

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



Iron-manganese phosphates: from pegmatites to lithium-ion batteries

Prof. Dr. Frédéric Hatert

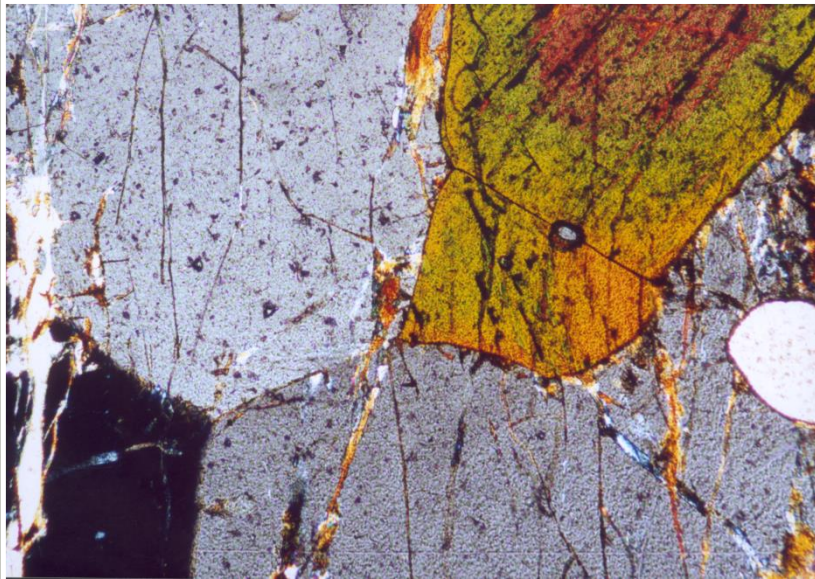
Jena, November 30th, 2015

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2. Olivine-type phosphates
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4. Alluaudite- and wyllieite-type phosphates
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6. Conclusions

