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

Structural Variations of Olivine-type Phosphates: A good Example of how Minerals can inspire the Development of new Materials

F. Hatert, F. Dal Bo, M. Baijot

Warwick, August 27th, 2013

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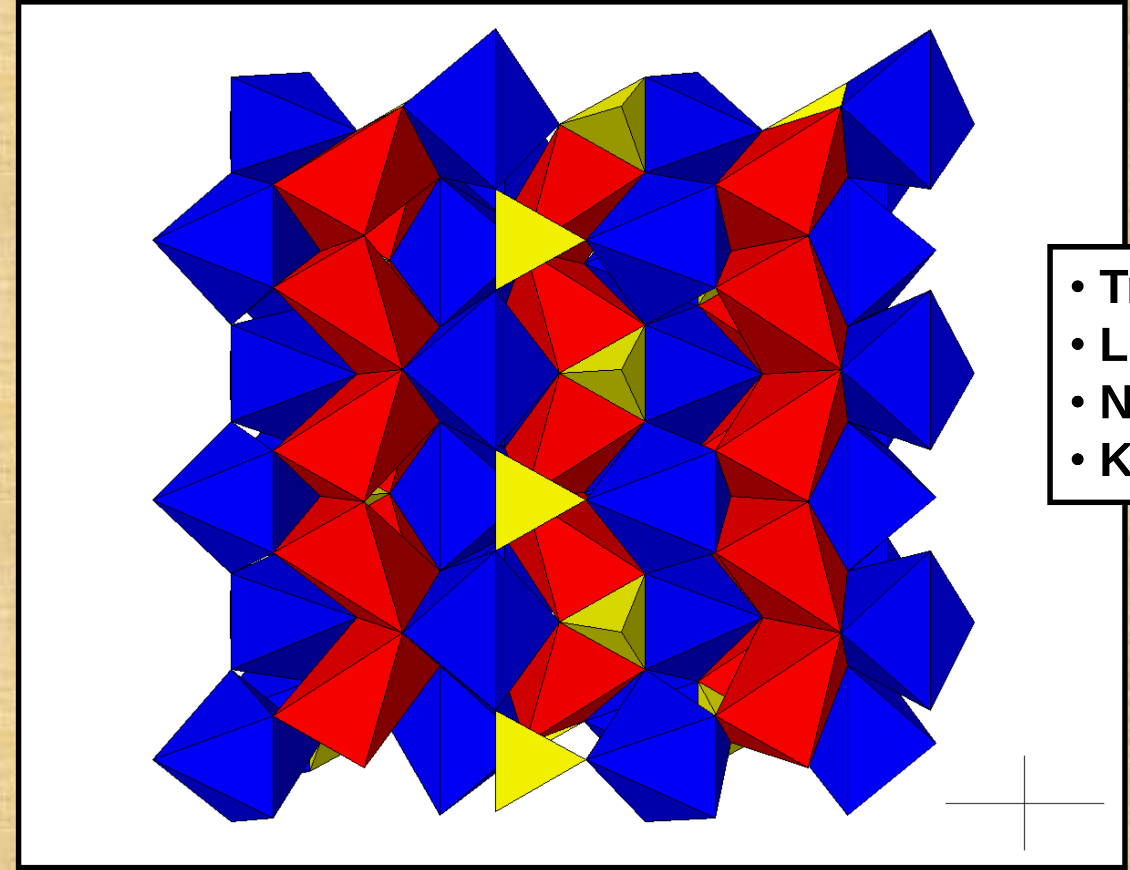
Natural phosphates with the olivine structure



- Triphylite, $LiFe^{2+}(PO_4)$
- Lithiophilite, $LiMn(PO_4)$
- Natrophilite, $NaMn(PO_4)$
- Karenwebberite, $NaFe^{2+}(PO_4)$

S.G. *Pmnb*
***a* = 6.092, *b* = 10.429, *c* = 4.738 Å**

Red octahedra: M1 (Li, Na)
Blue octahedra: M2 (Fe^{2+}, Mn, Mg)

Occurrence: Granitic pegmatites

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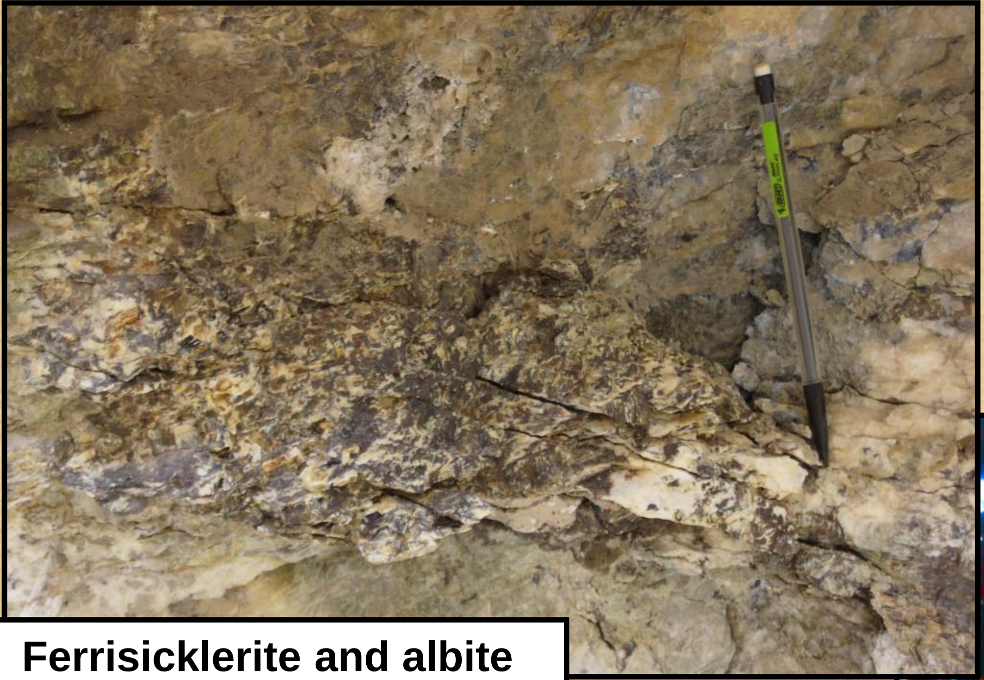
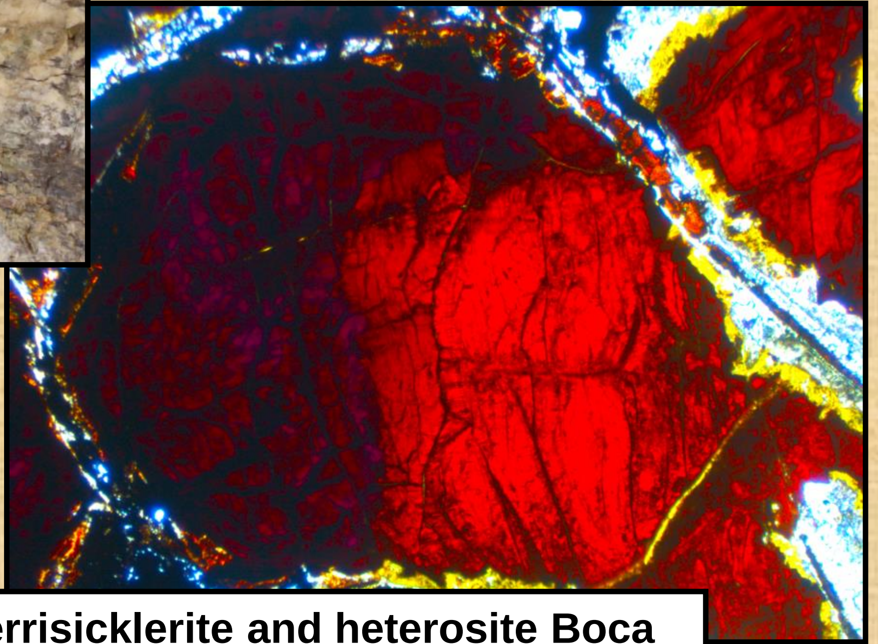
Lithiophilite, La Empleada pegmatite, Argentina

Triphylite and albite, Sapucaia pegmatite, Brazil

Oxidized compositions



Ferrisicklerite and albite
Sapucaia pegmatite, Brazil



Ferrisicklerite and heterosite Boca Rica pegmatite, Brazil

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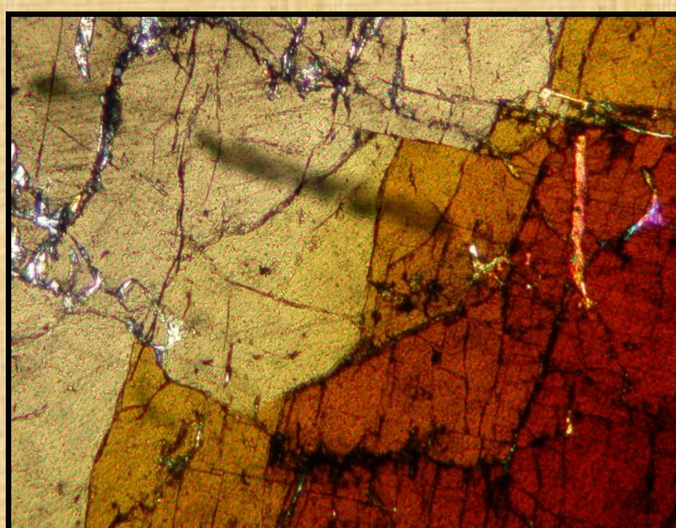
Oxidation of olivine-type phosphates: the « Quensel-Mason » sequence

