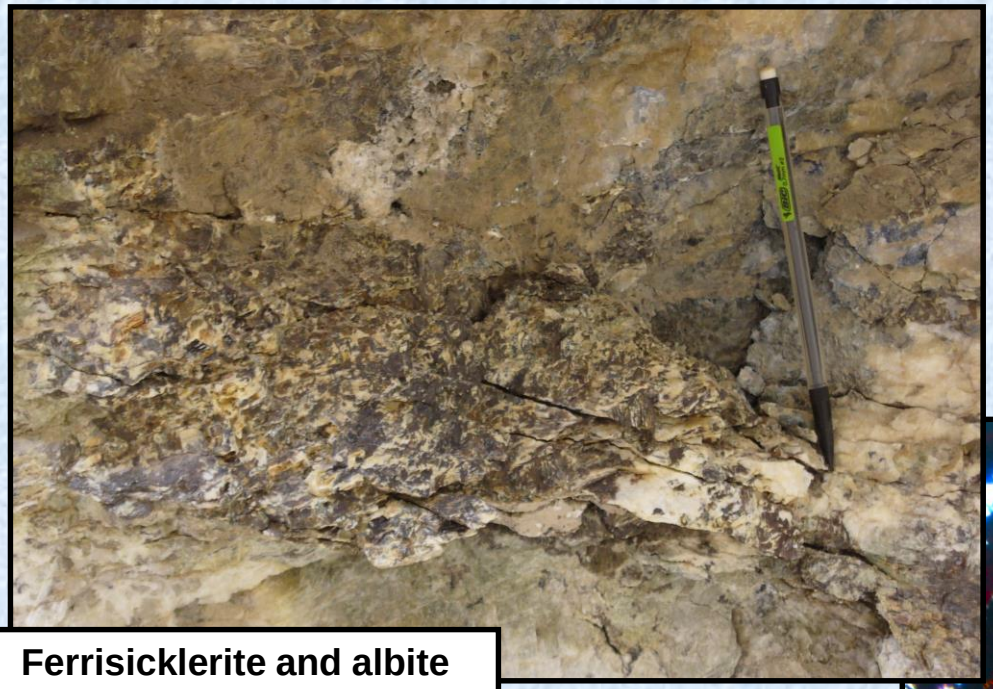
Université de Liège
Faculté des Sciences
Département de Géologie
Laboratoire de Minéralogie

The Crystal Chemistry of Olivine-type Phosphates

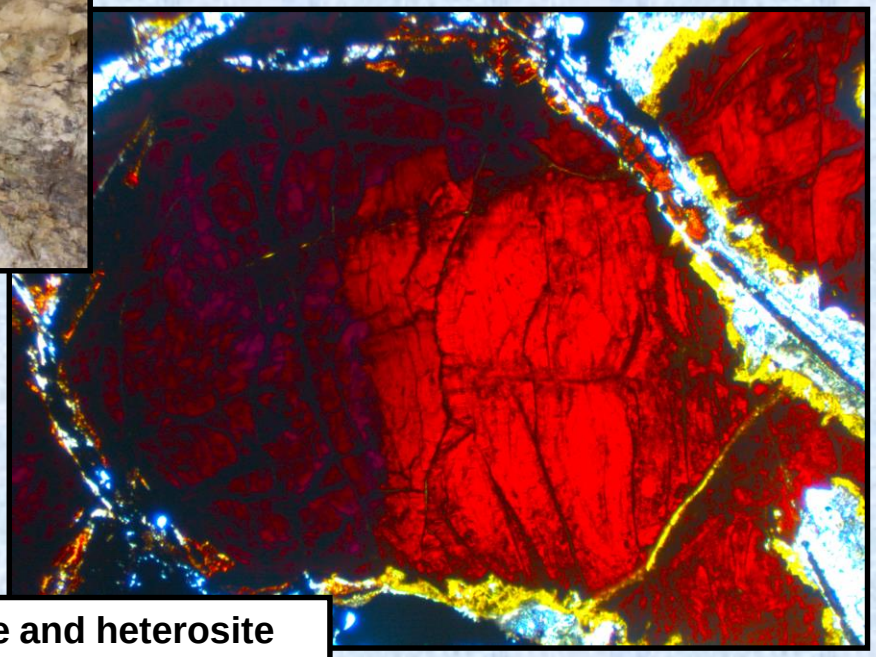
F. Hatert, L. Ottolini, F. Fontan, P. Keller, E. Roda-Robles, A.-M. Fransolet

Mendoza, February 21st, 2011

Occurrence: Granitic pegmatites



Ferrisicklerite and albite
Sapucaia pegmatite, Brazil



Ferrisicklerite and heterosite
Boca Rica pegmatite, Brazil

Oxidation of olivine-type phosphates: the « Quensel-Mason » sequence

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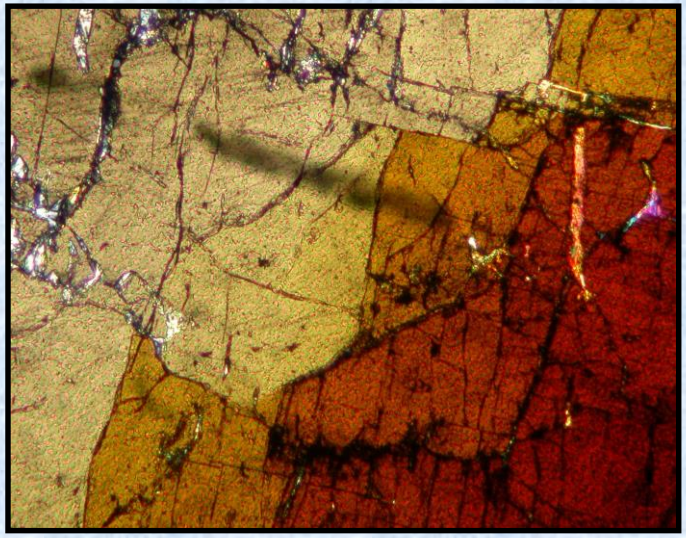
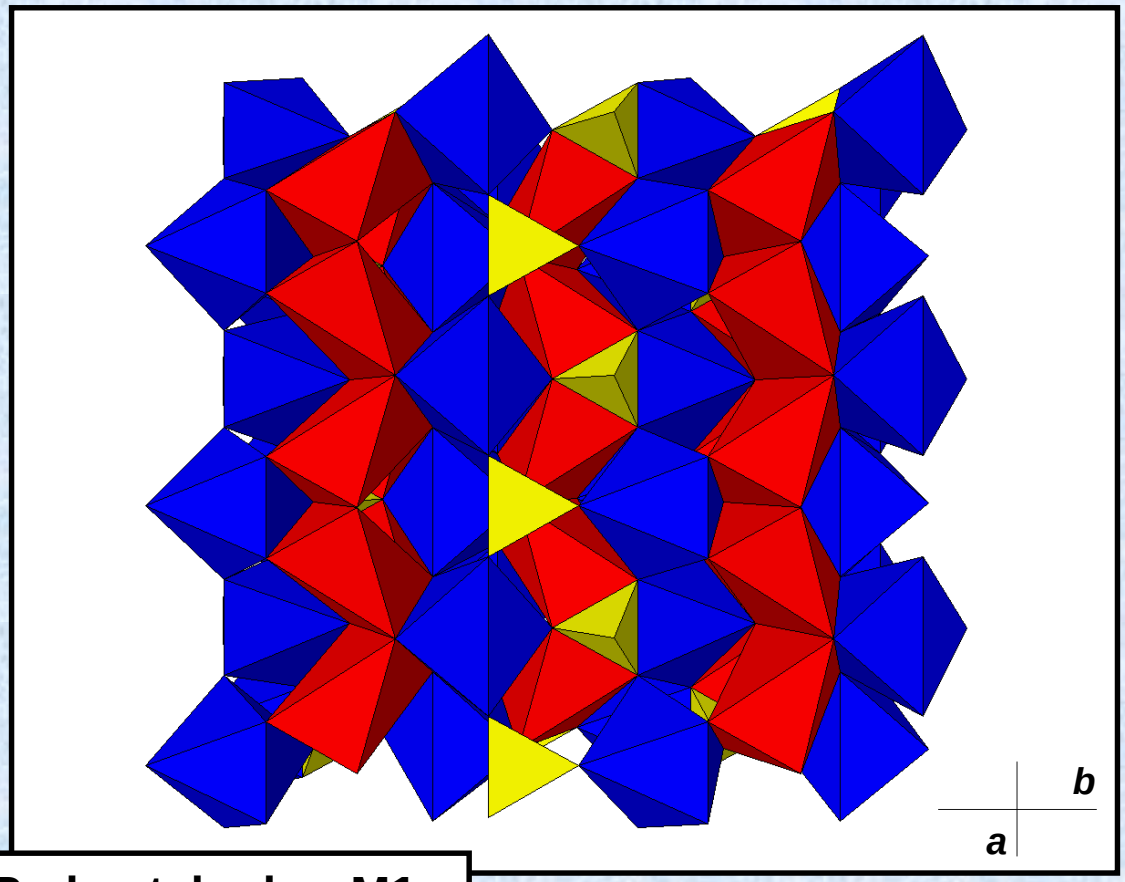
$Li(Mn^{2+},Fe^{2+})PO_4 \Rightarrow {}_{x}^{\bullet}Li_{1-x}(Mn^{2+},Fe^{3+})PO_4 \Rightarrow (Mn^{3+},Fe^{3+})PO_4$
(Lithiophilite) (Sicklerite) (Purpurite)