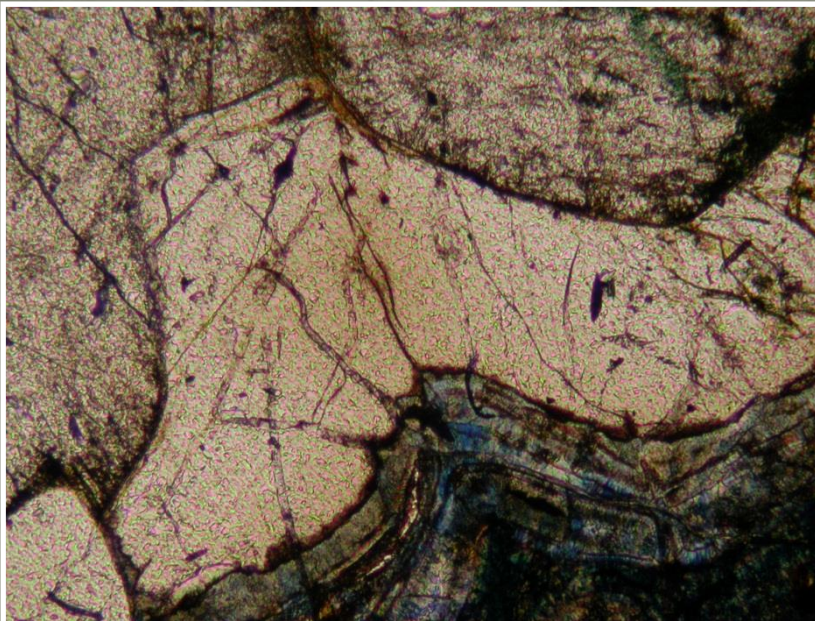
Occurrence

- Granitic pegmatites
- Metamorphic rocks
- Meteorites

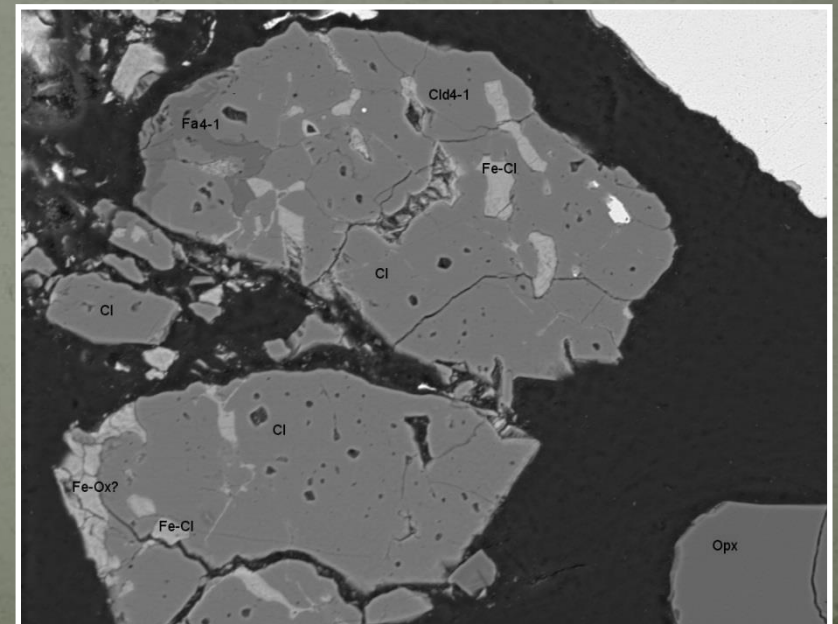


Fillowite + alluaudite, Kabira pegmatite, Uganda

Chladniite, GRA 95209 meteorite



Johnsomervilleite, Loch Quoich, Scotland



Fe-Mn phosphates in pegmatites

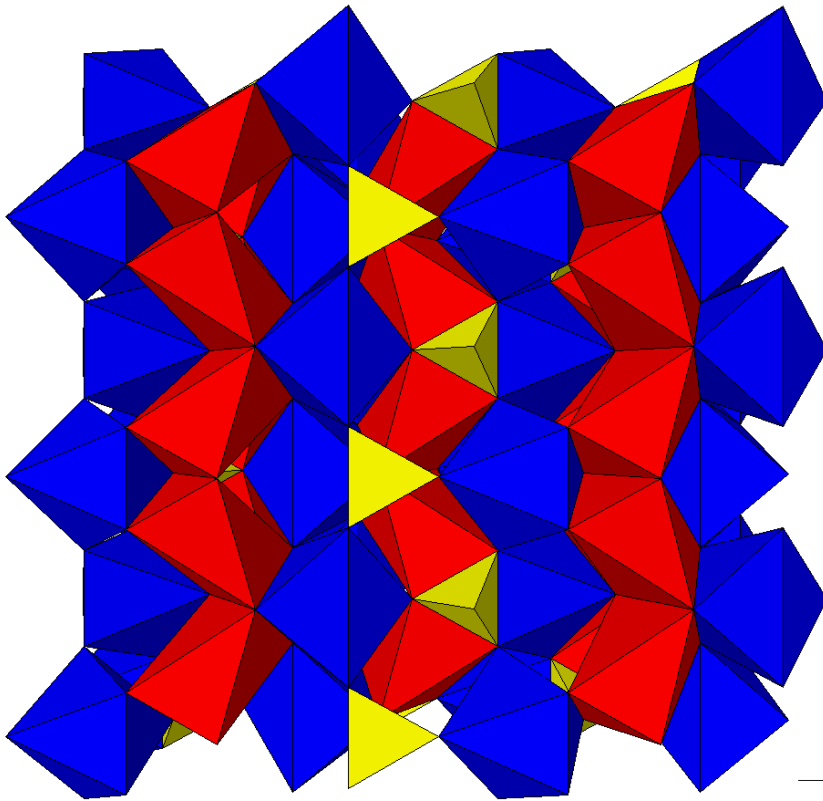


Buranga pegmatite, Rwanda

Sapucaia pegmatite, Brazil



The triphylite structure



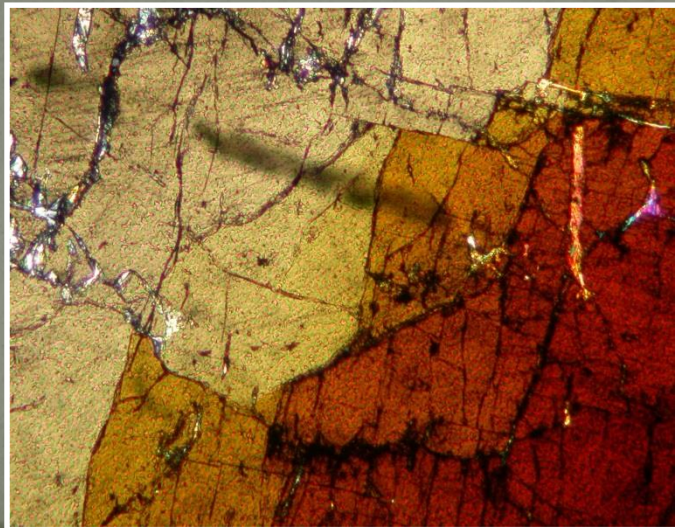
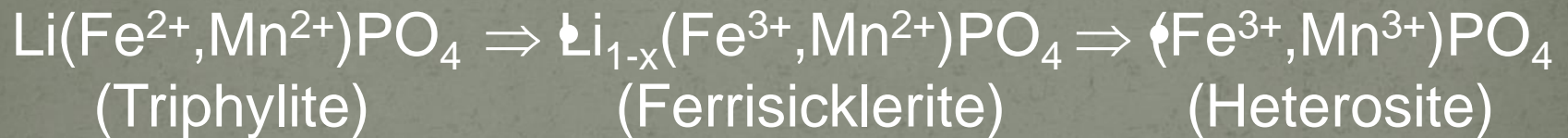
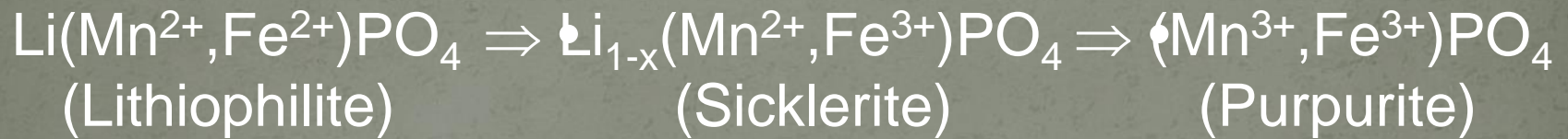
- Triphylite, $\text{LiFe}^{2+}(\text{PO}_4)$
- Lithiophilite, $\text{LiMn}(\text{PO}_4)$