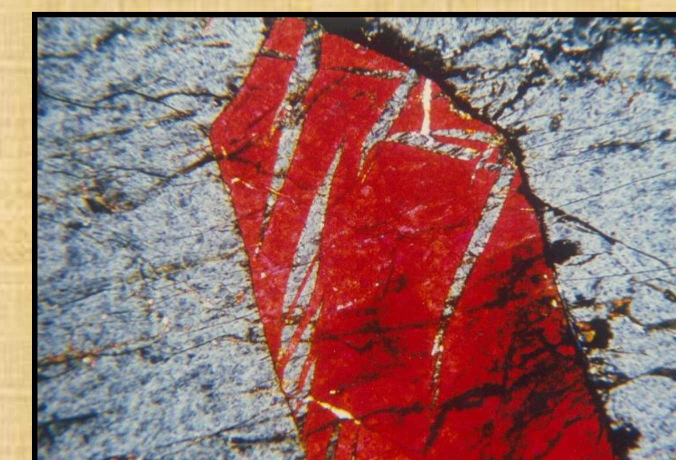
$Li(Mn^{2+},Fe^{2+})PO_4 \Rightarrow \bullet_x Li_{1-x}(Mn^{2+},Fe^{3+})PO_4 \Rightarrow \bullet(Mn^{3+},Fe^{3+})PO_4$

(Lithiophilite) (Sicklerite) (Purpurite)

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

(Triphylite) (Ferrisicklerite) (Heterosite)





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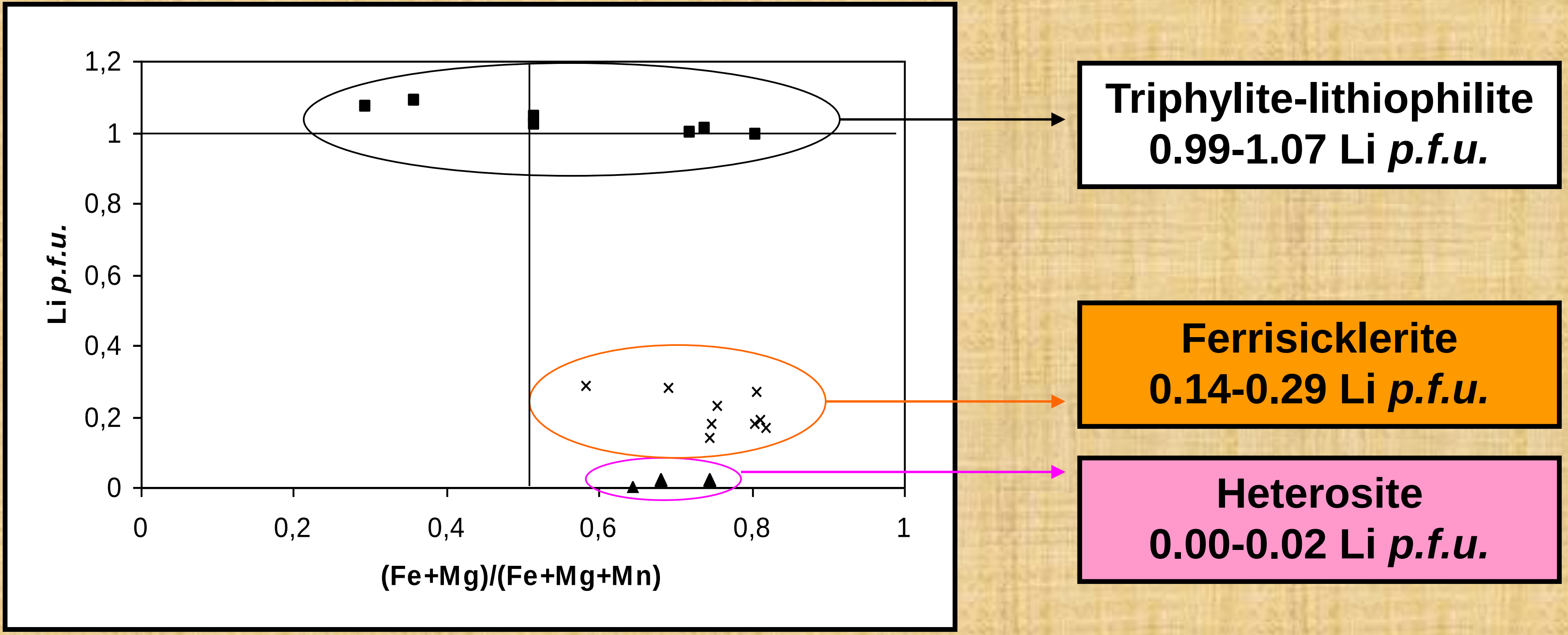
Natural sample selection

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



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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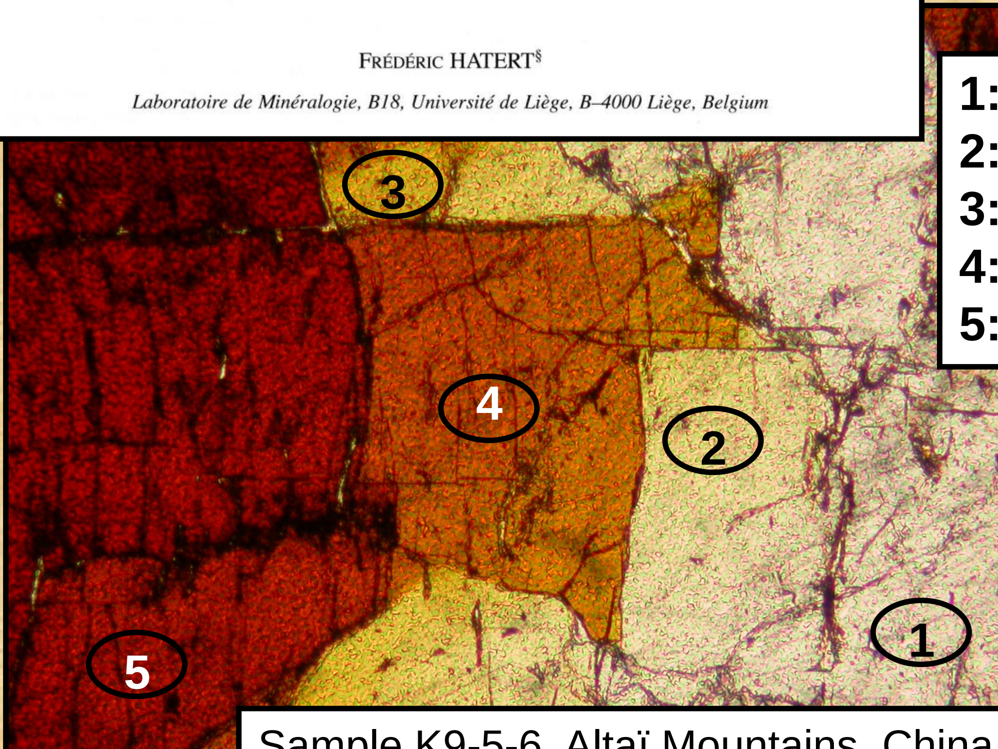
A STRUCTURAL STUDY OF THE LITHIOPHILITE–SICKLERITE SERIES

FRÉDÉRIC HATERT§

Laboratoire de Minéralogie, B18, Université de Liège, B–4000 Liège, Belgium



Sample K9-5-6, Altaï Mountains, China

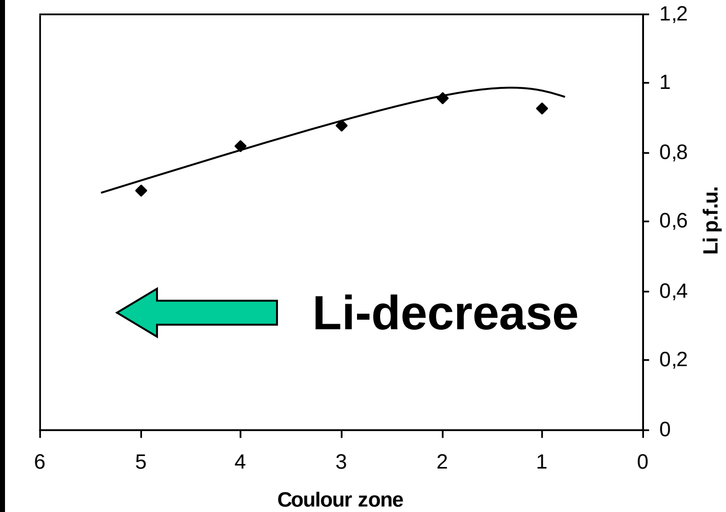
1: $Li_{0.93}(Fe^{2+}_{0.03}Fe^{3+}_{0.13}Mn^{2+}_{0.80})(PO_4)$