$Li(Fe^{2+},Mn^{2+})PO_4 \Rightarrow {}_{x}^{\bullet}Li_{1-x}(Fe^{3+},Mn^{2+})PO_4 \Rightarrow (Fe^{3+},Mn^{3+})PO_4$
(Triphylite) (Ferrisicklerite) (Heterosite)



The triphylite structure



Red octahedra: M1
Blue octahedra: M2

S.G. *Pbnm*

***a* = 4.690, *b* = 10.286, *c* = 5.987 Å**

- **M1: Li, []**
- **M2: Fe^{2+}, Mn, Mg**

$LiFePO_4$-based batteries

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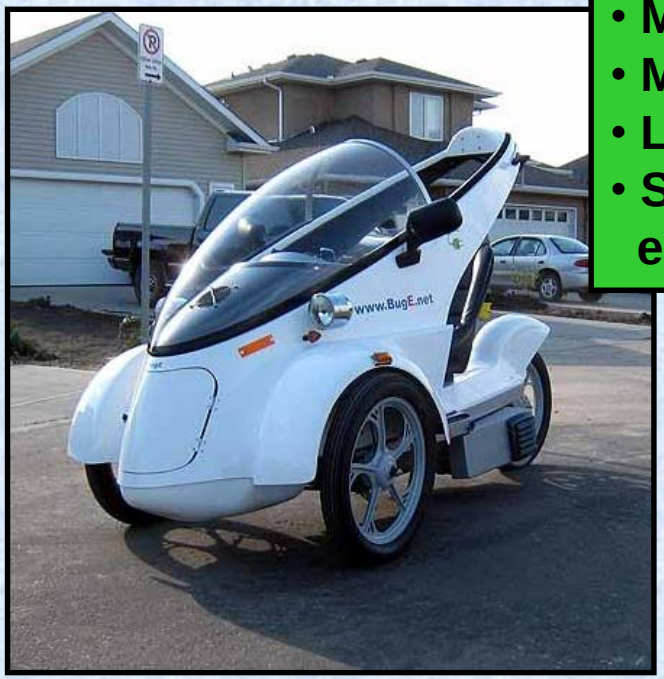
nature Vol 458|12 March 2009|doi:10.1038/nature07853

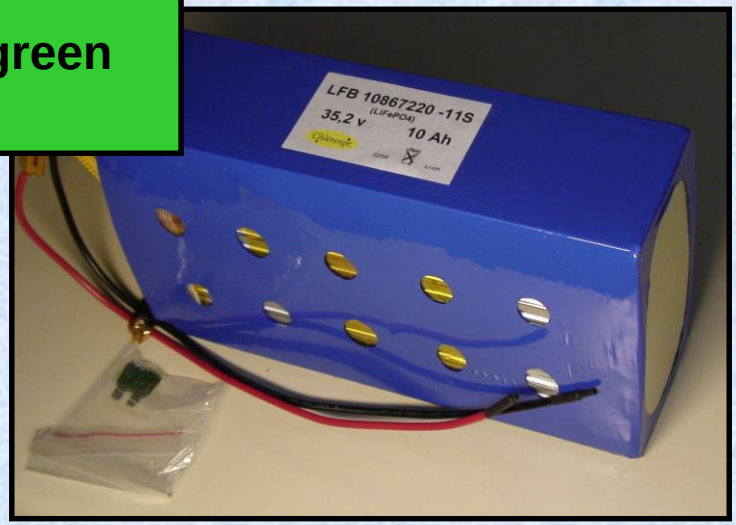
LETTERS

Battery materials for ultrafast charging and discharging

Byoungwoo Kang[1] & Gerbrand Ceder[1]

- Cars
- Bicylces
- Motorbikes
- Mobile phones
- Laptops
- Storage of green energy





Sample selection

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Sample	Locality
PK-17	Hagendorf-Süd, Germany
PK-20	Engelbrechts Claim, Brandberg, Namibia
PK-1	McDonalds Claim, Brandberg, Namibia
PK-18	Strathmore tin mine, Namibia
PK-3	Ariakas, Usakos, Namibia
PK-15	Sandamap, Usakos, Namibia
K9-5-6 (5 zones)	Koktokay #3 pegmatite, Altai, China
AB-2-2	Cañada pegmatite, Spain
AB-X1-2-ME-3	Cañada pegmatite, Spain
AB-X1-2-TB-5	Cañada pegmatite, Spain

- **Electron microprobe**
- **Ion probe (SIMS)**
- **Single-crystal structure refinements**

Sample	Mineral	Composition
PK-17	Triphylite	$Li_{0.99}(Fe^{2+}_{0.73}Fe^{3+}_{0.05}Mn^{2+}_{0.19}Mg_{0.01})PO_4$
PK-20	Triphylite	$Li_{1.06}(Fe^{2+}_{0.65}Mn^{2+}_{0.34})PO_4$
PK-1	Ferrisicklerite	$Li_{0.18}(Fe^{3+}_{0.67}Mn^{2+}_{0.13}Mn^{3+}_{0.12}Mg_{0.07})PO_4$
PK-18	Ferrisicklerite	$Li_{0.18}(Fe^{3+}_{0.73}Mn^{2+}_{0.11}Mn^{3+}_{0.10}Mg_{0.06})PO_4$
PK-3	Heterosite	$(Fe^{3+}_{0.64}Mn^{2+}_{0.05}Mn^{3+}_{0.31}Mg_{0.01})PO_4$
PK-15	Heterosite	$Li_{0.02}(Fe^{3+}_{0.70}Mn^{3+}_{0.25}Mg_{0.03})PO_4$
AB-2-2	Ferrisicklerite	$Li_{0.17}(Fe^{3+}_{0.75}Mn^{2+}_{0.08}Mn^{3+}_{0.10}Mg_{0.06})PO_4$
AB-X1-2-ME-3	Ferrisicklerite	$Li_{0.19}(Fe^{3+}_{0.57}Mn^{3+}_{0.19}Mg_{0.24})PO_4$
AB-X1-2-TB-5	Ferrisicklerite	$Li_{0.23}(Fe^{3+}_{0.67}Mn^{2+}_{0.14}Mn^{3+}_{0.10}Mg_{0.07})PO_4$