- Natrophilite, $\text{NaMn}(\text{PO}_4)$
- Karenwebberite, $\text{NaFe}^{2+}(\text{PO}_4)$

S.G. $Pmnb$

$a = 6.092 \text{ \AA}$
 $b = 10.429 \text{ \AA}$
 $c = 4.738 \text{ \AA}$

Red octahedra: M1 (Li, Na)
 Blue octahedra: M2 (Fe, Mn)

Phosphates with the olivine structure: the « Quensel-Mason » sequence



Questions:

- ➔ A. Is the « Quensel-Mason » sequence a progressive oxidation process ?
- ➔ B. Is ferrisicklerite of primary or secondary origin ?
- ➔ C. Which are the stability fields of karenwebberite and marićite ?

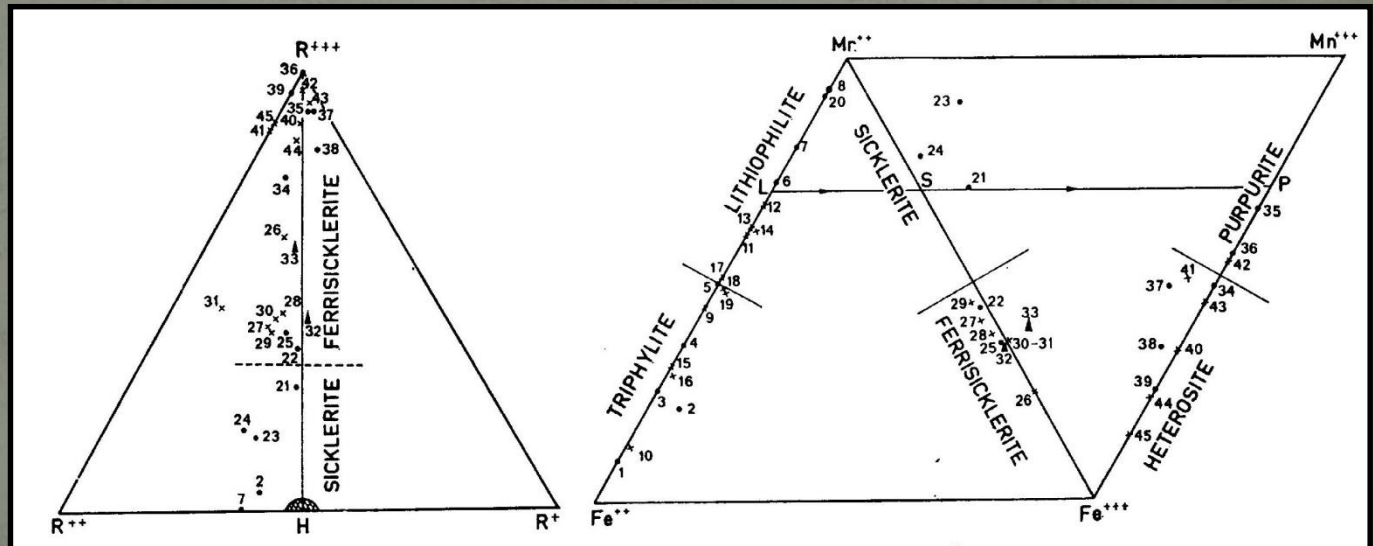
A. The oxidation of triphylite-lithiophilite