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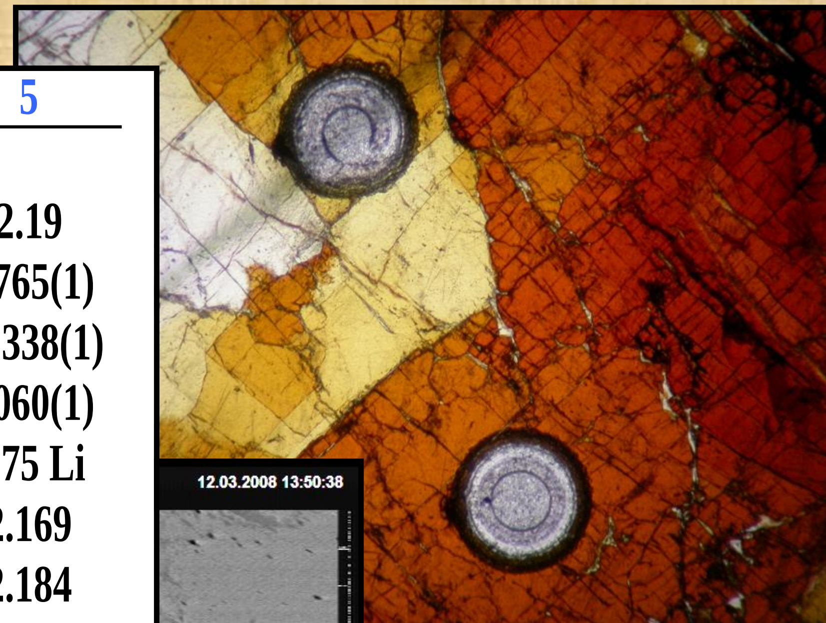
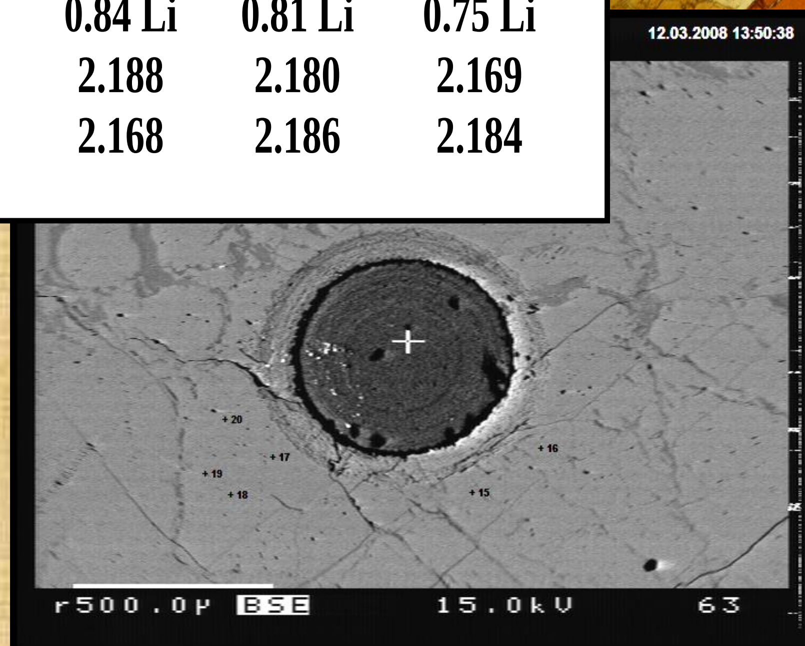
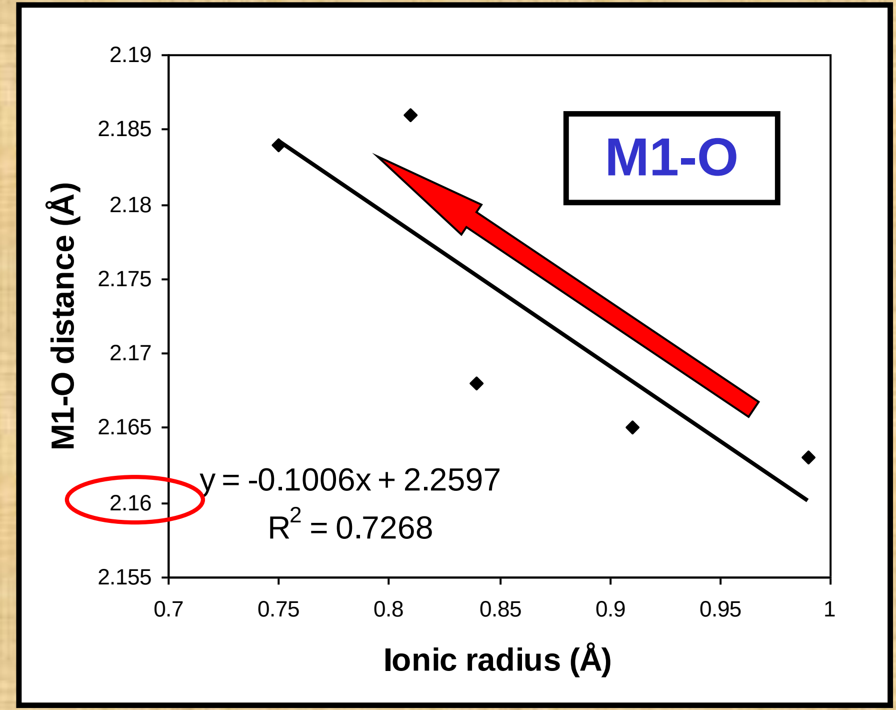
	1	2	3	4	5
R_1 (%)	2.53	2.36	2.94	2.67	2.19
a (Å)	4.736(1)	4.734(1)	4.740(1)	4.767(1)	4.765(1)
b (Å)	10.432(2)	10.423(2)	10.415(1)	10.403(2)	10.338(1)
c (Å)	6.088(1)	6.094(1)	6.080(1)	6.072(1)	6.060(1)
M(2)	0.99 Li	0.91 Li	0.84 Li	0.81 Li	0.75 Li
M(1)-O	2.193	2.193	2.188	2.180	2.169
M(2)-O	2.163	2.165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

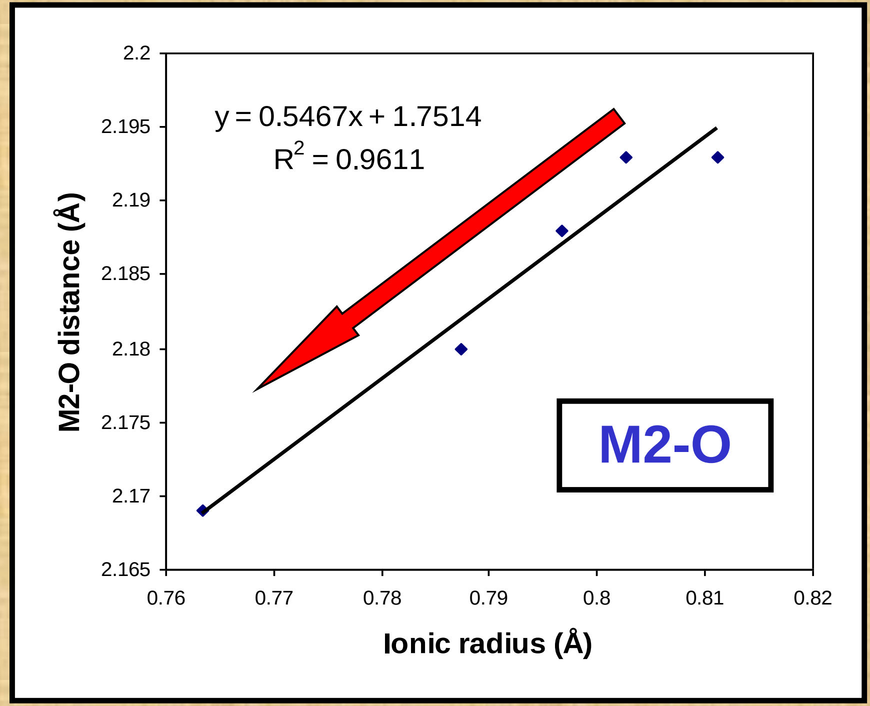




- **Micro-drilling**
- **Single-crystal structure refinements**

Variations of M-O bond lengths





- 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!

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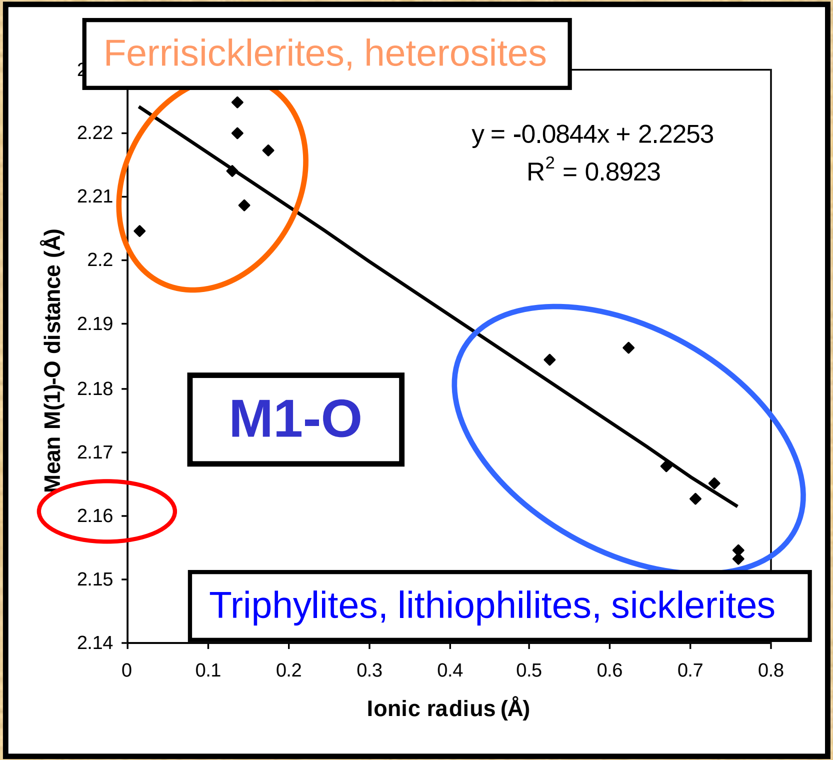
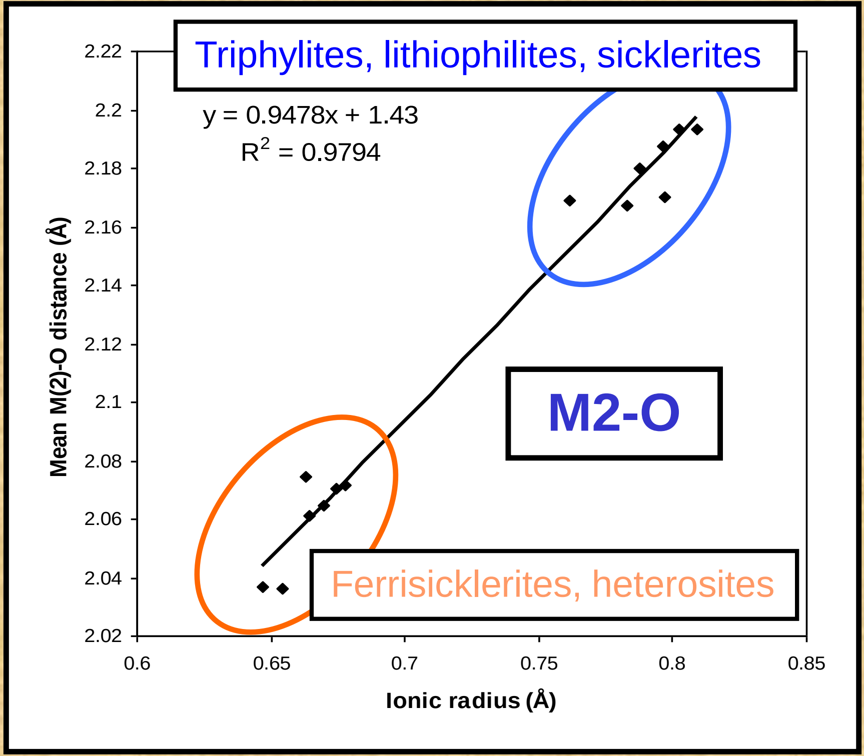
Single-crystal structure refinements of natural olivine-type phosphates

