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

Crystal chemistry and nomenclature of the triphylite group of phosphates

Prof. Frédéric Hatert

Dublin, August 23rd, 2024

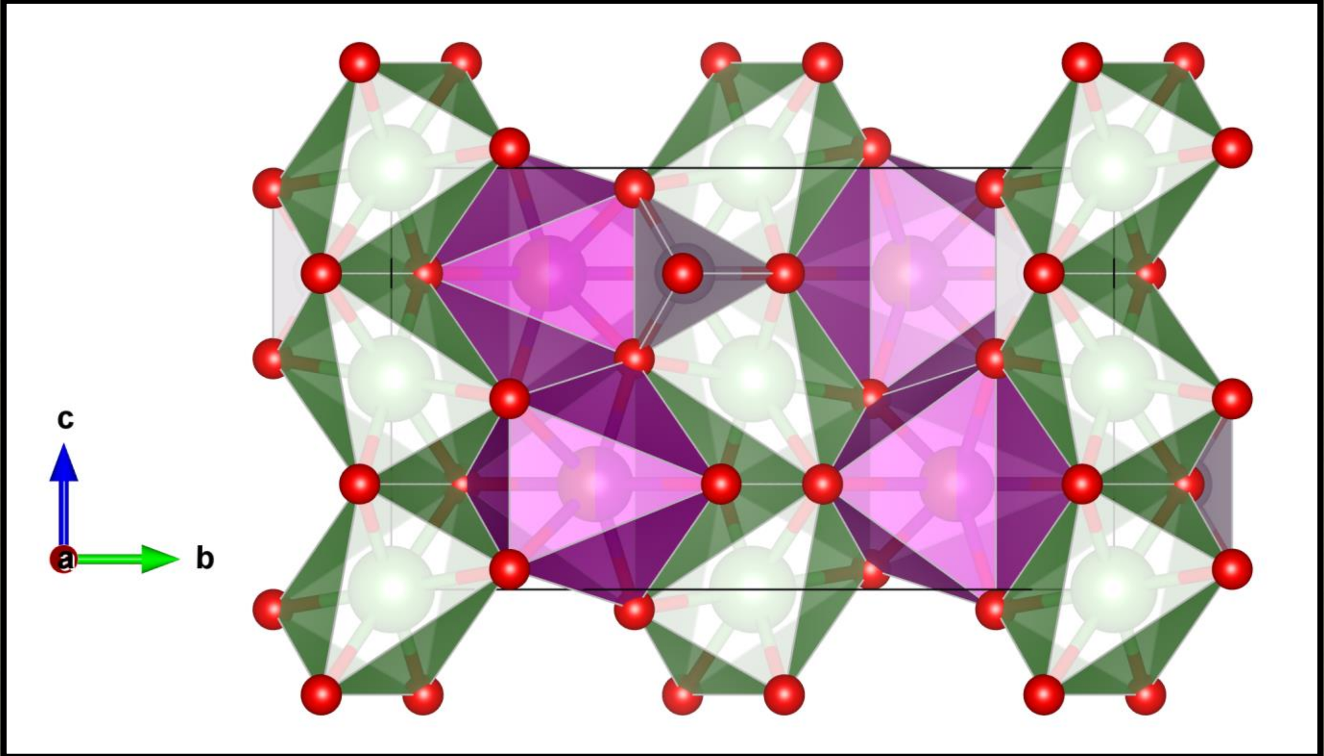
Triphylite-type phosphates in pegmatites

Heterosite, Buranga, Rwanda

Triphylite, Palermo, NH, USA

Ferrisicklerite, Sapucaia, Brazil

The triphylite structure



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

Isostructural with olivine

S.G. *Pnma*

a = 4.738 Å
b = 10.429 Å
c = 6.092 Å

Green octahedra: M1 (Li, Na)
Purple octahedra: M2 (Fe, Mn)

The Quensel-Mason oxidation sequence

Percy Quensel (1881-1966)

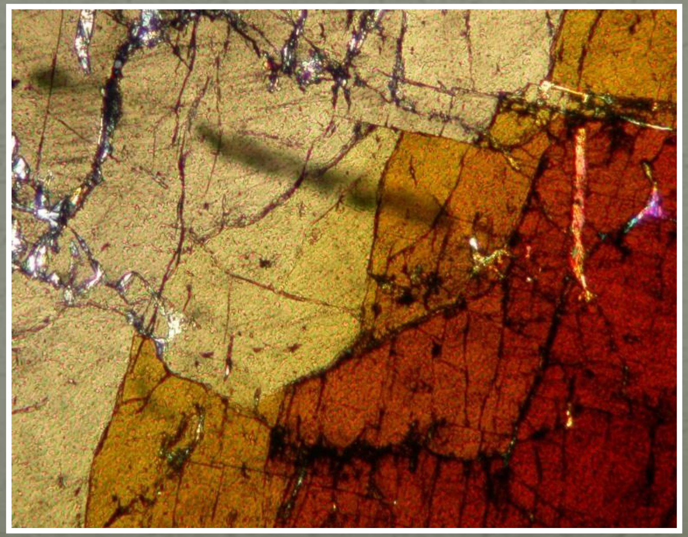
Brian Mason (1917-2009)