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 *.

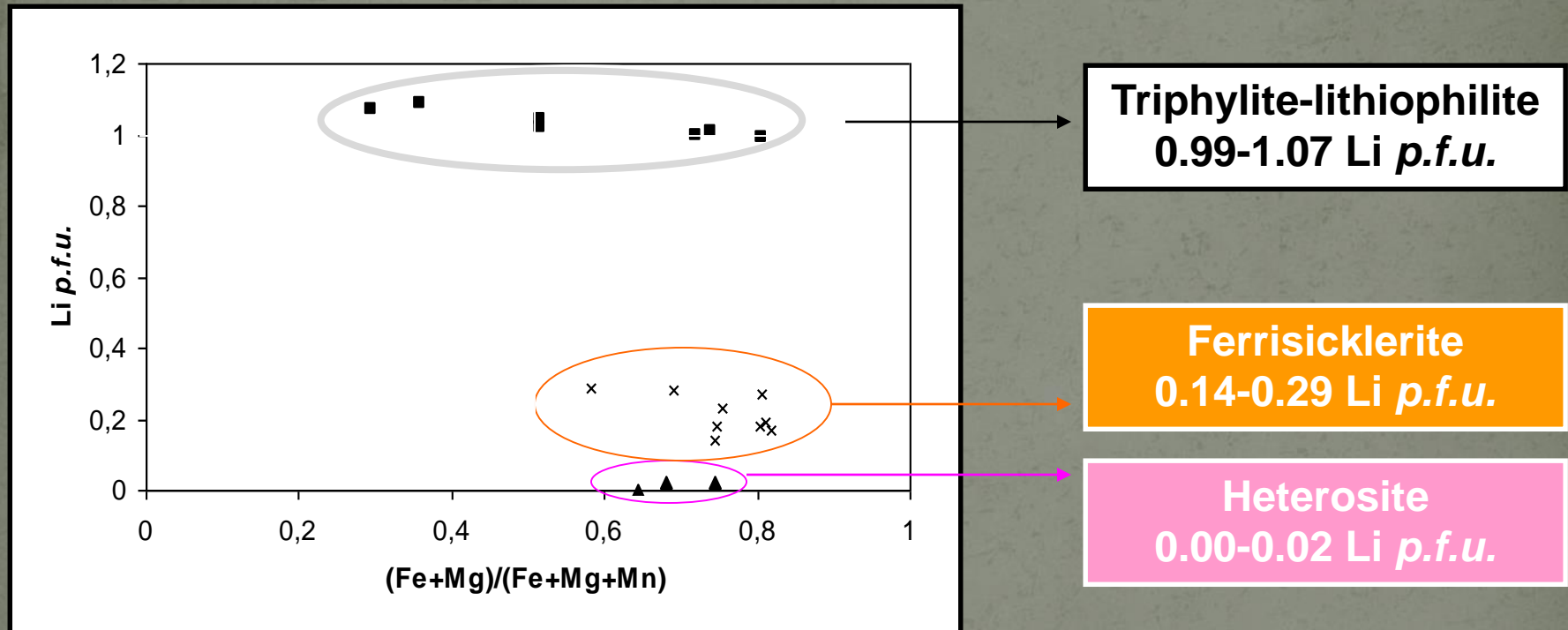
1976



This oxidation is not a continuous process!