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

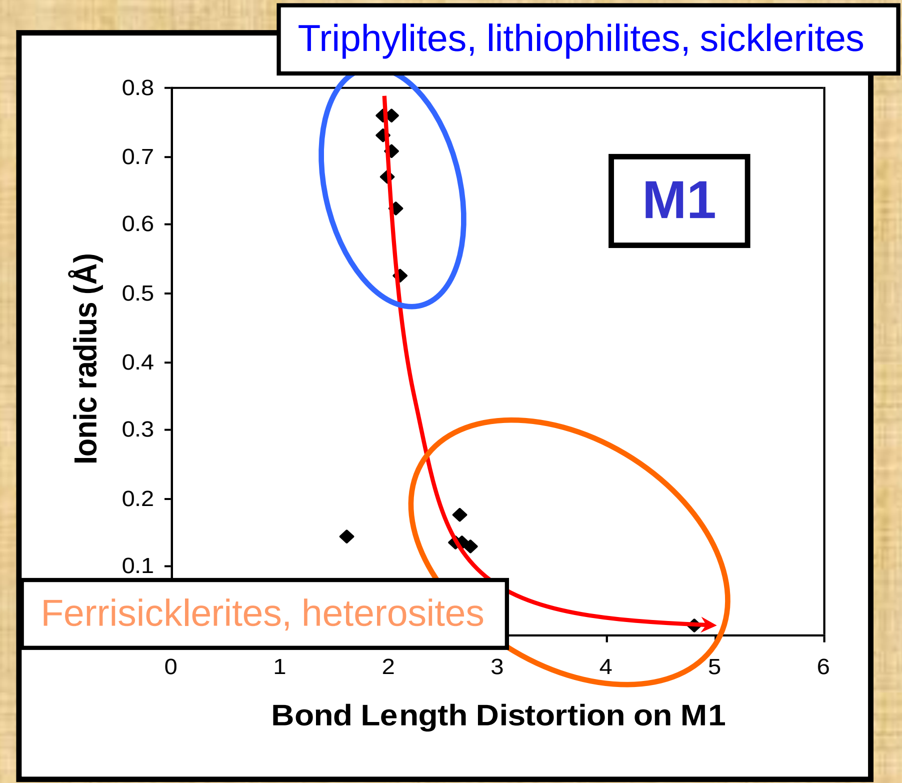
Variations of M-O bond lengths

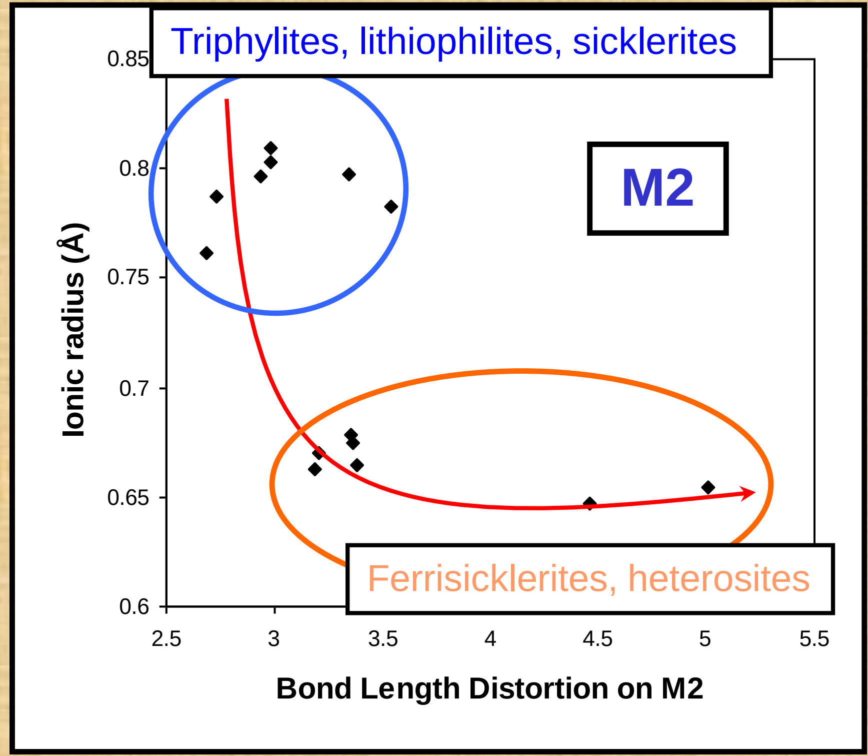




- Decrease of the M2-O due to the progressive oxidation of iron and manganese
- Increase of the M1-O due to leaching of lithium

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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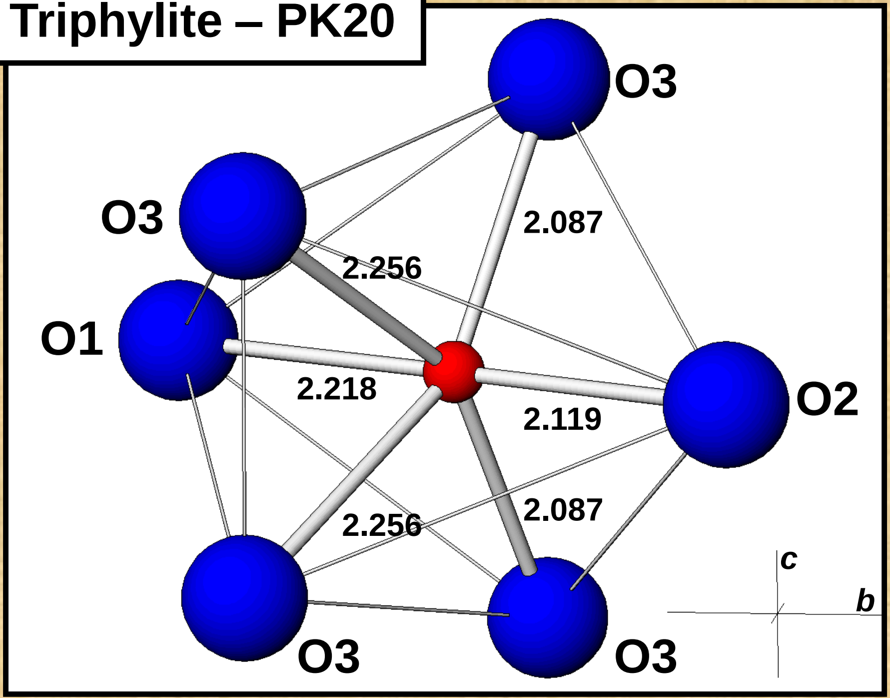
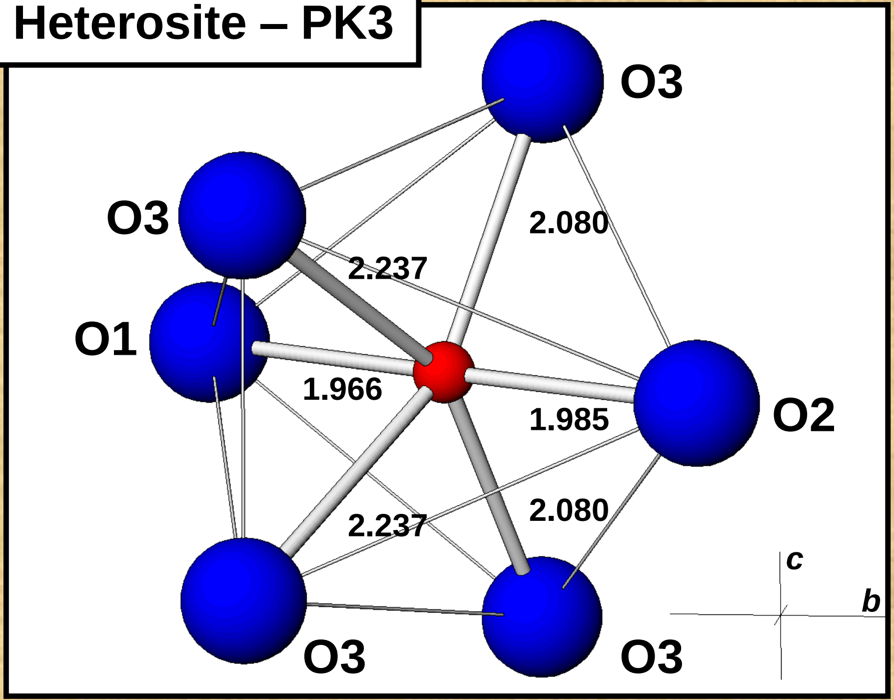
Triphylite – PK20