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

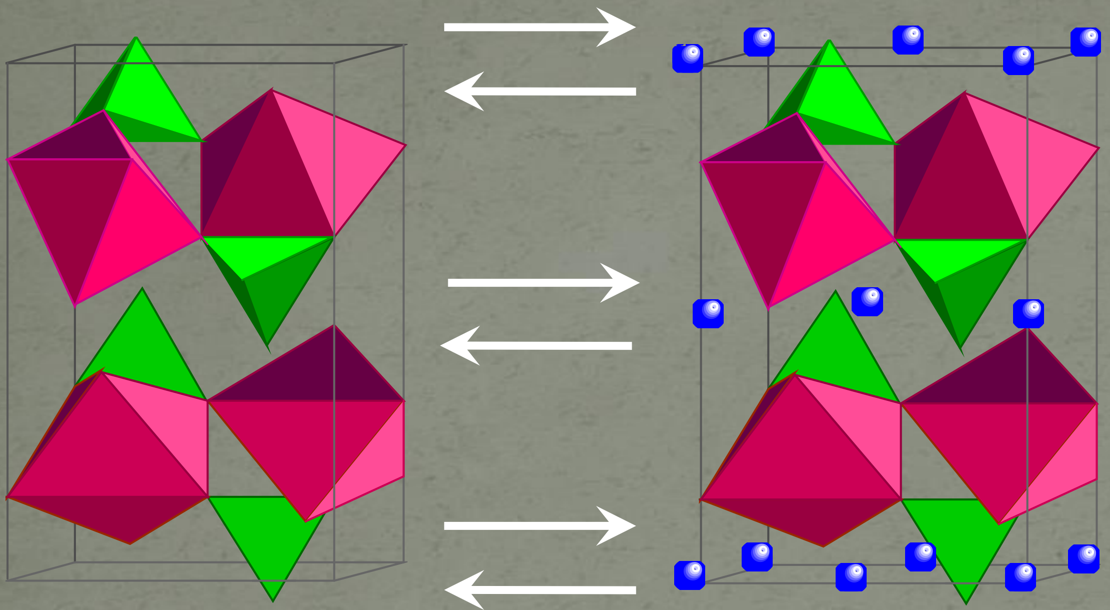
(Lithiophilite) (Sicklerite) (Purpurite)

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

(Triphylite) (Ferrisicklerite) (Heterosite)



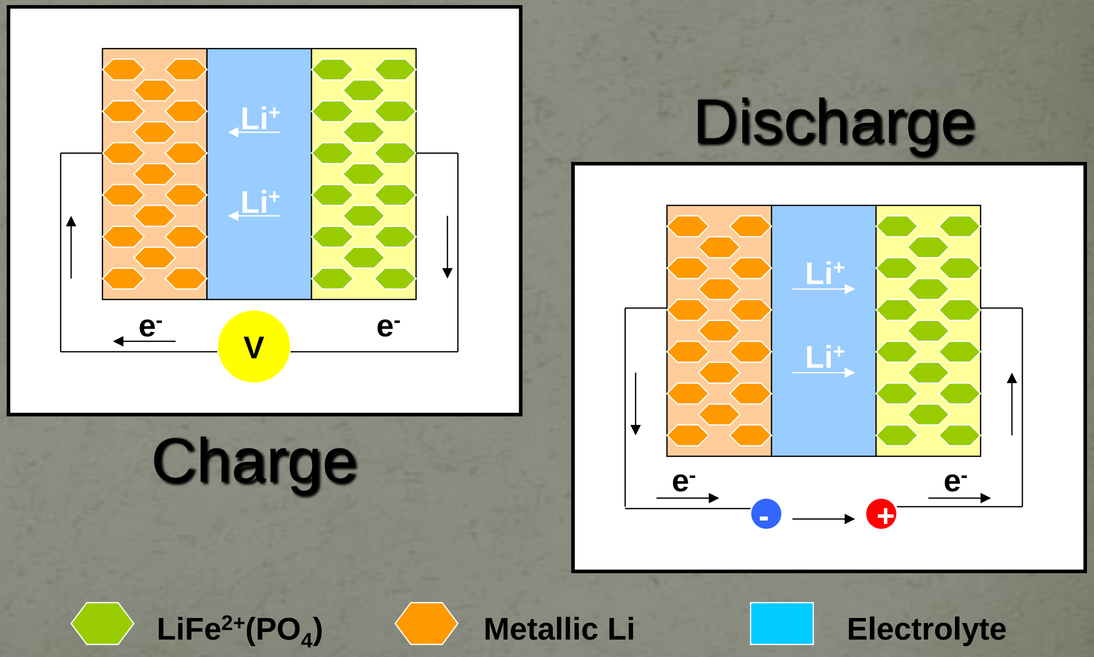
Electrochemical properties



Hétérosite
$Fe^{3+}(PO_4)$

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

Padhi *et al*. (1997)