A. SIMS analyses of natural samples

EMPA, SIMS and crystal-structure analysis of 19 samples

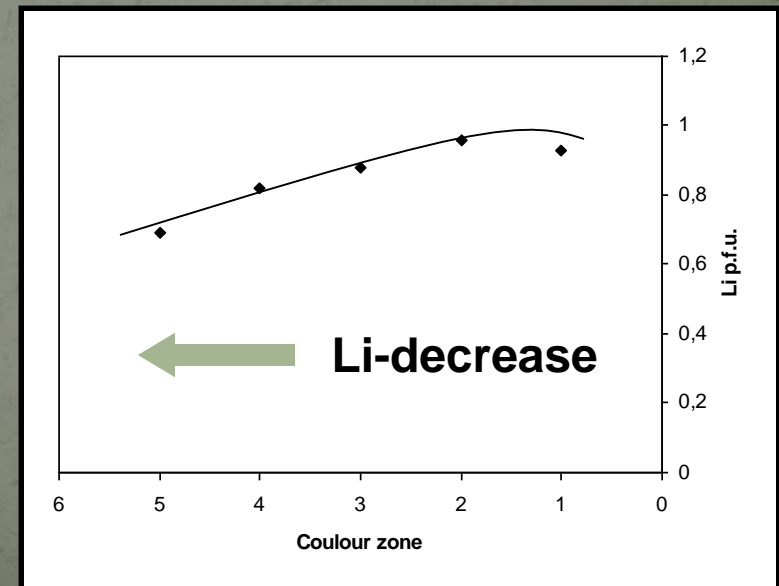
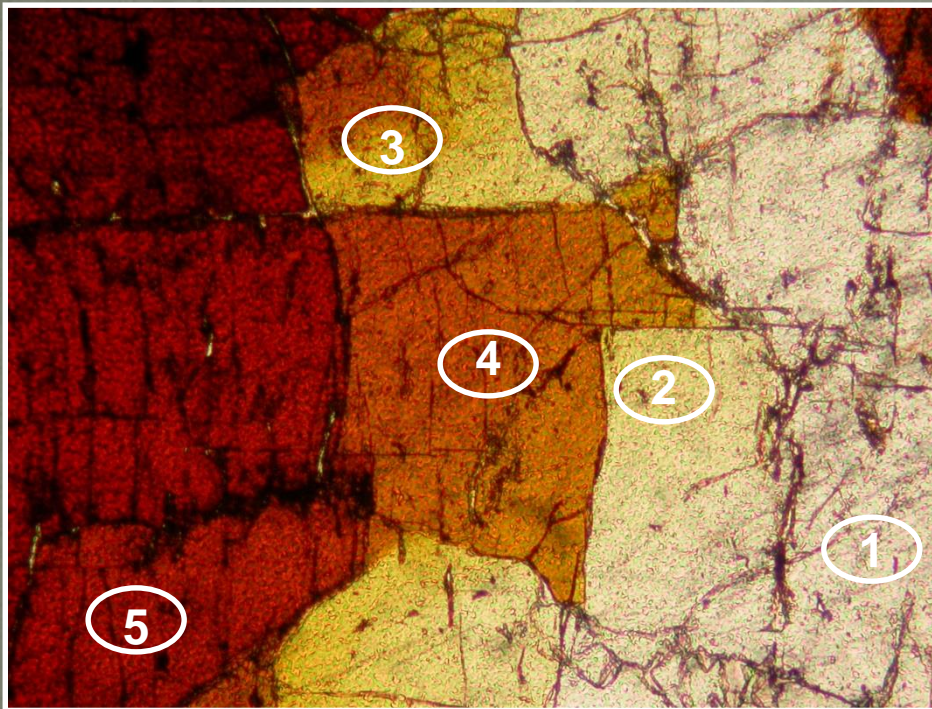


Heterosite may contain up to 0.21 wt. % Li_2O , and ferrisicklerite may show a low Li-content of 1.31 wt. % Li_2O

Close Li-contents!