The Li content of natural olivine-type phosphates

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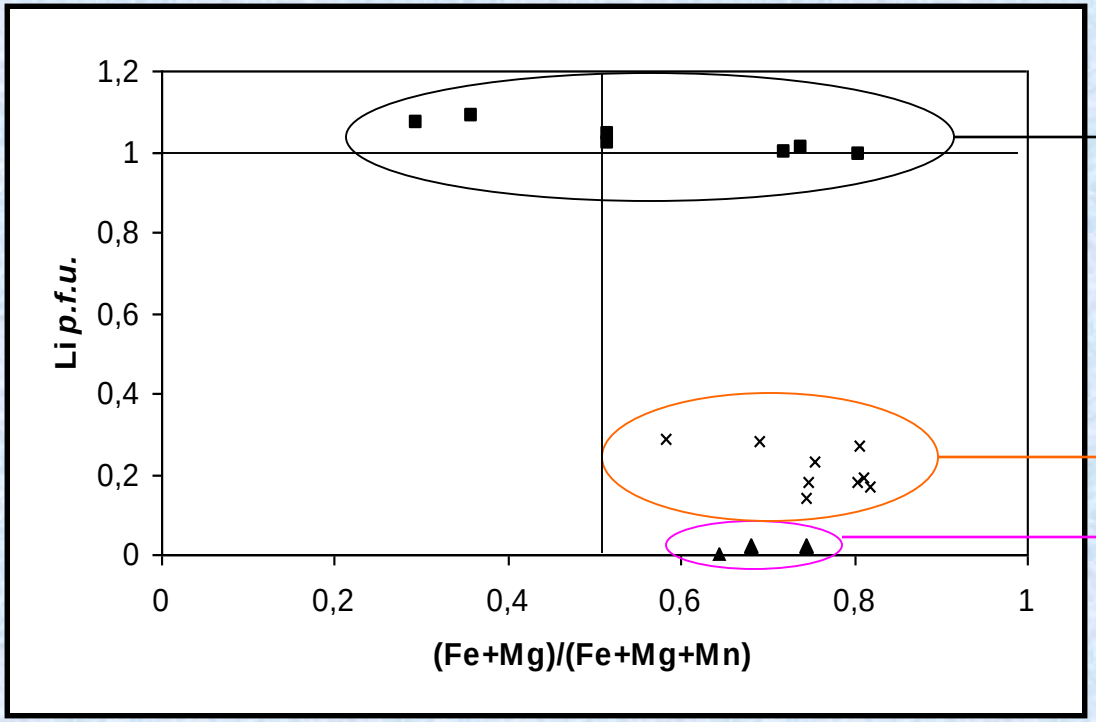

Triphylite-lithiophilite
0.99-1.07 Li *p.f.u.*

Ferrisicklerite
0.14-0.29 Li *p.f.u.*

Heterosite
0.00-0.02 Li *p.f.u.*

Heterosite may contain up to 0.21 wt. % Li_2O, and ferrisicklerite may show a low Li-content of 1.31 wt. % Li_2O

Close Li-contents!

The progressive transition from lithiophilite to sicklerite

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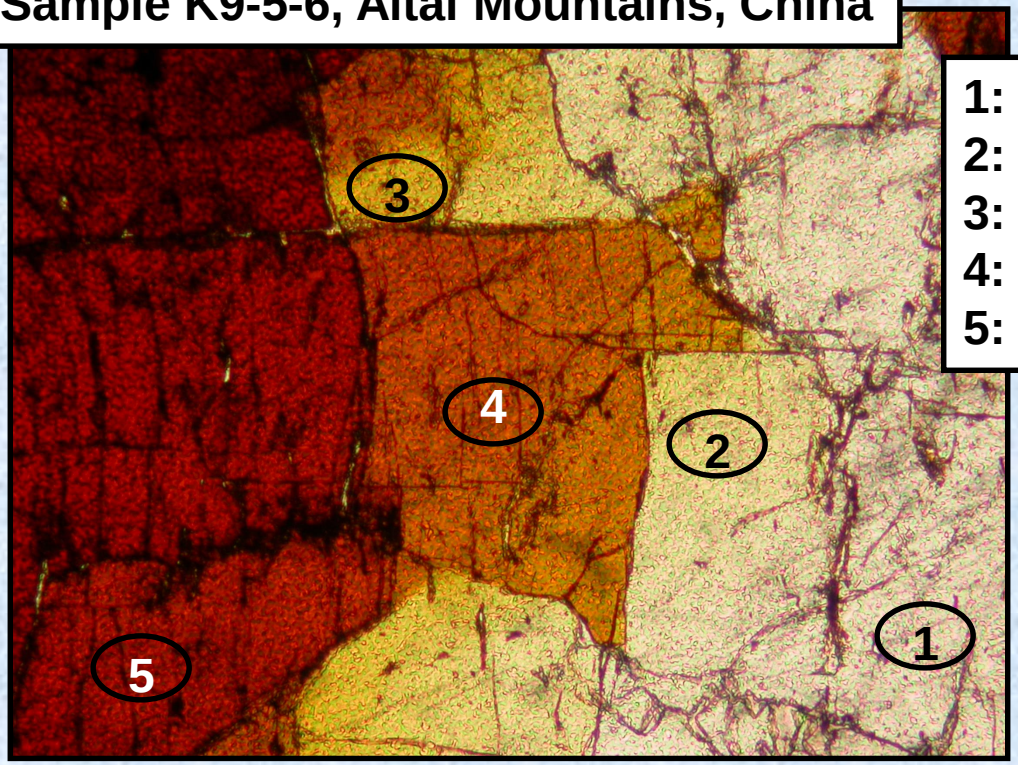
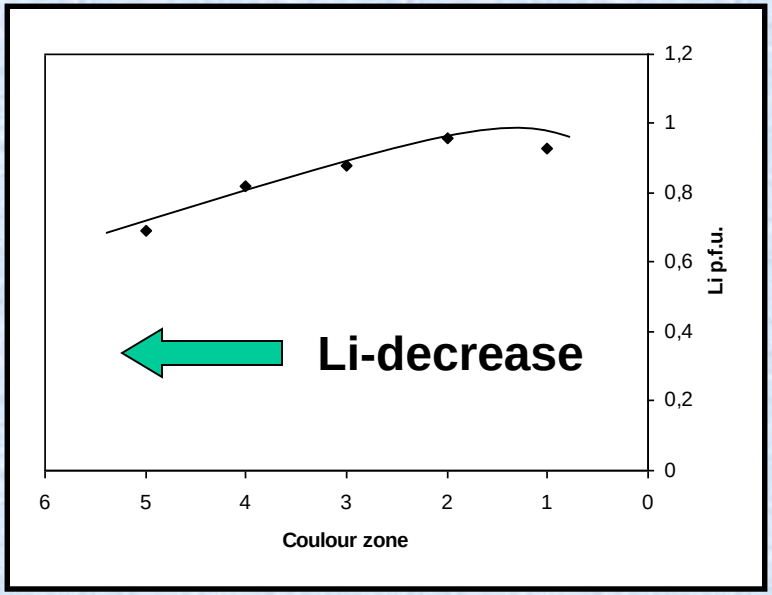
Sample K9-5-6, Altaï Mountains, China



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: $Li_{0.69}(Fe^{3+}_{0.16}Mn^{2+}_{0.62}Mn^{3+}_{0.19})(PO_4)$



- The transition from lithiophilite to sicklerite is progressive
- The change in colour is due to the presence of Mn^{3+}