Li-ion batteries based on LFP

LFP Li-ion batteries

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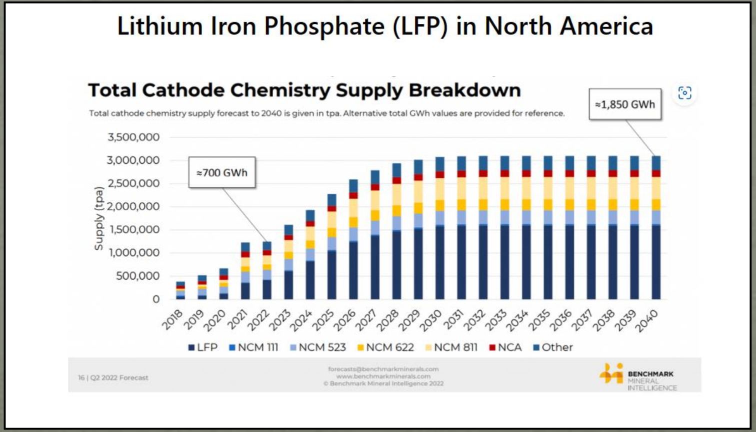
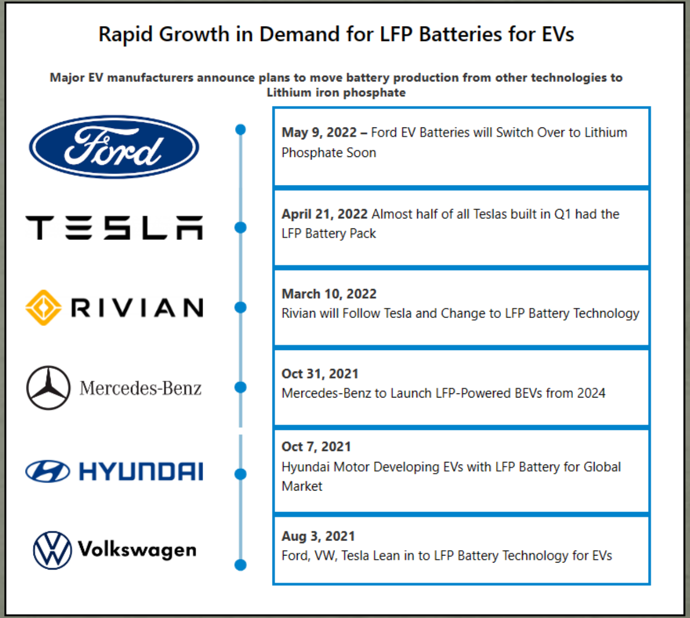
	Layered struct.		Spinel	Triphylite
	$LiCoO_2$	$LiNiCoO_2$	$LiMn_2O_4$	$LiFePO_4$
Capacity (mAh/g)	140-150	170-180	110-120	160-170
Potentiel (V)	3,9	3,8	4,0	3,4
Resistance to cycling	Poor	Poor	+/-	Good
Exchange speed	Good	Good	Good	Good
Electrode density	Good	+/-	+/-	Poor
Security	+/-	?	Good	Good
Cost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





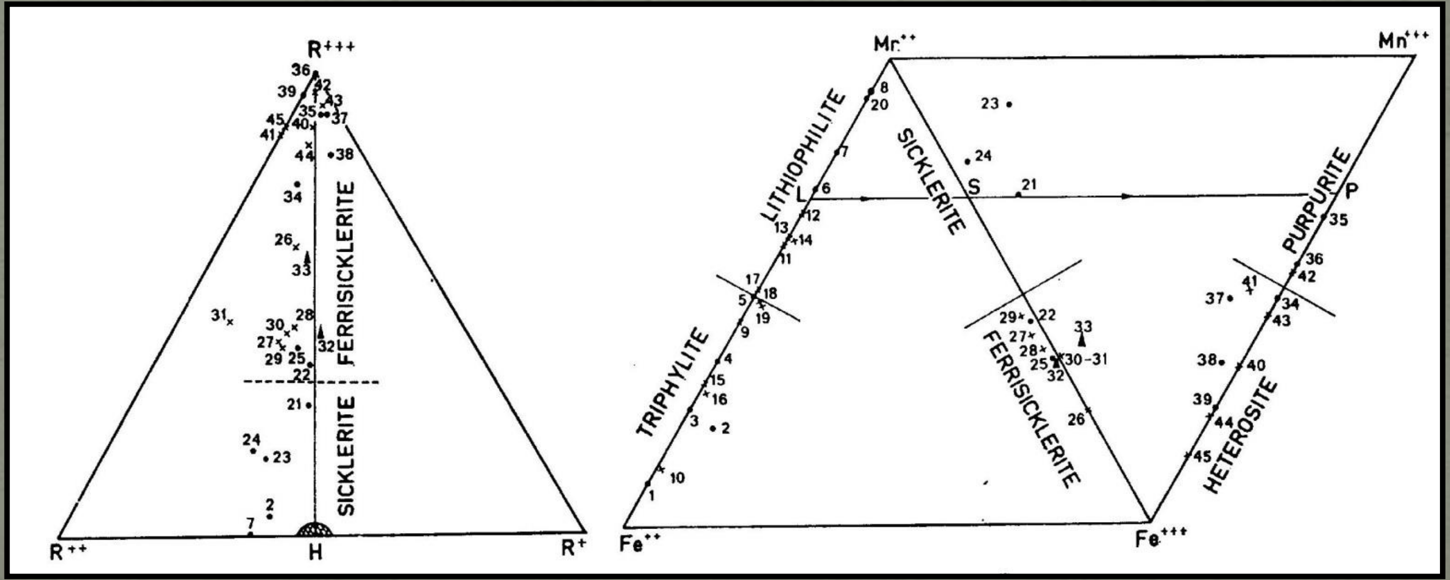
The Quensel-Mason oxidation sequence

François Fontan (1942-2007)