A. The lithiophilite-sicklerite series

Sample from the Altaï Mountains, China



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

B. The stability of ferrisicklerite

Phosphate paragenesis

Primary Crystallization
~ 600°C - 500°C



High Temperature Metasomatic Alteration
Hydroxylation and cation exchange
~ 500°C - 300°C



Low Temperature Metasomatic Alteration
Hydration, hydroxylation and cation exchange
~ 300°C - 100°C

- Crystallization temperatures of ferrisicklerite?
- Degree of oxidation?

High Temperature Metasomatic Alteration

Triphylite-lithiophilite
 $\text{Li}(\text{Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$

~ 500°C - 300°C

Non-oxidizing conditions

Leaching of Li^+
Addition of OH^-
Wolfeite-trioplidite

Addition of Al^{3+}
Griphite, Scorzalite

Addition of Ca^{2+}
Whitlockite

Addition of Na^+
Natrophilite

Oxidizing conditions

Oxidation of Fe^{2+} to Fe^{3+}
Ferrisicklerite-sicklerite

Leaching of Li^+
Heterosite-purpurite

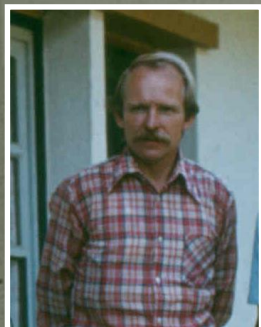
Addition of Na^+ and Ca^{2+}
Alluaudite group

Simmons *et al.* 2003

Preliminary hydrothermal experiments

- 200-600°C, 1-3 kbar
- Low $f\text{O}_2$: triphylite
- High $f\text{O}_2$: $\text{LiFe}^{3+}\text{PO}_4(\text{OH})$