A structural study of the lithiophilite-sicklerite series

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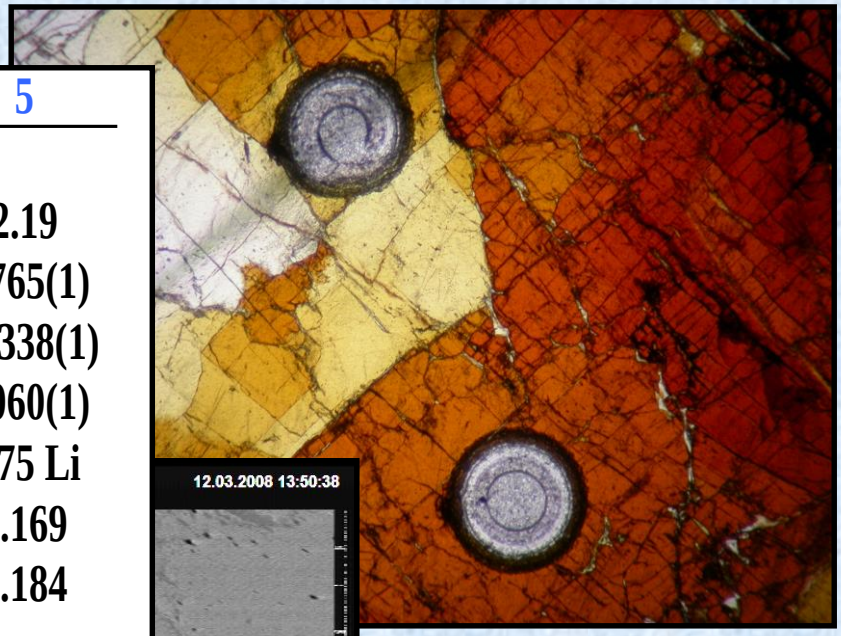
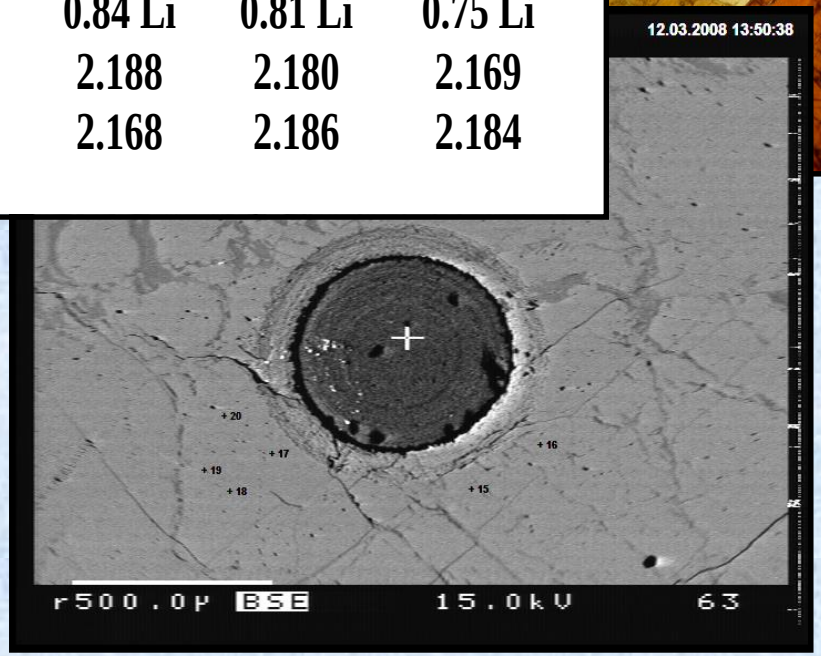
	1	2	3	4	5
R_1 (%)	2.53	2.36	2.94	2.67	2.19
a (Å)	4.736(1)	4.734(1)	4.740(1)	4.767(1)	4.765(1)
b (Å)	10.432(2)	10.423(2)	10.415(1)	10.403(2)	10.338(1)
c (Å)	6.088(1)	6.094(1)	6.080(1)	6.072(1)	6.060(1)
M(2)	0.99 Li	0.91 Li	0.84 Li	0.81 Li	0.75 Li
M(1)-O	2.193	2.193	2.188	2.180	2.169
M(2)-O	2.163	2.165	2.168	2.186	2.184





- **Micro-drilling**
- **Single-crystal structure refinements**

Variations of M-O bond lengths

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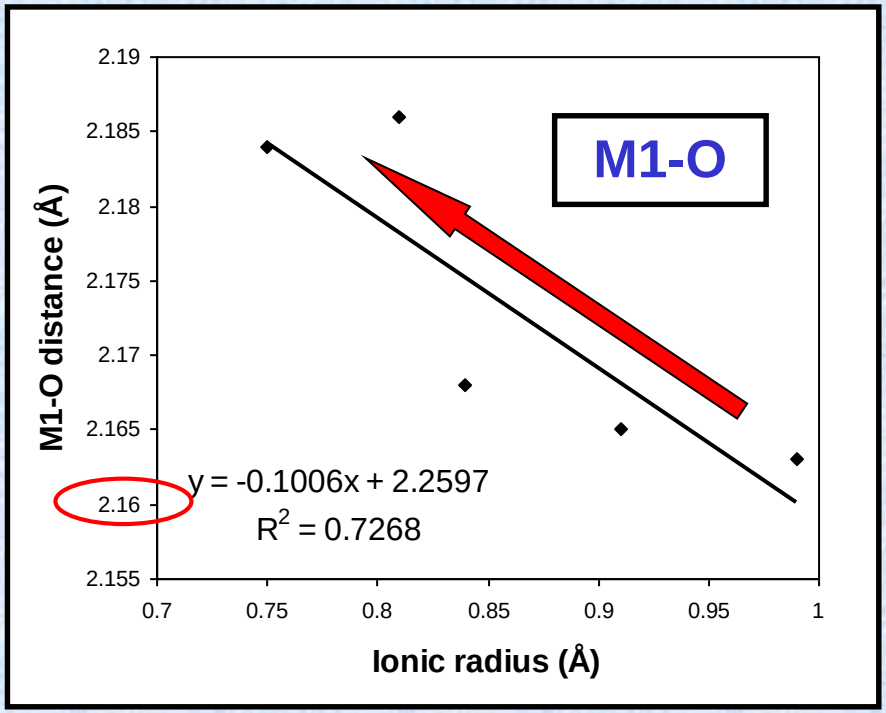

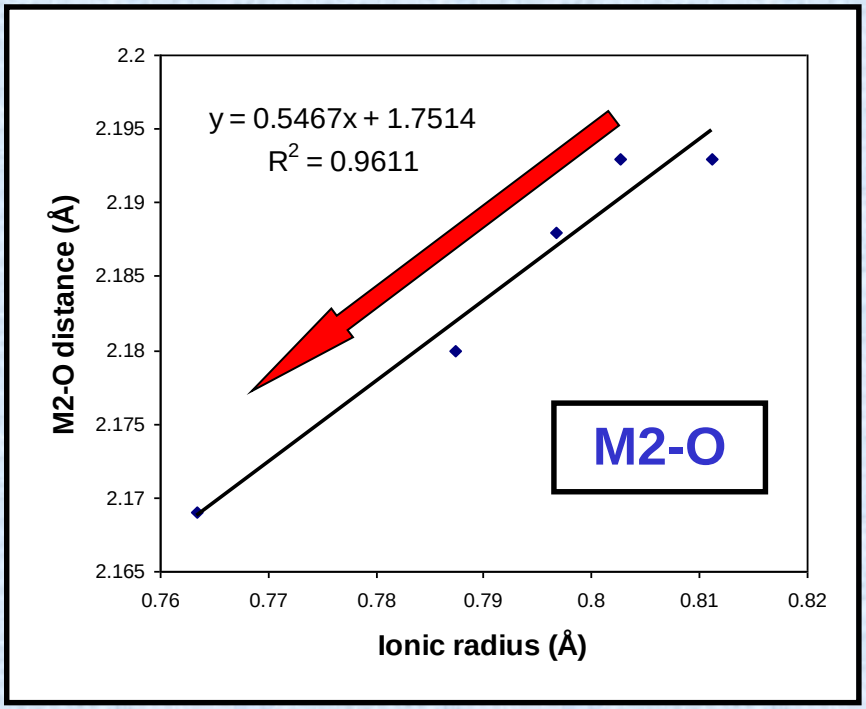

- Decrease of the M2-O bond lengths, due to the progressive oxidation of iron and manganese
- Increase of the M1-O bond lengths, due to leaching of lithium (decrease of bond valence sums correlated with the increasing number of vacancies)
- Correlation between M1-O and M2-O!