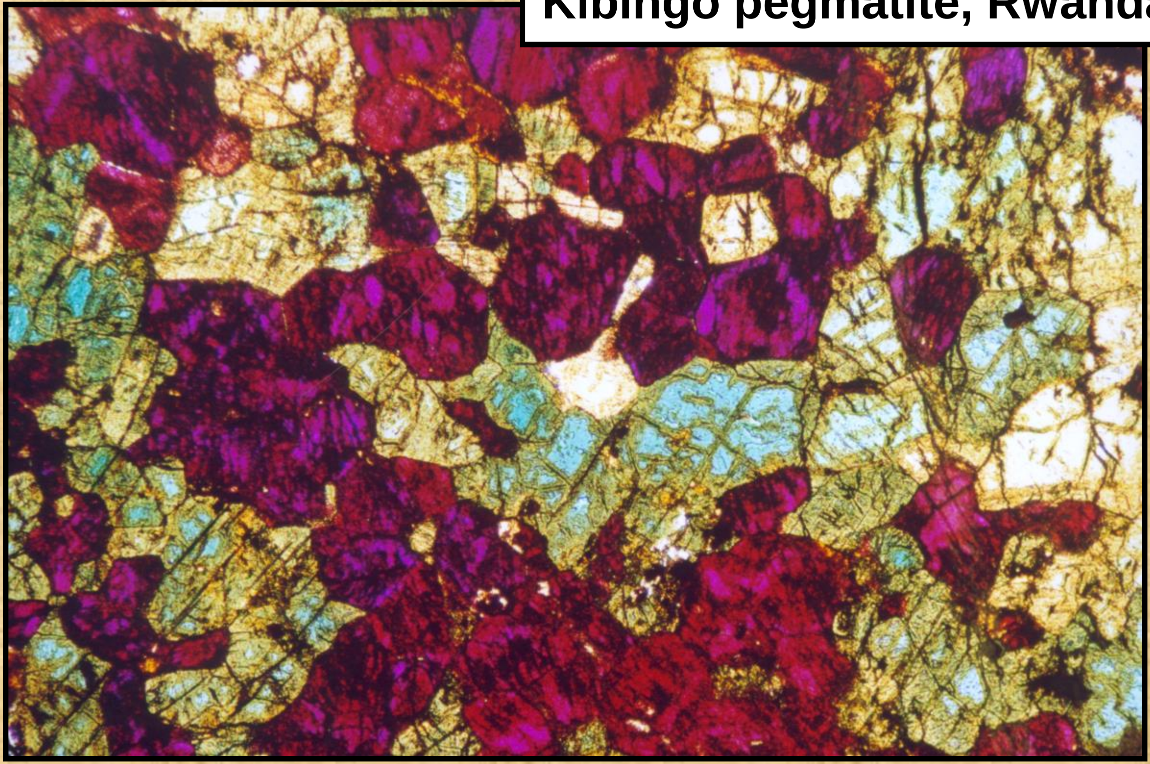
Heterosite – PK3

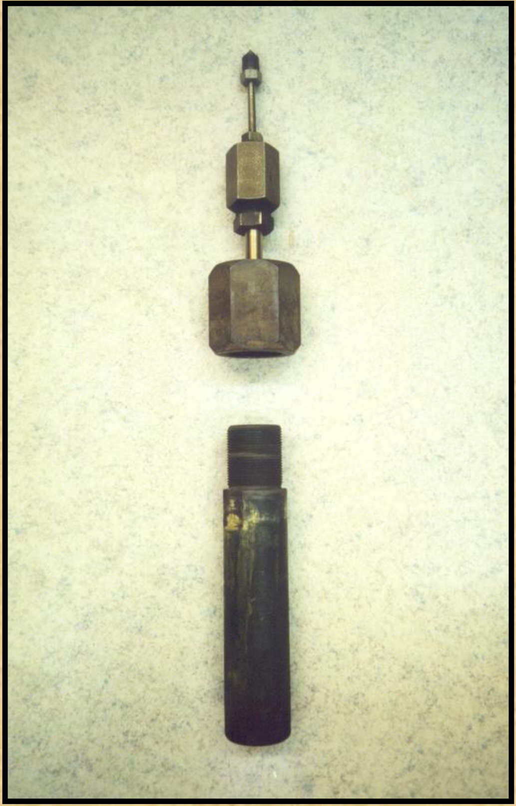


→ **Jahn-Teller distortion, due to the presence of Mn^{3+} in heterosite**

Experimental investigations: the alluaudite + triphylite assemblage

Kibingo pegmatite, Rwanda





Hydrothermal synthesis

T = 400-800 °C, P = 1 kbar

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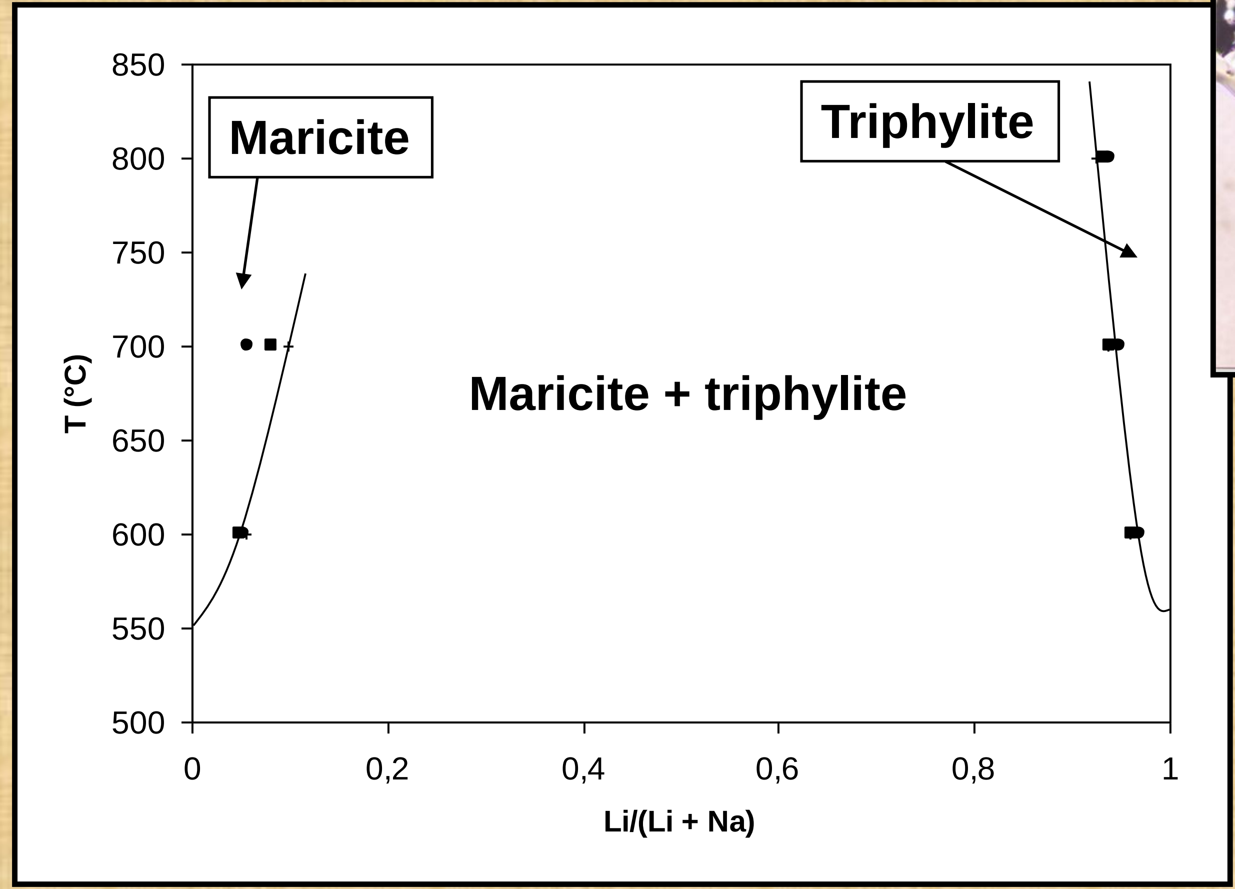
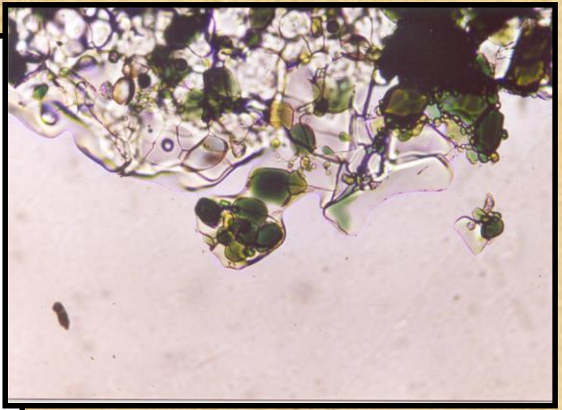
Presence of Na in synthetic triphylite

Maricite $NaFe(PO_4)$

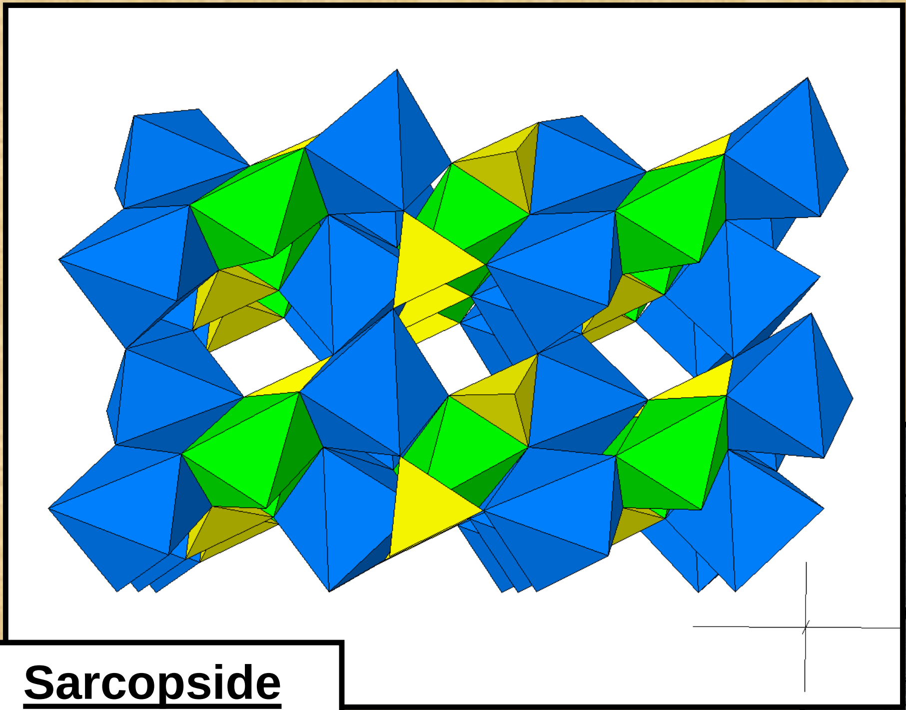




- **In triphylite, Na can reach 0.08 *a.p.u.f.* at 800°C**
- **In maricite, Li can reach 0.10 *a.p.u.f.* at 700°C**

Na already observed in natrophilite, $NaMnPO_4$, and in karenwebberite, $NaFePO_4$!