La ferrisicklérite des pegmatites de Sidi Bou Othmane
(Jebilet, Maroc)
et le groupe des minéraux à structure de triphylite

par FRANÇOIS FONTAN *, PAUL HUVELIN **, MARCEL ORLIAC * et FRANÇOIS PERMINGEAT *.

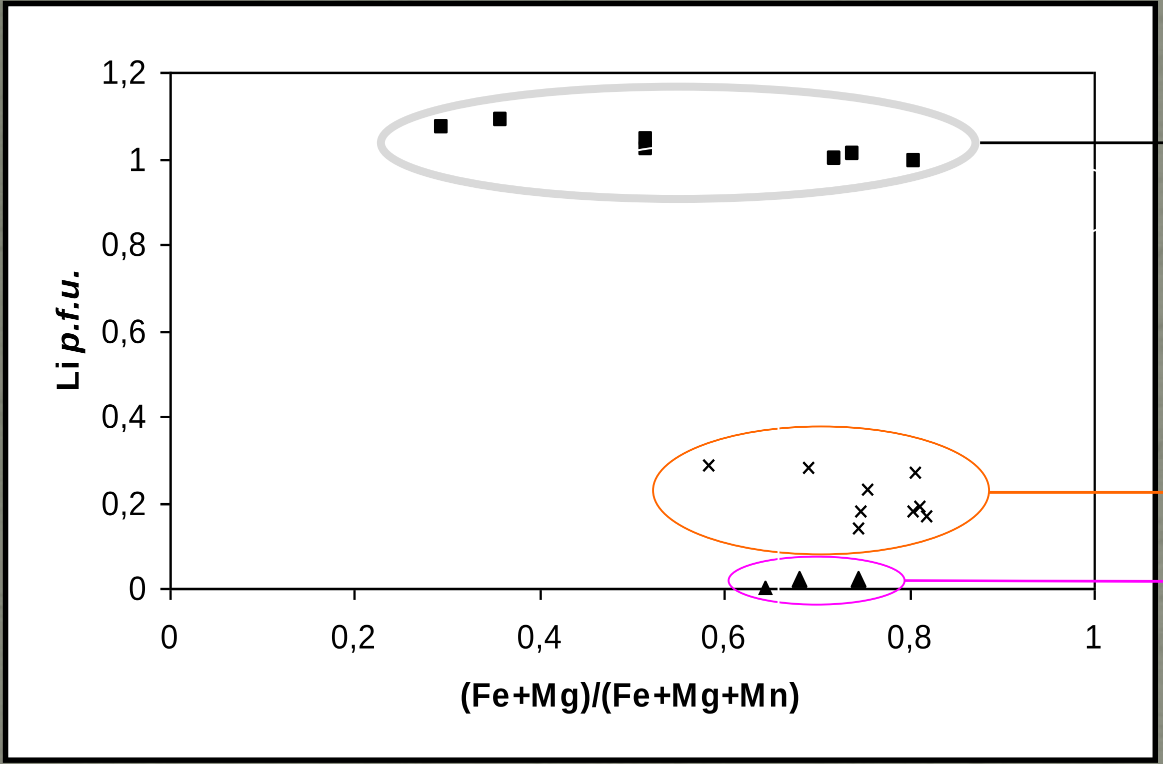
1976



This oxidation is not a continuus process!

New analyses of natural samples

EMPA, SIMS and crystal-structure analysis of 19 samples



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.*

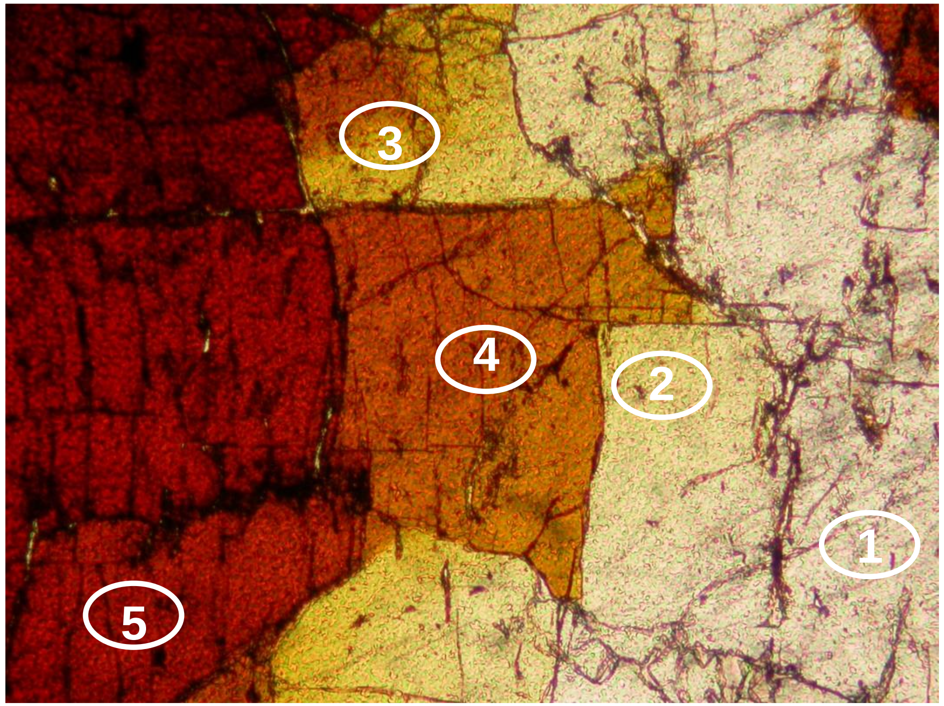
Heterosite may contain up to 0.21 wt. % Li_2O, and ferrisicklerite may show a low Li-content of 1.31 wt. % Li_2O