Single-crystal structure refinements of natural olivine-type phosphates

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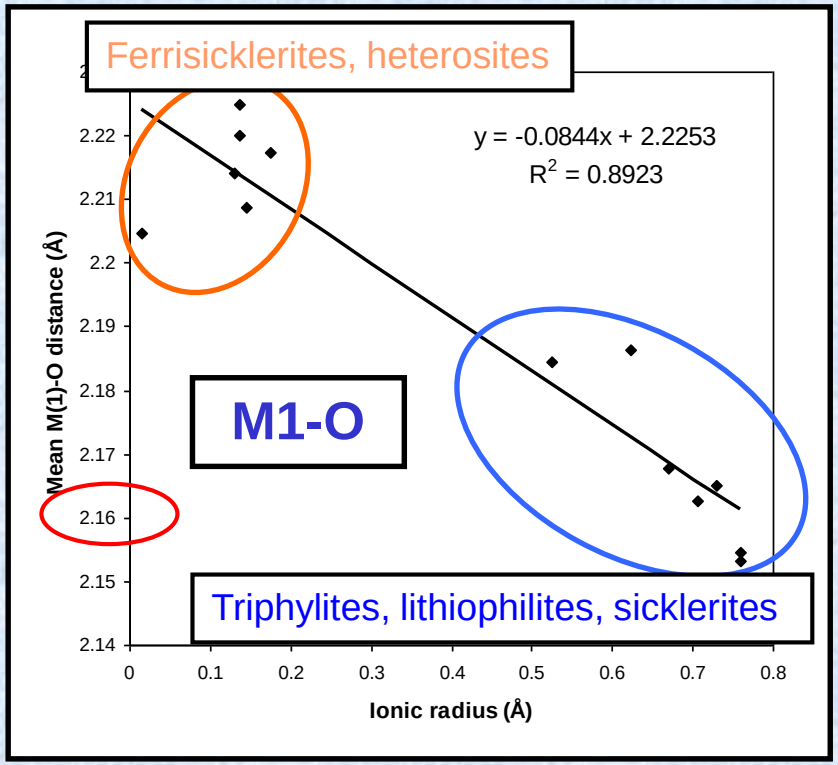
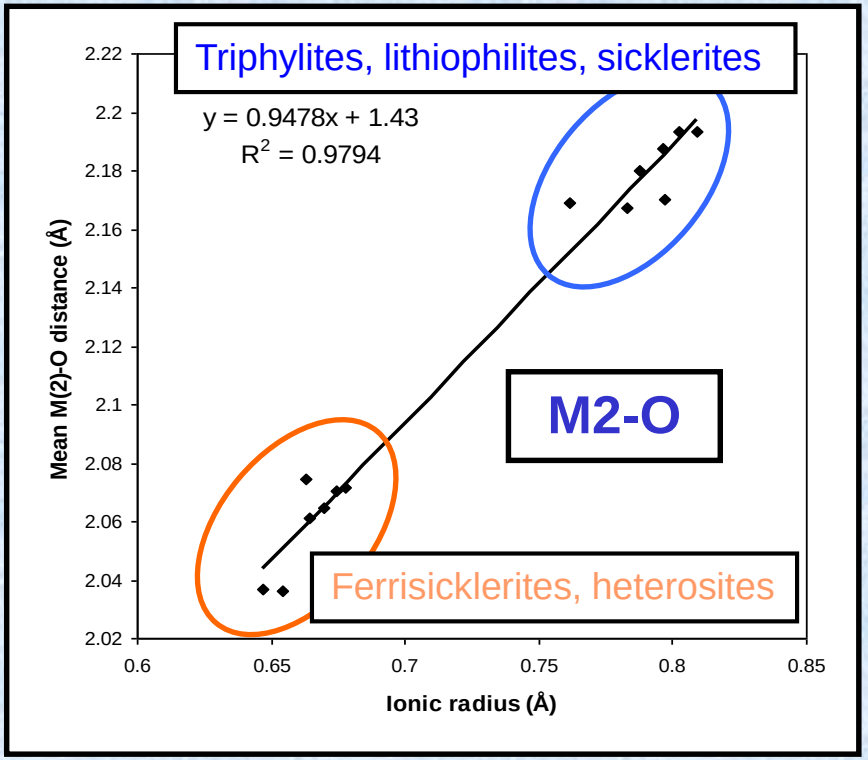
Sample	*a* (Å)	*b* (Å)	*c* (Å)	V (Å^3)	R_1 (%)
PK-17	4.704(1)	10.365(1)	6.025(1)	293.7(1)	4.07
PK-20	4.711(1)	10.369(1)	6.038(7)	294.9(1)	3.56
PK-1	4.795(1)	9.979(2)	5.890(1)	281.8(1)	4.01
PK-18	4.795(2)	9.959(6)	5.892(3)	281.3(3)	4.92
PK-3	4.776(3)	9.732(3)	5.826(3)	270.8(2)	6.32
PK-15	4.777(2)	9.776(3)	5.817(2)	271.7(2)	5.76
AB-2-2	4.787(2)	9.954(3)	5.875(2)	280.0(2)	5.87
AB-X1-2-ME-3	4.776(3)	10.035(3)	5.883(3)	282.0(3)	8.24
AB-X1-2-TB-5	4.797(3)	9.978(5)	5.881(3)	281.5(3)	6.92

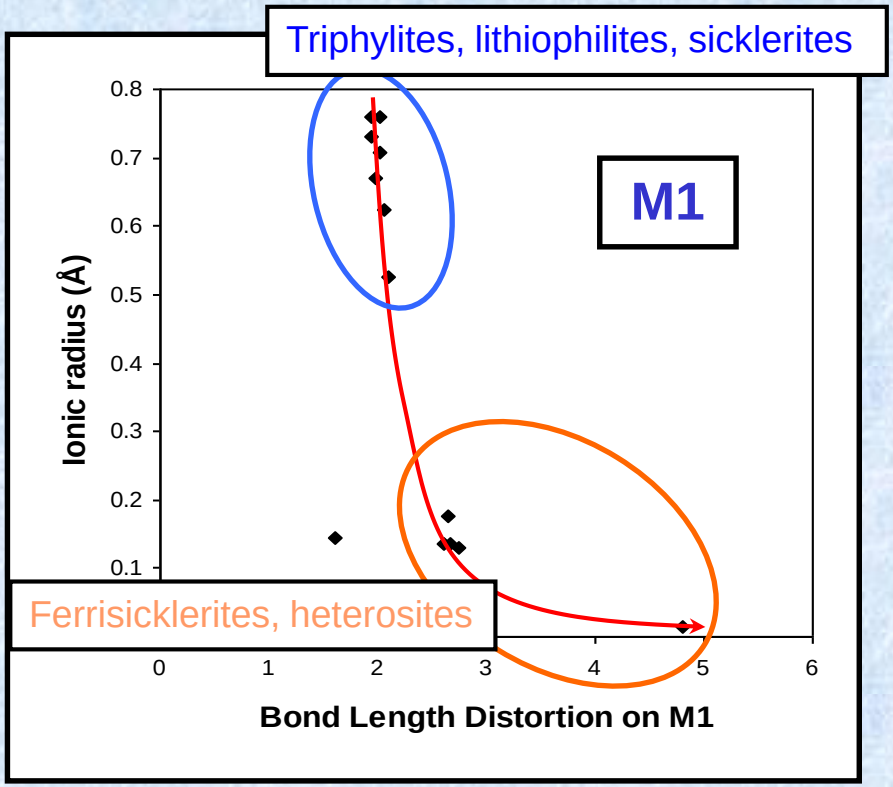
Variations of M-O bond lengths

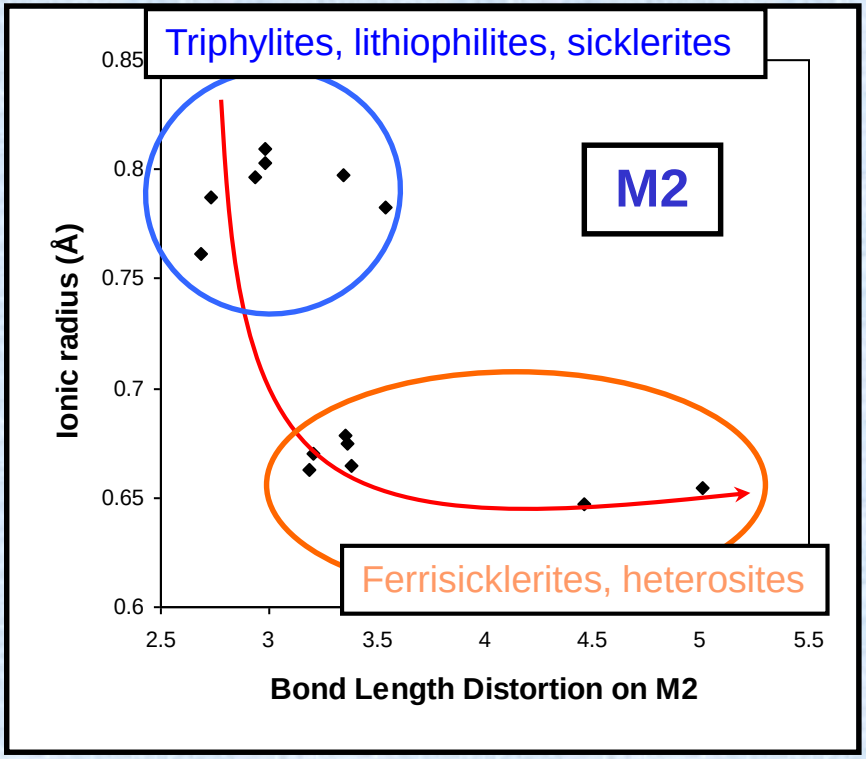




- Decrease of the M2-O due to the progressive oxidation of iron and manganese
- Increase of the M1-O due to leaching of lithium