The triphylite + sarcopside assemblage



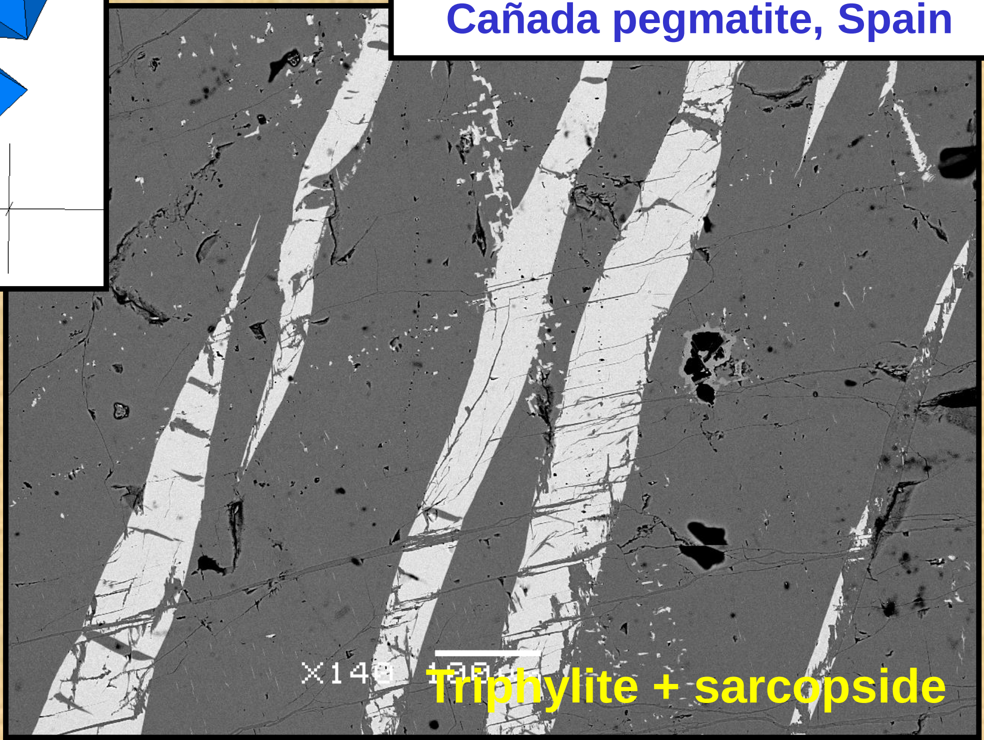
Sarcopside
a = 6.088(1) Å
b = 4.814(1) Å
c = 10.484(2) Å
β = 89.42(3)°
S.G. $P2_1/c$

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

Lamellar textures

EXSOLUTION!

Cañada pegmatite, Spain



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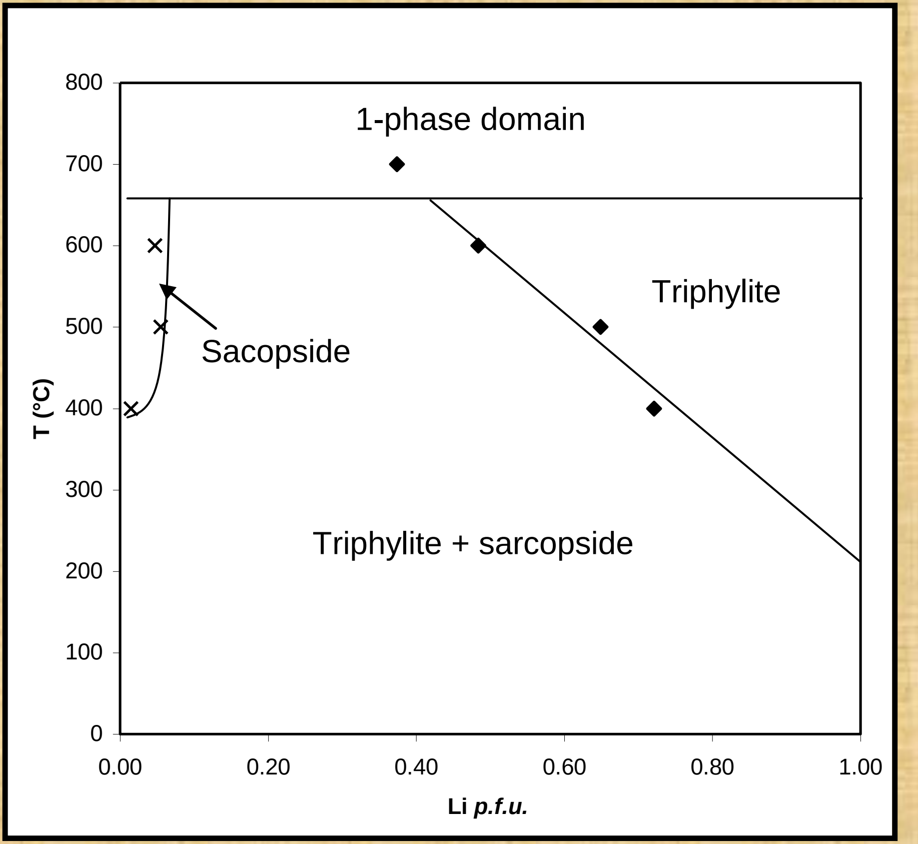
Stability of the triphylite + sarcopside assemblage



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

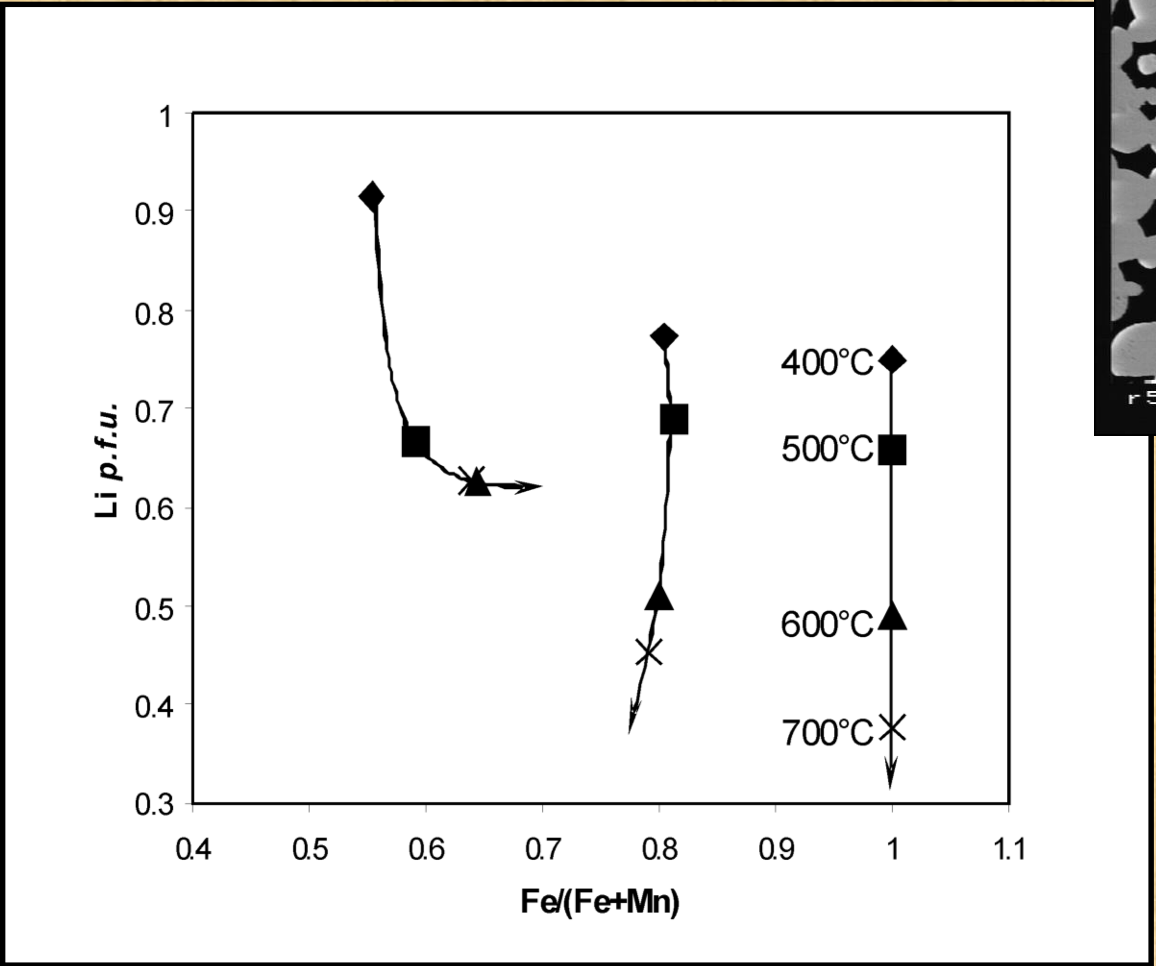
- **Decrease of the Li-content of triphylite, from 0.72 *a.p.f.u.* at 400°C, to 0.48 *a.p.f.u.* at 600°C**
- **1-phase domain above 650°C**

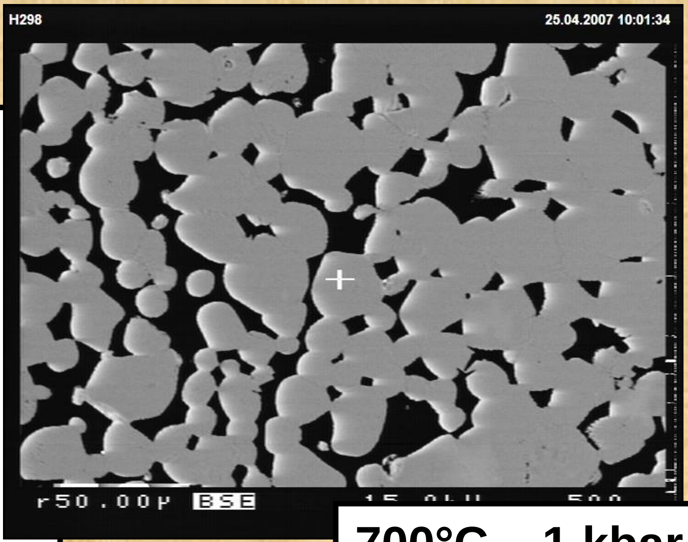
$2Li^{+} = [] + Fe^{2+}$

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

The triphylite-sarcopside miscibility

$Li_2Fe^{2+}{}_2(PO_4)_2$ – $Fe^{2+}{}_3(PO_4)_2$





700°C – 1 kbar

- **Stability of pure $LiFe(PO_4)$?**
- **No chemical data (Li) in the literature!**