Close Li-contents!

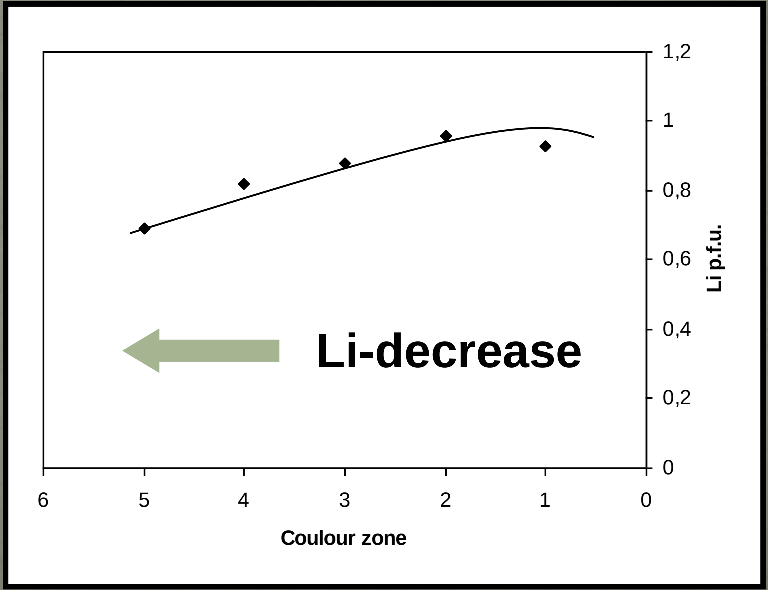
Ferrisicklerite is a variety of heterosite?

The lithiophilite-sicklerite series

Sample from the 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+}
- Sicklerite is a variety of lithiophilite?

Karenwebberite, a new mineral species

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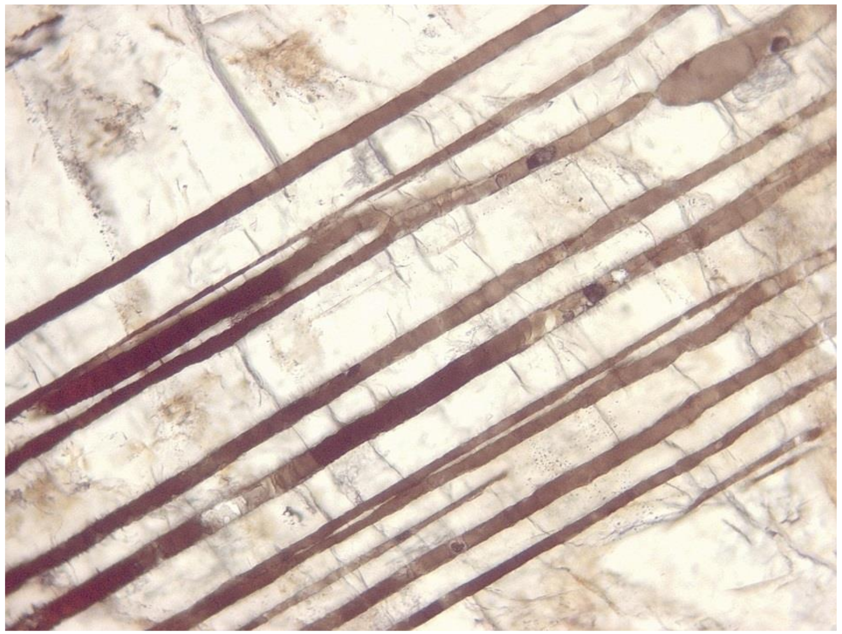
American Mineralogist, Volume 98, pages 767–772, 2013

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]