B. The stability of ferrisicklerite

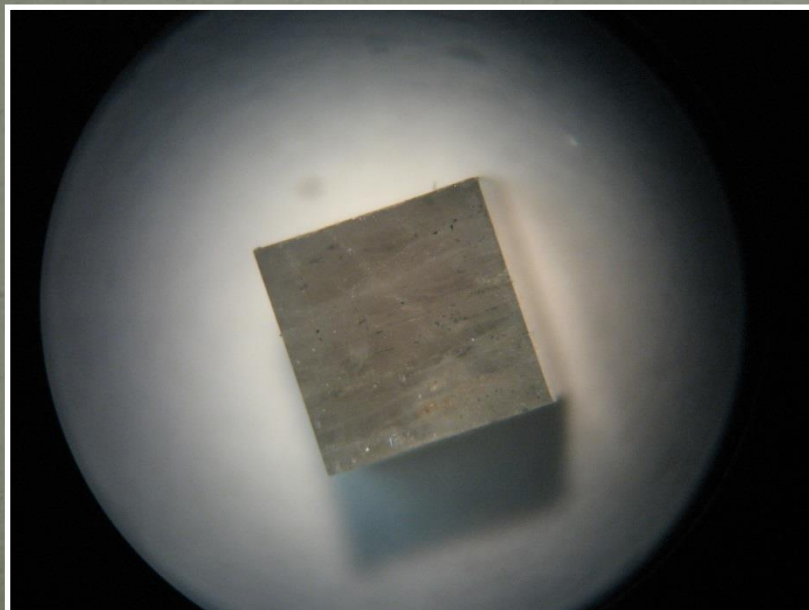


Sample 9706.41, Palermo, N.H., USA
Collection Paul Keller, Stuttgart

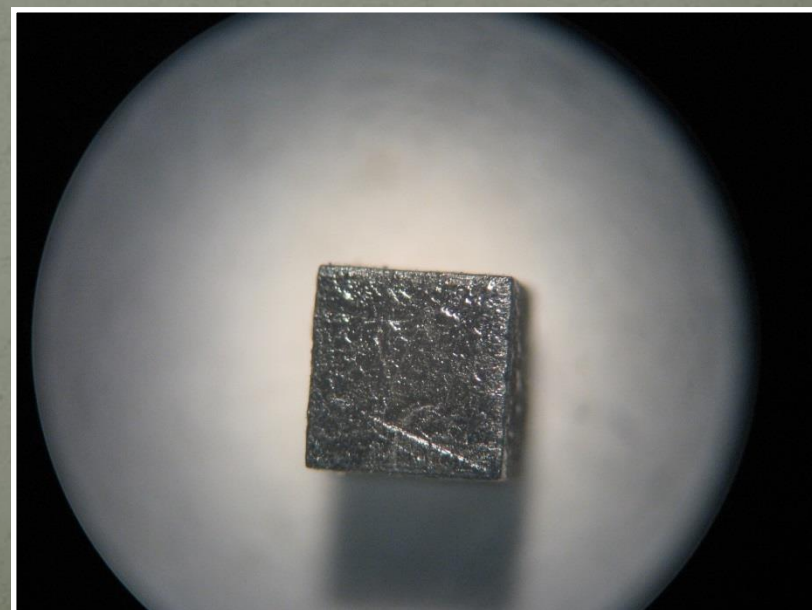
X LiFePO_4 = 0.74(1) 100% Fe^{2+}
X LiMnPO_4 = 0.21(1)
X LiMgPO_4 = 0.05(1)

0.1n HCl, 21mg KMnO_4 , 120°C, 28 d

Before run

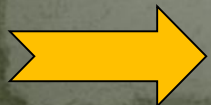
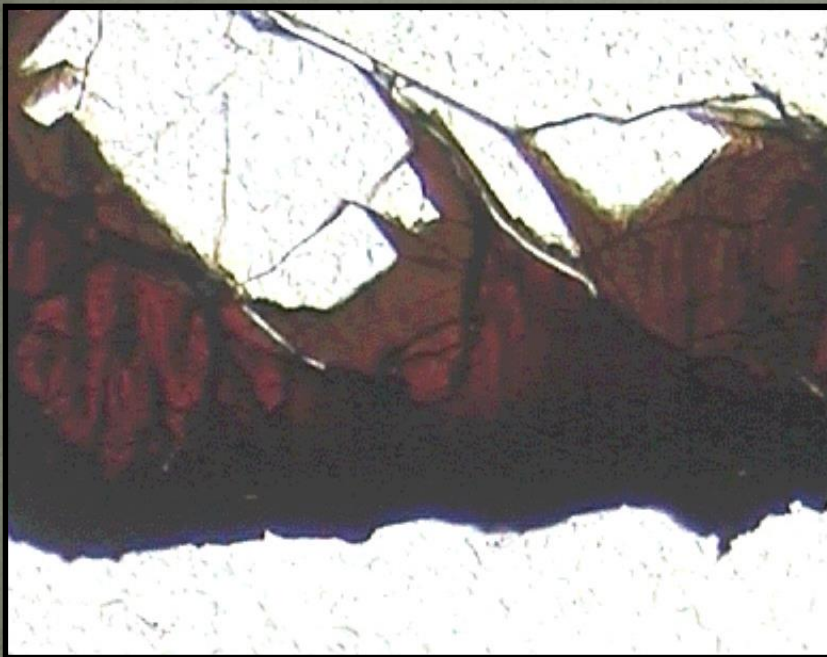