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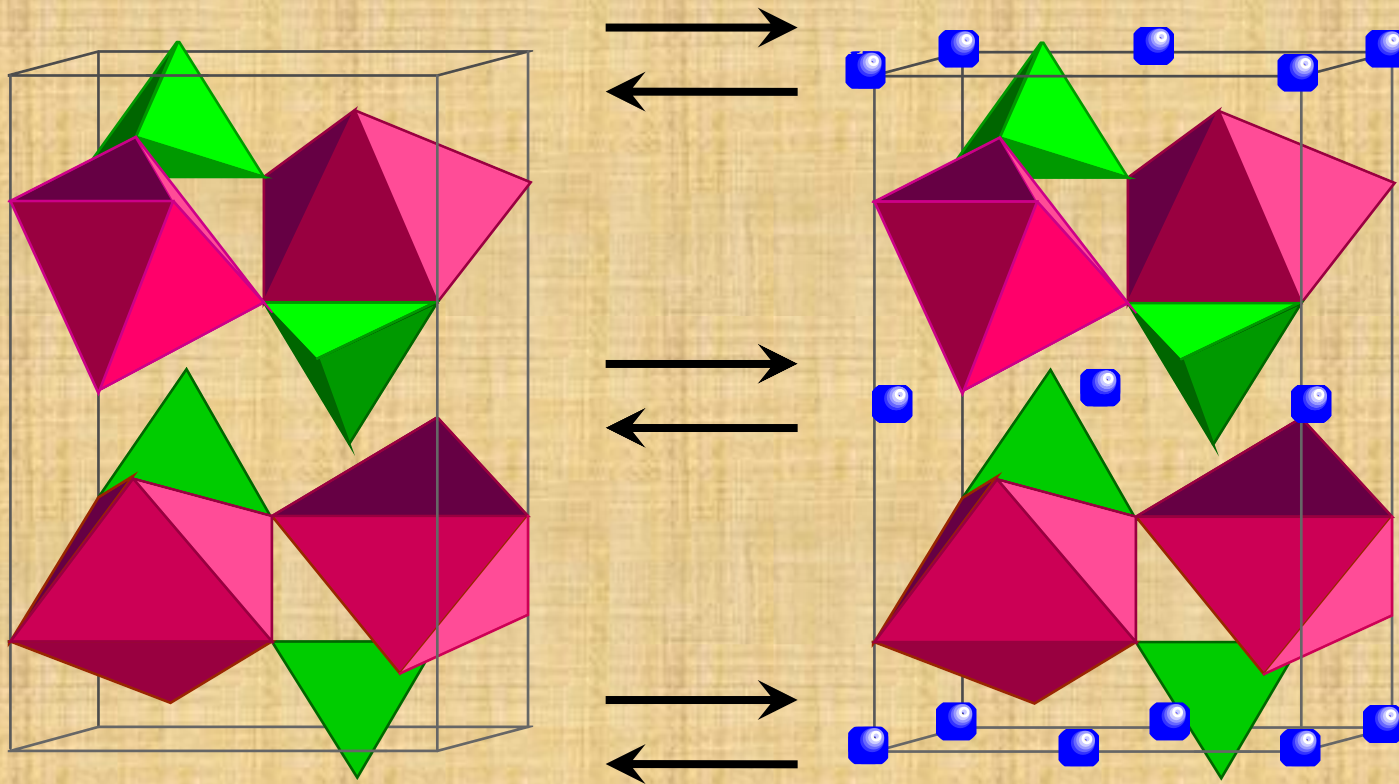
Intercalation – extraction of Li

Electrochemical properties demonstrated by Padhi *et al*. (1997)



Heterosite, $Fe^{3+}(PO_4)$

Triphylite, $LiFe^{2+}(PO_4)$

Natural oxydation mechanism described by Quensel (1937) and Mason (1941) !

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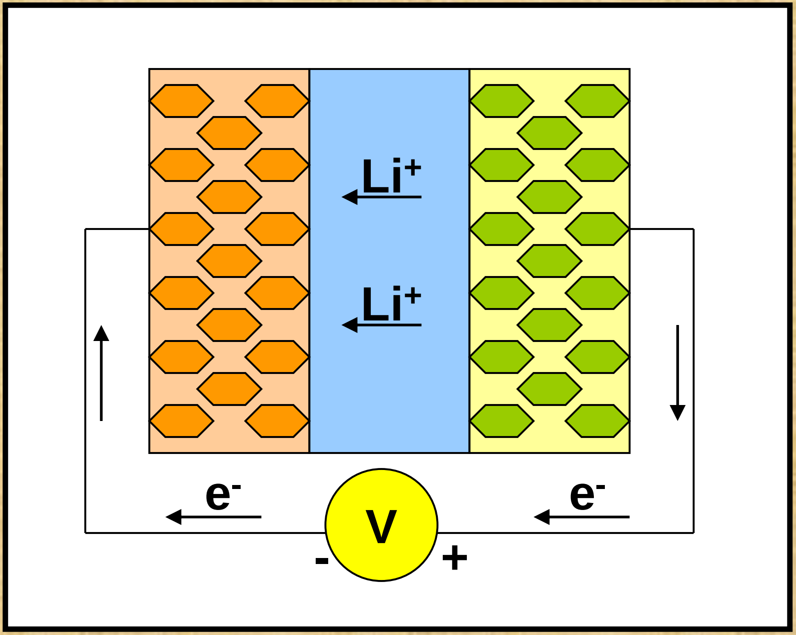
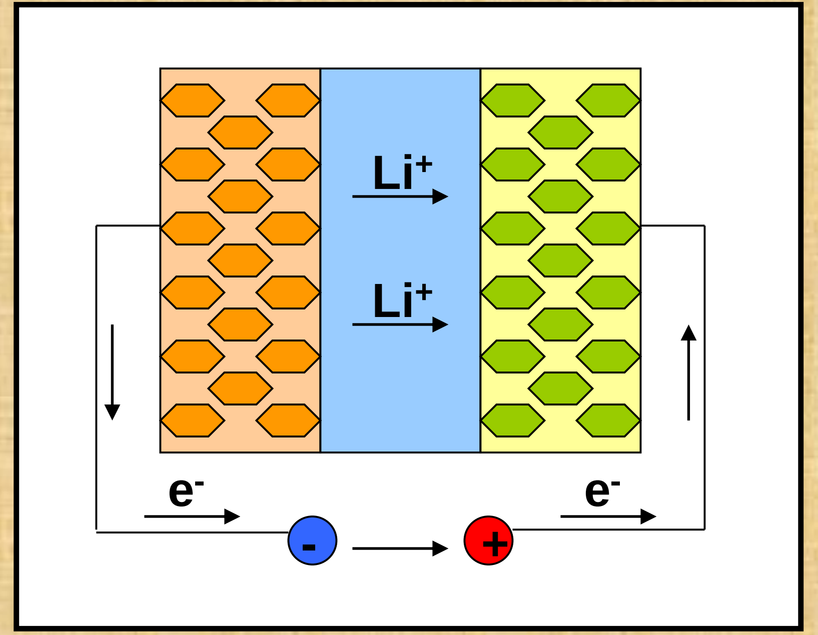
Principle of Li-ion batteries



Charge

Discharge



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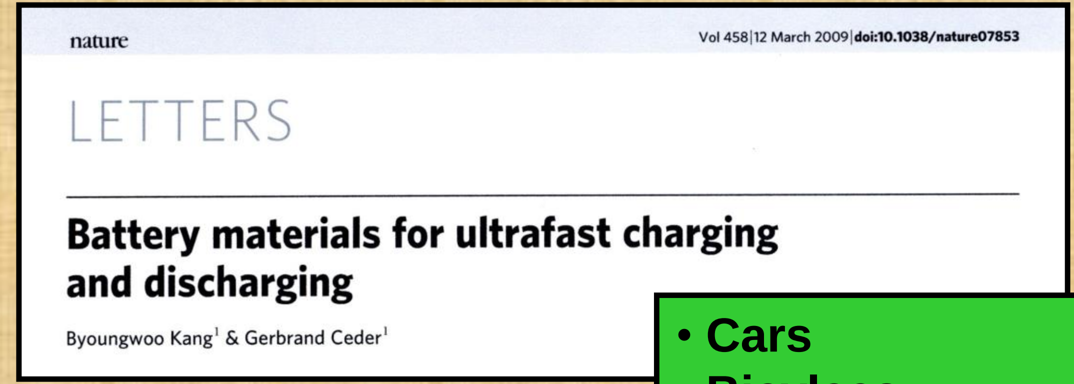
LiFePO$_4$-based batteries