$NaFe^{2+}PO_4$

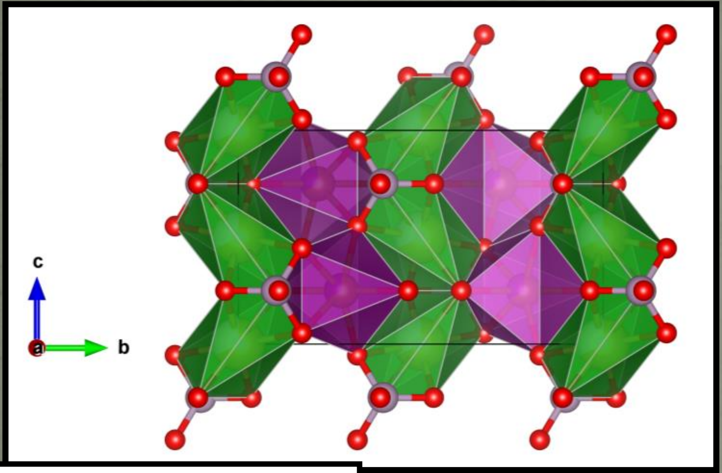
a = 4.882(1), *b* = 10.387(2), *c* = 6.091(1) Å
Pnma



Malpensata pegmatite, Italy

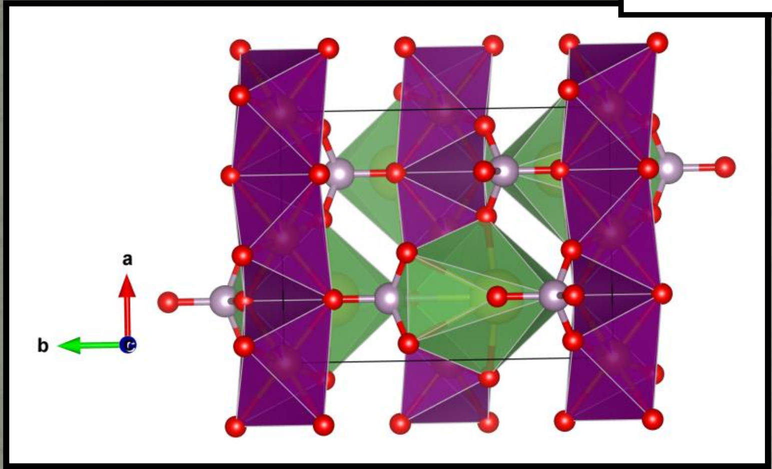
Karen Louise Webber

Stability and oxidation of karenwebberite

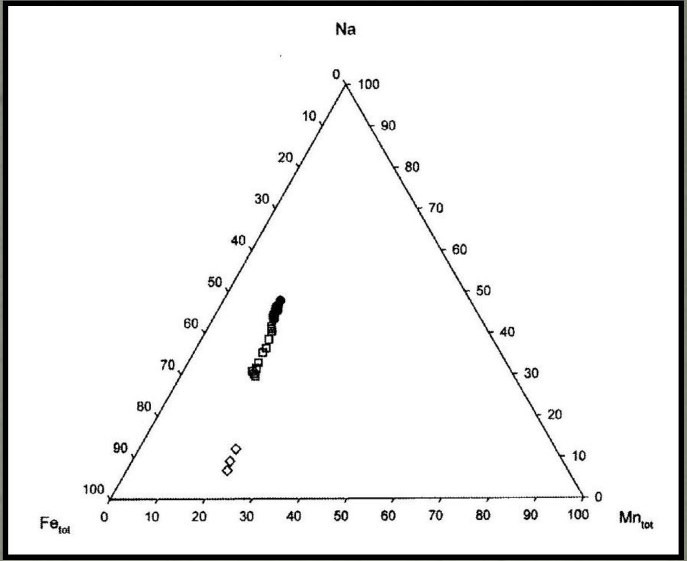


Karenwebberite

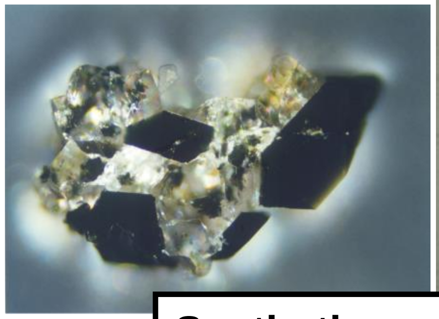
Maricite



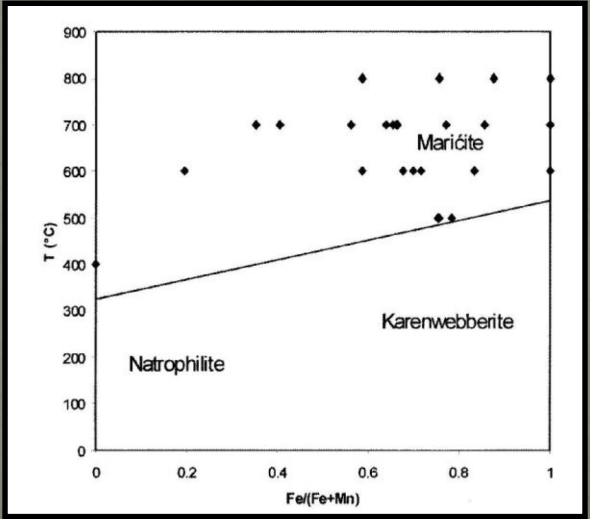
$Na^{+} + Fe^{2+} = [] + Fe^{3+}$



- Marićite is the high temperature polymorph of karenwebberite
- Transition temperature ~ 500°C