Distortion coefficients





Increase of the M1 and M2 bond length distortion coefficients for the oxidized compositions (ferrisicklerites, heterosites)

Topology of the M2 site

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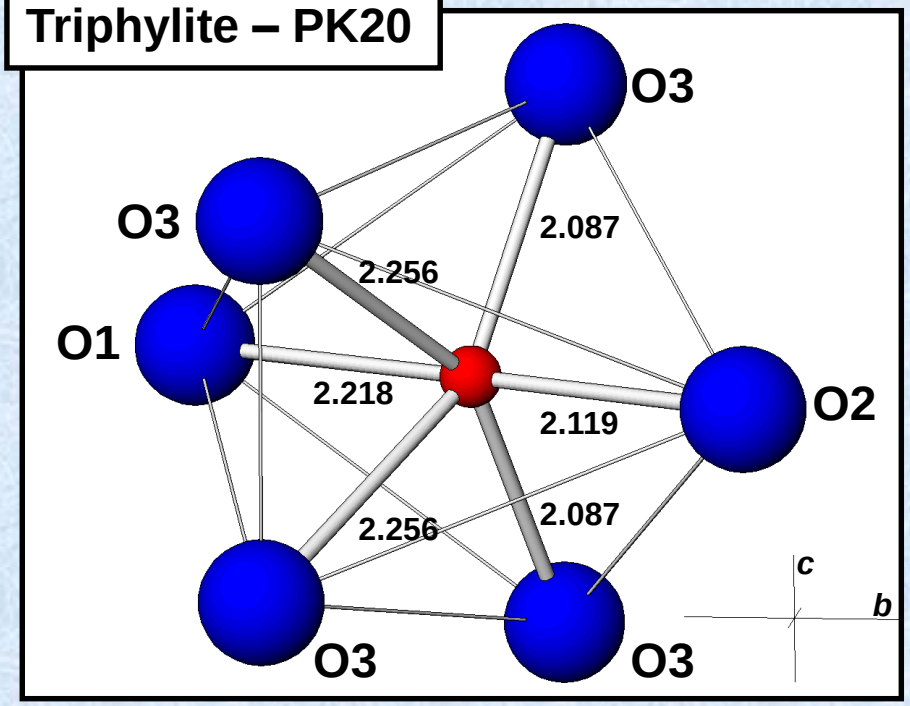
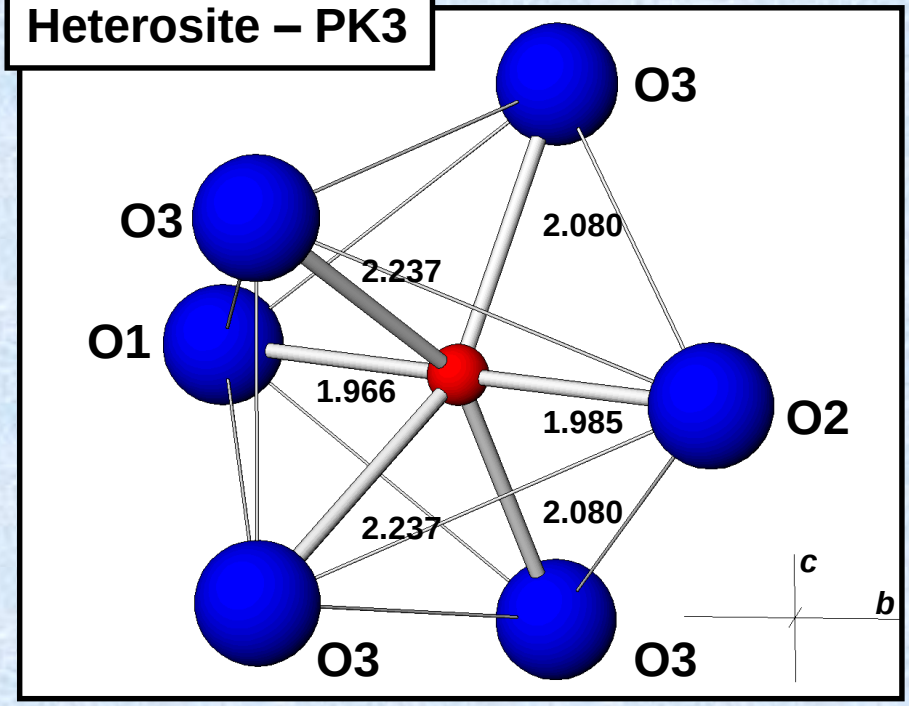
Triphylite – PK20

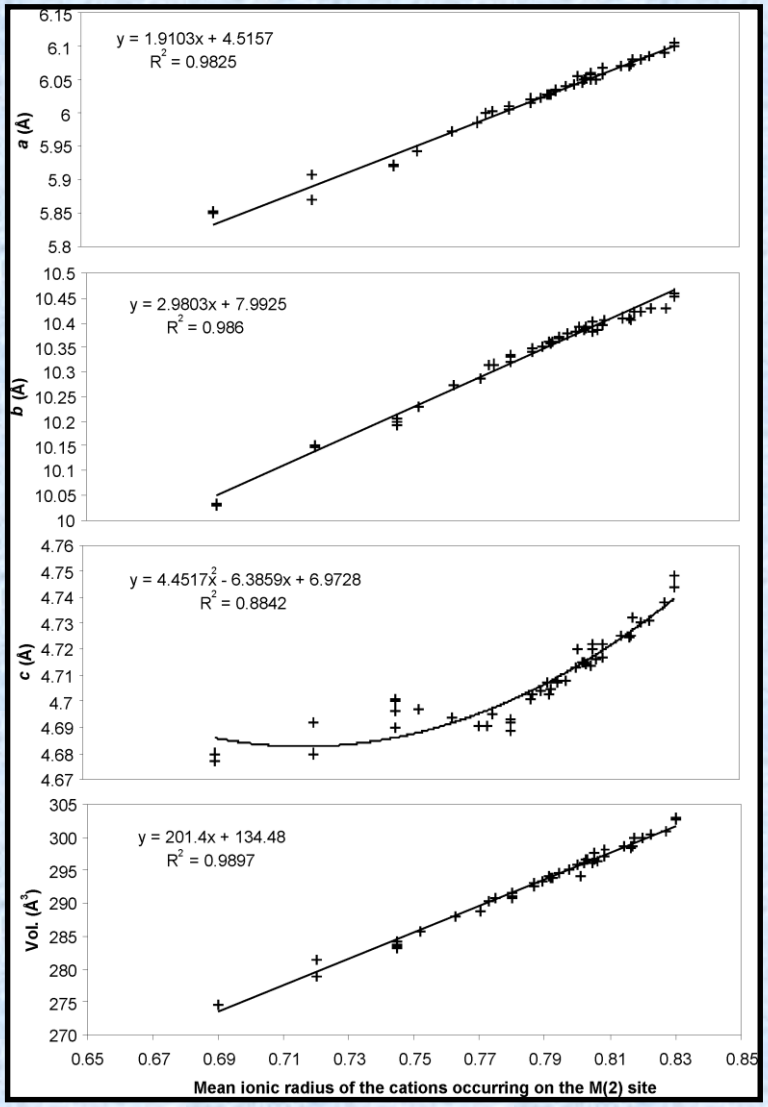


Heterosite – PK3



Jahn-Teller distortion, due to the presence of Mn^{3+} in heterosite

Variations of unit-cell parameters



Good correlations

Accurate estimation of the Fe/Mn ratio of natural members of the triphylite-lithiophilite series, when the Mg content is lower than 0.016 *a.p.f.u.* (accuracy +/- 7 %)