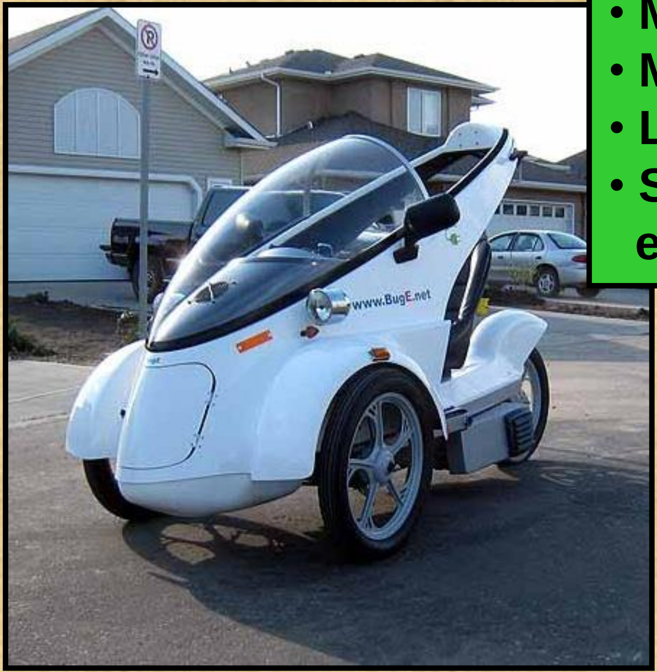

nature   Vol 458 | 12 March 2009 | doi:10.1038/nature07853

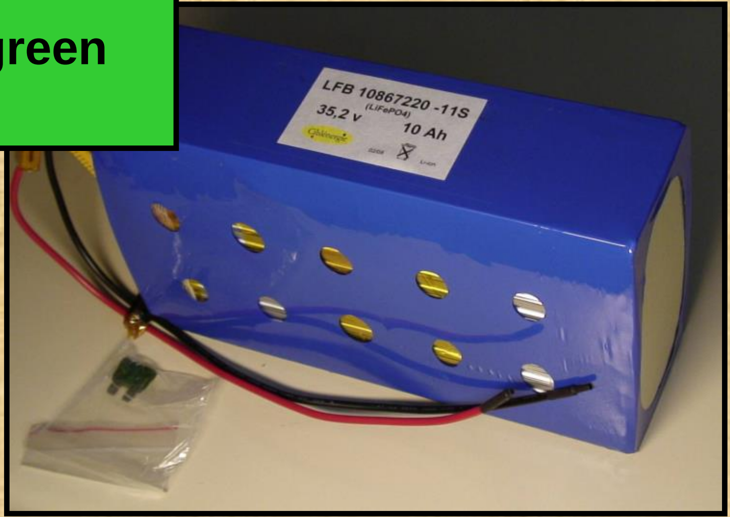
LETTERS

Battery materials for ultrafast charging and discharging

Byoungwoo Kang[1] & Gerbrand Ceder[1]

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





Karenwebberite, a new mineral...

American Mineralogist, Volume 98, pages 767–772, 2013

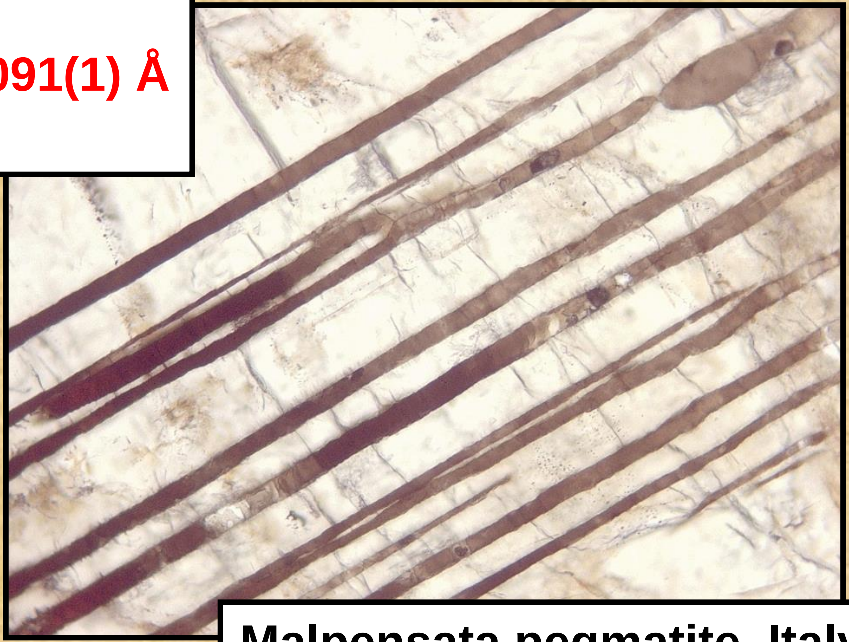
Karenwebberite, Na(Fe^{2+},Mn^{2+})PO_4, a new member of the triphylite group from the Malpensata pegmatite, Lecco Province, Italy

PIETRO VIGNOLA,[1] FRÉDÉRIC HATERT,[2,*] ANDRÉ-MATHIEU FRANSOLET,[2] OLAF MEDENBACH,[3] VALERIA DIELLA,[1] AND SERGIO ANDÒ[4]

$NaFe^{2+}PO_4$

***a* = 4.882(1), *b* = 10.387(2), *c* = 6.091(1) Å**
Pbnm

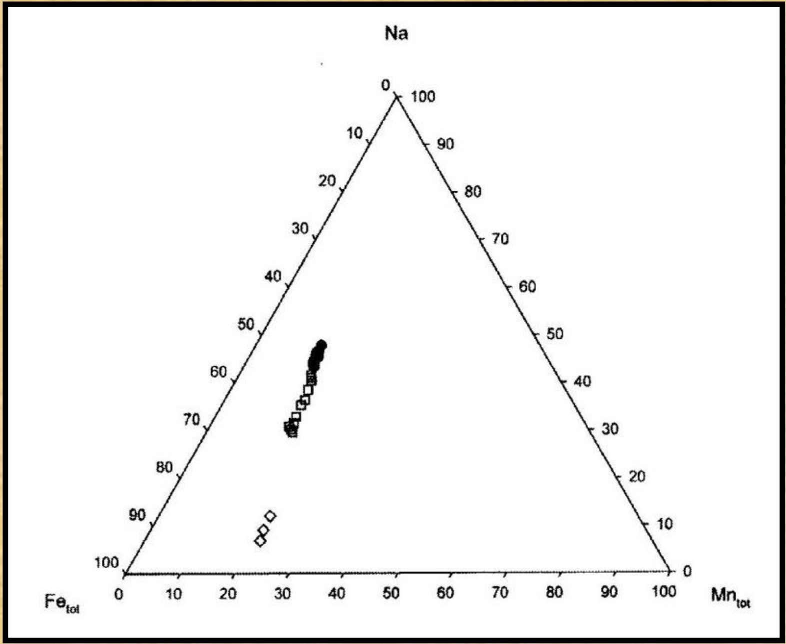
Karen Louise Webber



Malpensata pegmatite, Italy

The oxidation of karenwebberite

Progressive oxidation towards Na-bearing ferrisicklerite



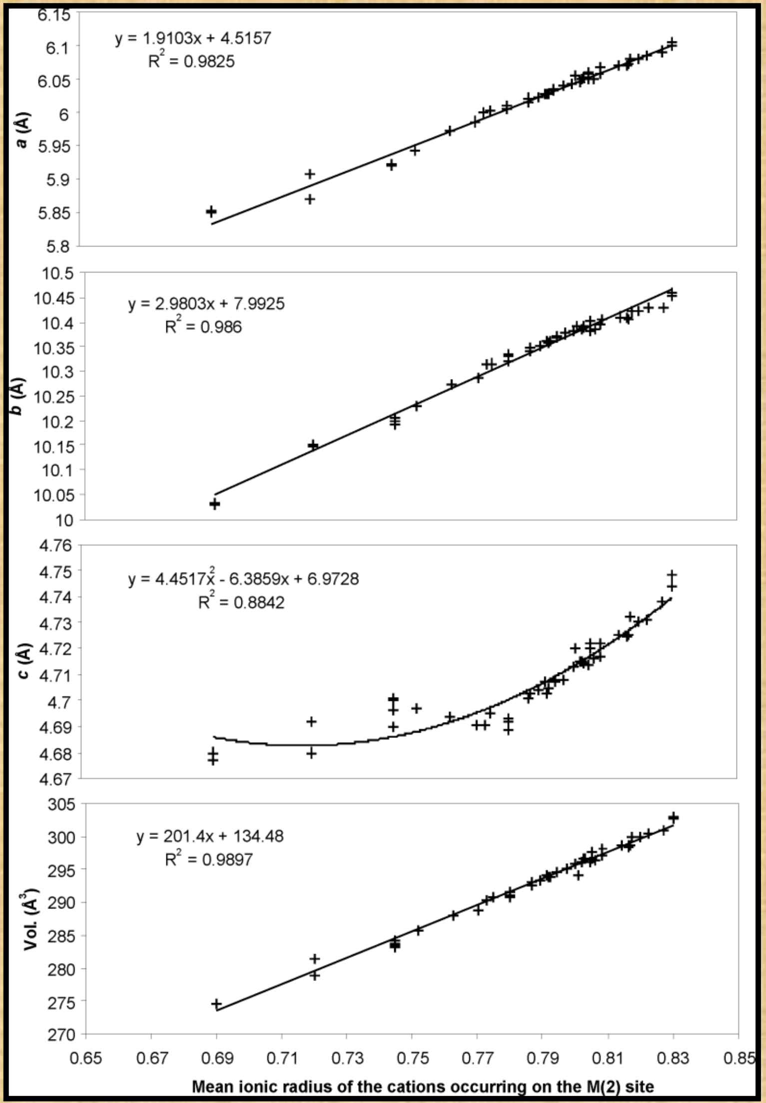
$Na^{+} + Fe^{2+} = [] + Fe^{3+}$

Use of karenwebberite as cathode material for sodium batteries??

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.
- Synthetic Na-bearing olivine-type phosphates, with compositions like those of karenwebberite, are good candidates as cathode material for sodium batteries.

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 %)

Li-ion batteries

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	Layered struct.		Spinel	Triphylite
	$LiCoO_2$	$LiNiCoO_2$	$LiMn_2O_4$	$LiFePO_4$
Capacity (mAh/g)	140-150	170-180	110-120	160-170
Potentiel (V)	3,9	3,8	4,0	3,4
Resistance to cycling	Poor	Poor	+/-	Good
Exchange speed	Good	Good	Good	Good
Electrode density	Good	+/-	+/-	Poor
Security	+/-	?	Good	Good
Cost of chemicals	High	+/-	Low	Low
Cost of synthesis	Low	High	+/-	Low
Abundance	Low	+/-	High	High
Toxicity	?	?	Low	Very low

Ref: N. Krins, Master thesis ULg, 2004 (LCIS)