Synthetic marićite



- Oxidation of karenwebberite to Na-bearing ferrisicklerite

Nomenclature revision for the triphylite group

Eur. J. Mineral., 35, 427–437, 2023
https://doi.org/10.5194/ejm-35-427-2023

European Journal of Mineralogy
Open Access

Nomenclature of the triphylite group of minerals

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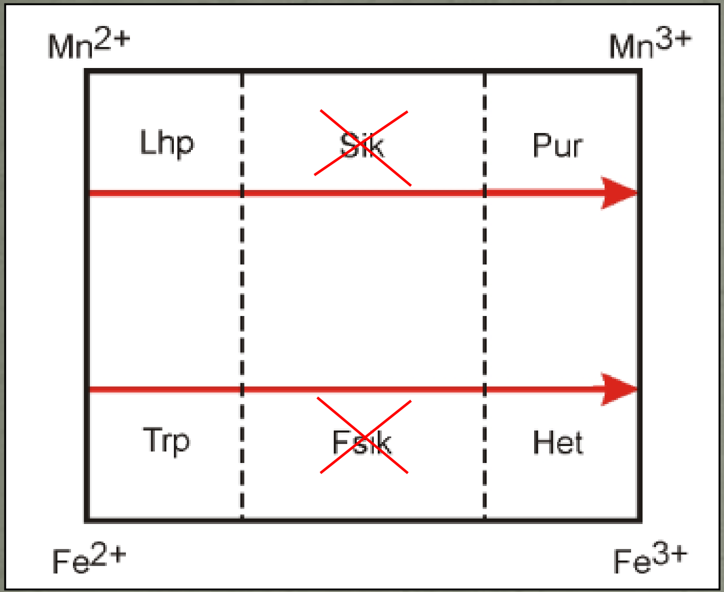
Mineral	IMA List of Minerals, December 2022	New end-member formulae
Triphylite	$LiFe^{2+}(PO_4)$	$LiFe^{2+}(PO_4)$
Lithiophilite	$LiMn^{2+}(PO_4)$	$LiMn^{2+}(PO_4)$
Heterosite	$Fe^{3+}(PO_4)$	$Fe^{3+}(PO_4)$
Purpurite	$Mn^{3+}(PO_4)$	$Mn^{3+}(PO_4)$
Sicklerite	$LiMn^{2+}(PO_4)$	Discredited
Ferrisicklerite	$Li_{1-x}(Fe^{3+},Mn^{2+})(PO_4)$	Discredited
Simferite	$Li(Mg,Fe^{3+},Mn^{3+})_2(PO_4)_2$	$LiMg(PO_4)$
Karenwebberite	$NaFe^{2+}(PO_4)$	$NaFe^{2+}(PO_4)$
Natrophilite	$NaMn^{2+}(PO_4)$	$NaMn^{2+}(PO_4)$

???

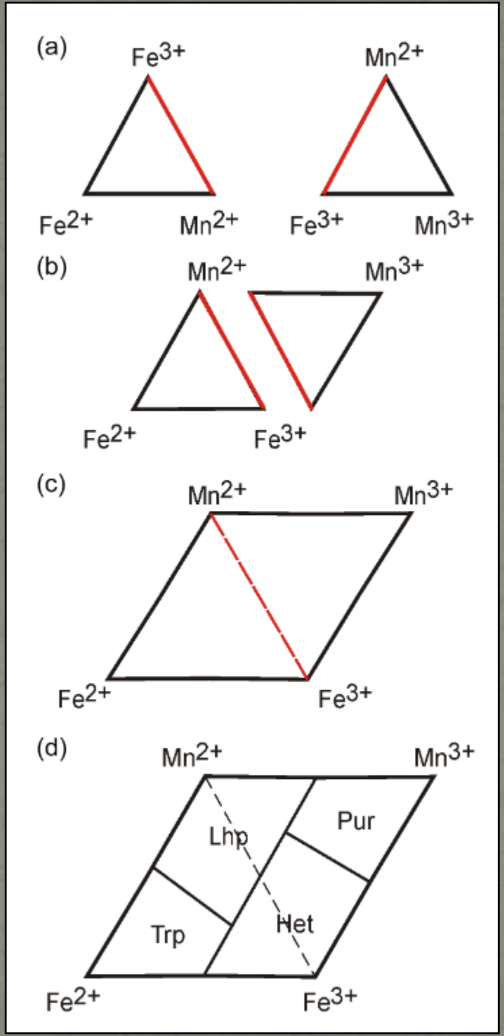
Sicklerite and ferrisicklerite are intermediate members in solid solutions