Experimental investigations: the alluaudite + triphylite assemblage

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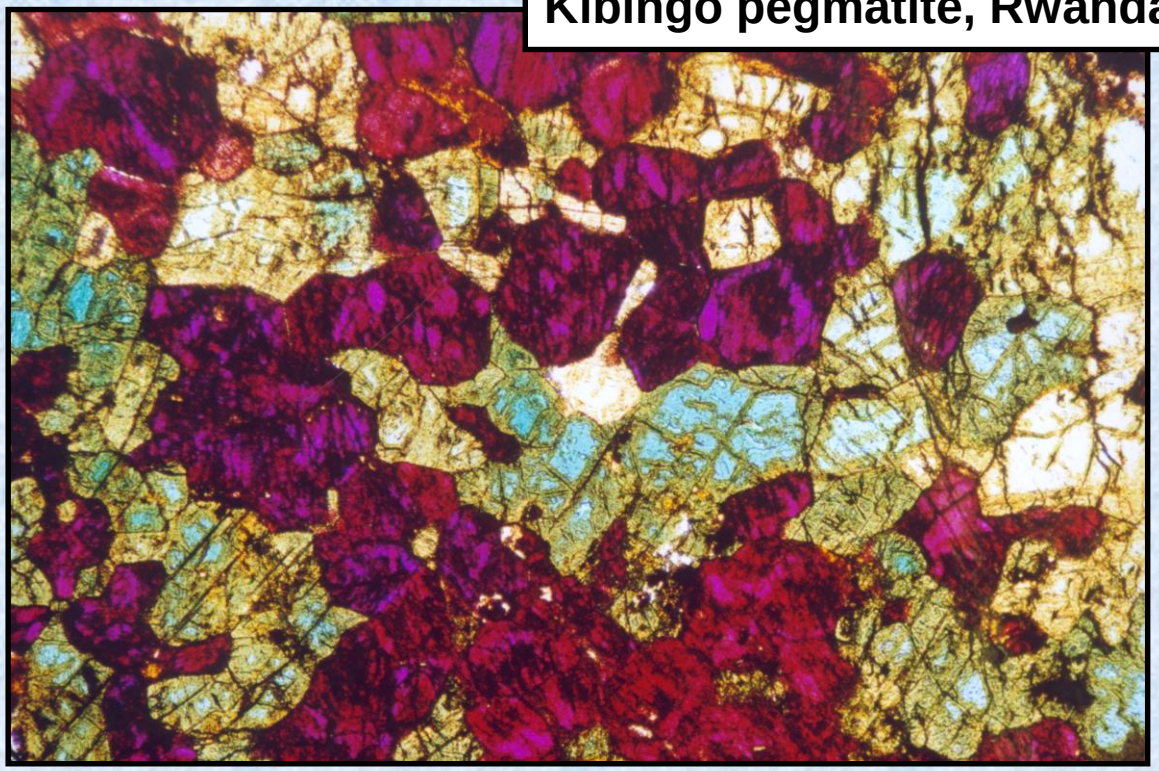
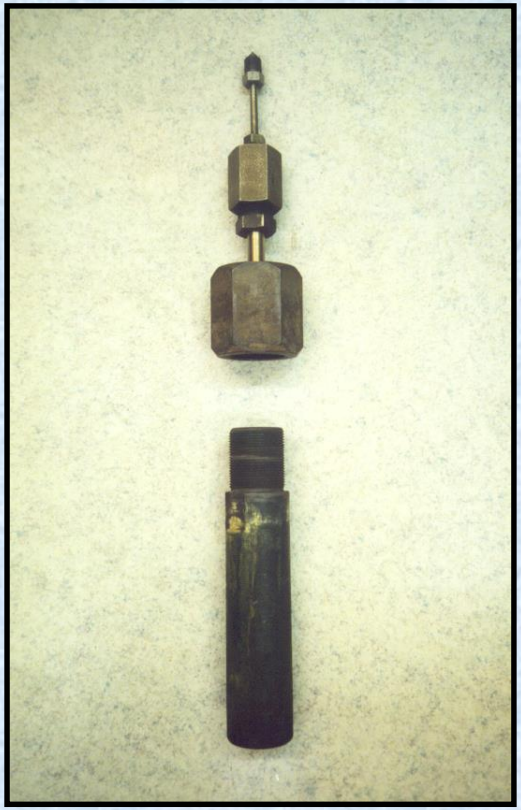
Kibingo pegmatite, Rwanda

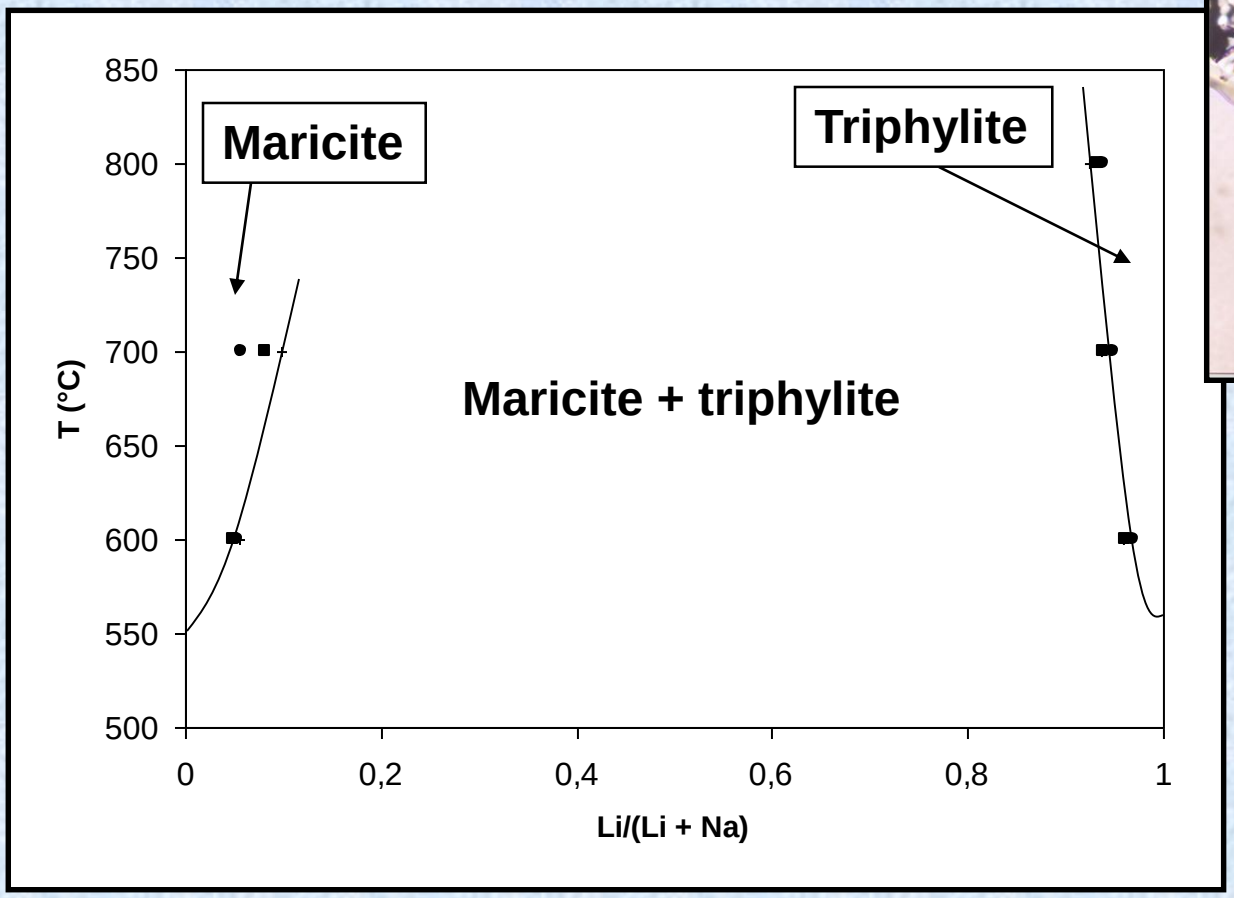


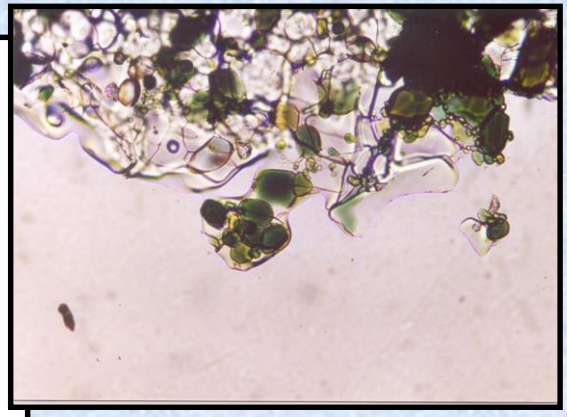


Hydrothermal synthesis

T = 400-800 °C, P = 1 kbar

Presence of Na in synthetic triphylite





- In triphylite, Na can reach 0.08 *a.p.u.f.* at 800°C
- In maricite, Li can reach 0.10 *a.p.u.f.* at 700°C

Na already observed in natrophilite, $NaMnPO_4$!

The triphylite + sarcopside assemblage

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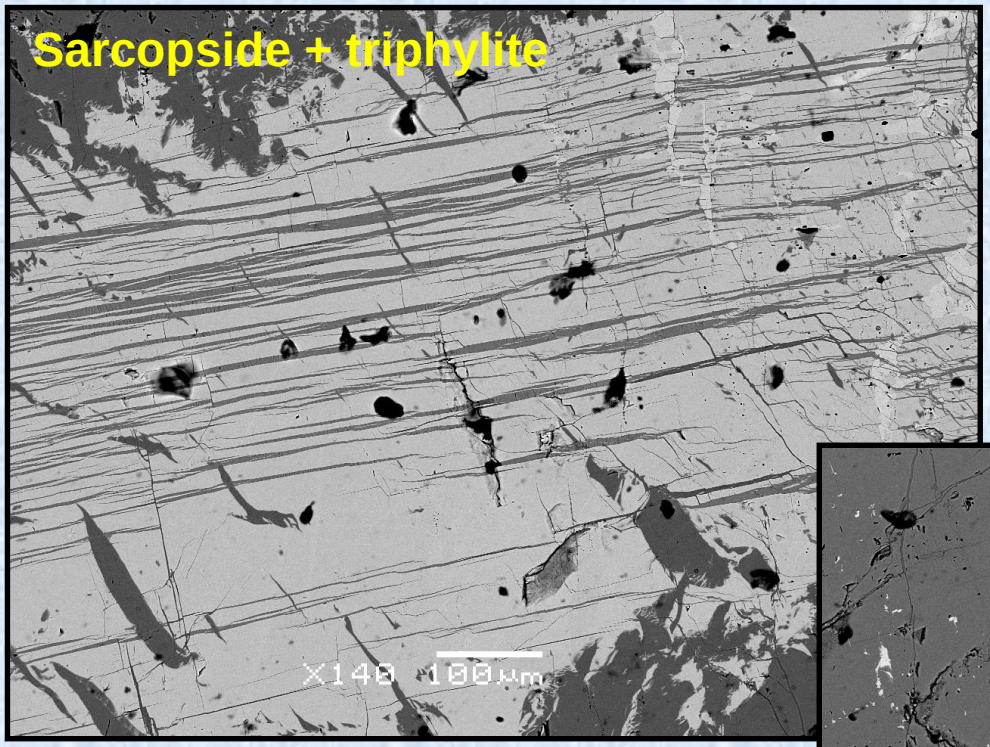


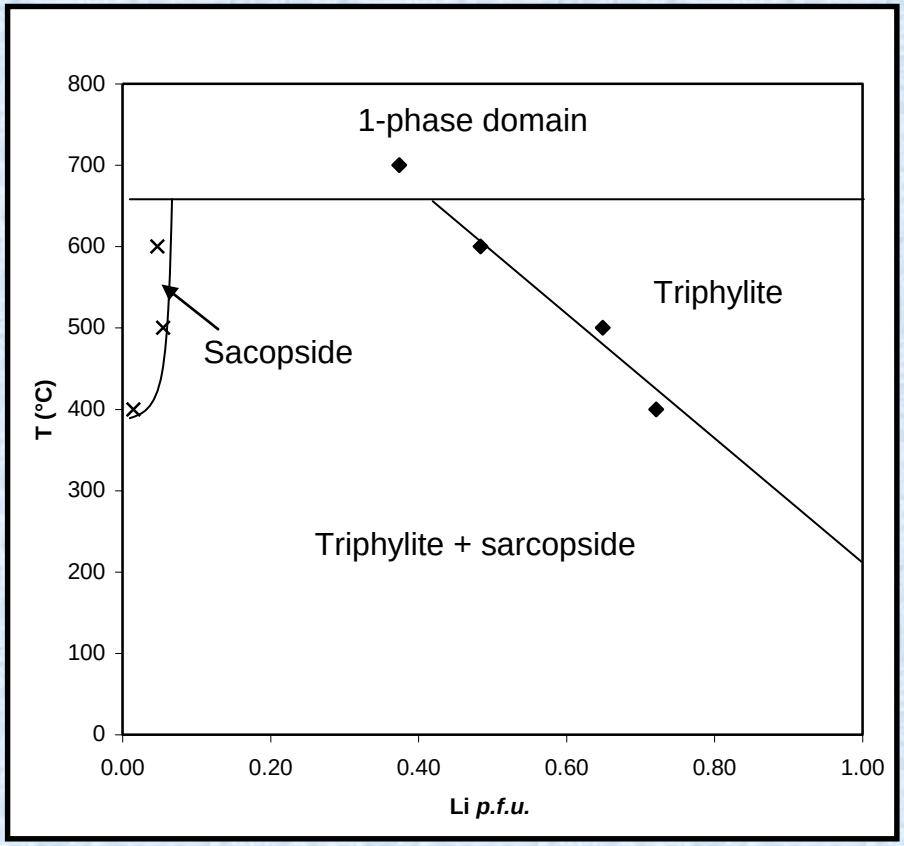
Cañada pegmatite, Spain

Lamellar textures

EXSOLUTIONS!!

Sarcopside $(Fe,Mn)_3(PO_4)_2$

Stability of the triphylite + sarcopside assemblage



$LiFe^{2+}_{2.5}(PO_4)_2$

- **Decrease of the Li-content of triphylite, from 0.72 *a.p.f.u.* at 400°C, to 0.48 *a.p.f.u.* at 600°C**
- **1-phase domain above 650°C**

$2Li^{+} = [] + Fe^{2+}$

- **The Li-content of triphylite decreases with the temperature**
- **The Fe-content of triphylite increases with the temperature**

Conclusions

- Natural and synthetic olivine-type phosphates were investigated by single-crystal X-ray diffraction, electron-microprobe, and ion probe (SIMS) techniques.
- The Li contents of ferrisicklerites and heterosites are very close to each other, and a progressive oxidation from lithiophilite to sicklerite is observed.
- The oxidation from triphylites to heterosites provokes a decrease of the M2-O bond lengths due to the oxidation of Fe and Mn, as well as an increase of the M1-O bond lengths due to the leaching of Li.
- A Jahn-Teller distortion of the M2 site is observed in heterosites, due to the presence of Mn^{3+}.
- Hydrothermal experiments have shown that significant amounts of Na may occur on the M1 site, and that Li may be replaced by Fe and vacancies according to the substitution mechanism $2Li^{+} = Fe^{2+} + []$.