Petrographic varieties, not valid mineral species according to the IMA-CNMNC

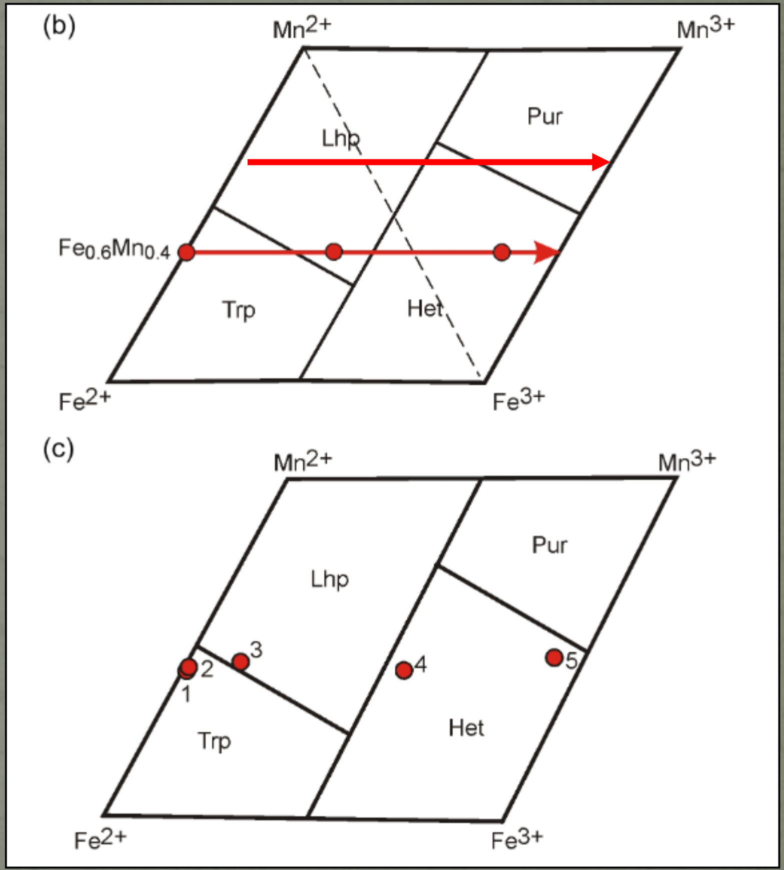
Revised oxidation process



Quensel-Mason sequence



Modified Fontan diagrams



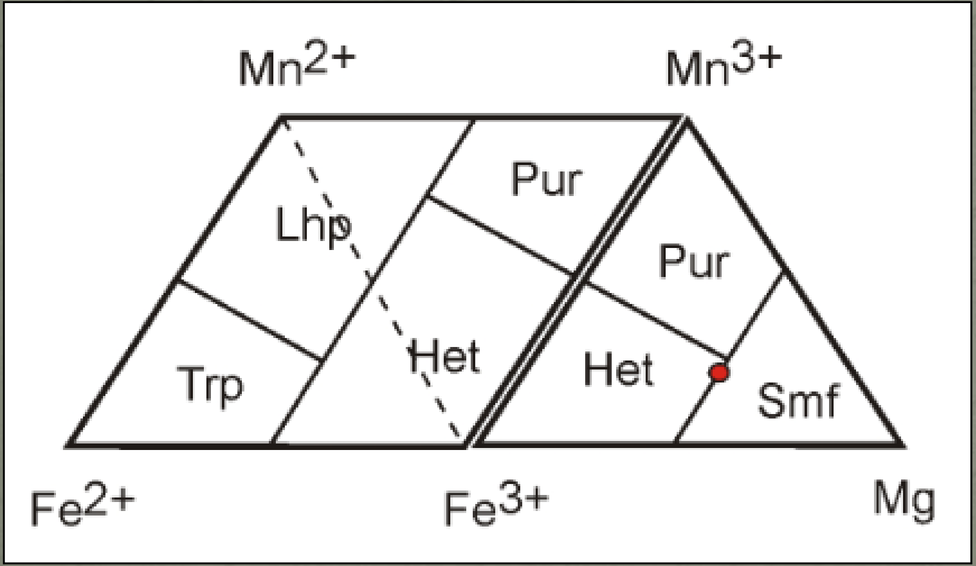
New oxidation sequence

The simferite problem

Yakubovich *et al.* (1989)
Single-crystal data

$Li_{0.5}(Mg_{0.5}Fe^{3+}_{0.3}Mn^{3+}_{0.2})(PO_4)$

- **Exactly at the boundary between heterosite and $LiMg(PO_4)$**
- **Impossible to determine an end-member formula**



Bayrakov *et al.* (2005)
EMPA and wet-chemical analysis for Li

 # 1: $Li_{0.56}(Mg_{0.54}Fe^{2+}_{0.01}Fe^{3+}_{0.29}Mn^{3+}_{0.16})(PO_4)$
 # 2: $Li_{0.57}(Mg_{0.43}Fe^{2+}_{0.12}Fe^{3+}_{0.30}Mn^{3+}_{0.14})(PO_4)$

- **Li dominant on the M1 site**
- **Mg dominant on the M2 site**
- **End-member formula redefined as $LiMg(PO_4)$**

Conclusions

- Triphylite-type phosphates occur in granitic pegmatites, where they constitute primary phosphates of crucial petrogenetic importance.
- Their oxidation process, called the Quensel-Mason sequence, is clearly visible on the field and in thin sections, and explains the exceptional electrochemical properties of these phases of huge economic significance.
- The nomenclature revision proposed herein,, and accepted by the CNMNC, has for consequence to discredit ferricicklerite and sicklerite, which are intermediate members in solid solutions.
- These discreditations significantly modify the Quensel-Mason sequence, thus briging new light on the oxidation mechanisms of these pegmatite phosphates.