After run



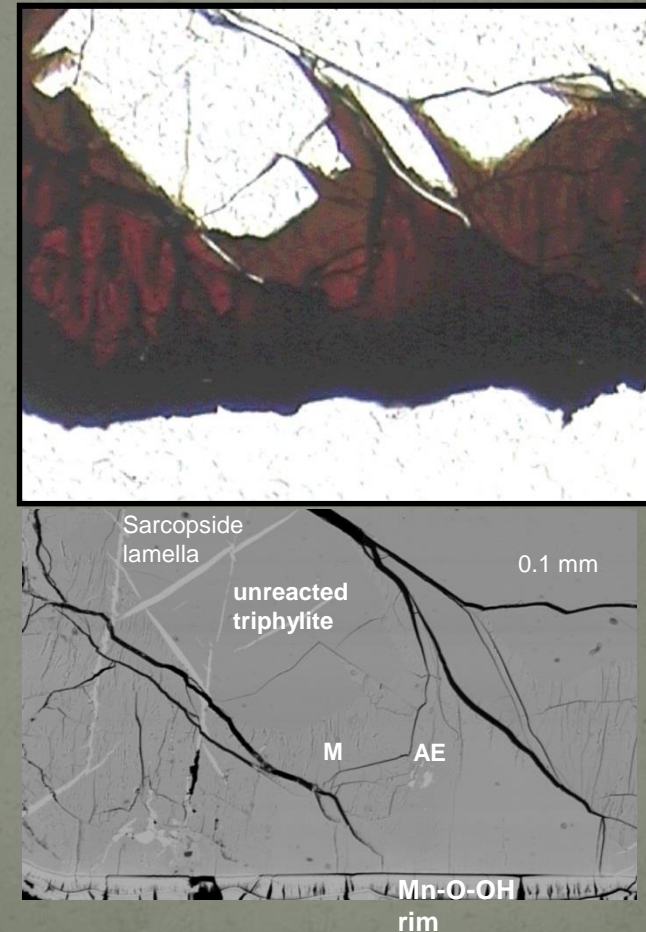
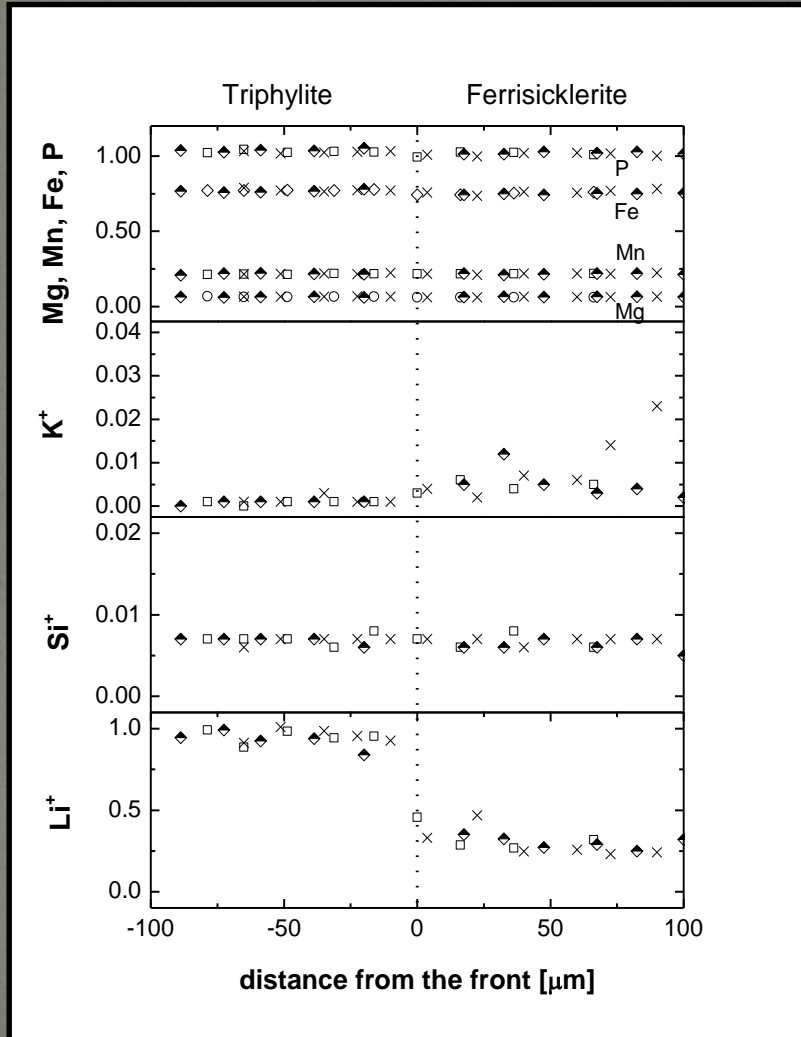
B. The stability of ferrisicklerite

- First hydrothermal synthesis of ferrisicklerite
- At very low temperature
- Under a very high fO_2



Ferrisicklerite is a low temperature metasomatic alteration mineral (?)

B. The stability of ferrisicklerite



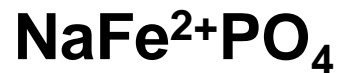
Sharp contact between triphylite and ferrisicklerite!

C. Karenwebberite, a new mineral...

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

Karenwebberite, $\text{Na}(\text{Fe}^{2+}, \text{Mn}^{2+})\text{PO}_4$, a new member of the triphylite group from the Malpensata pegmatite, Lecco Province, Italy

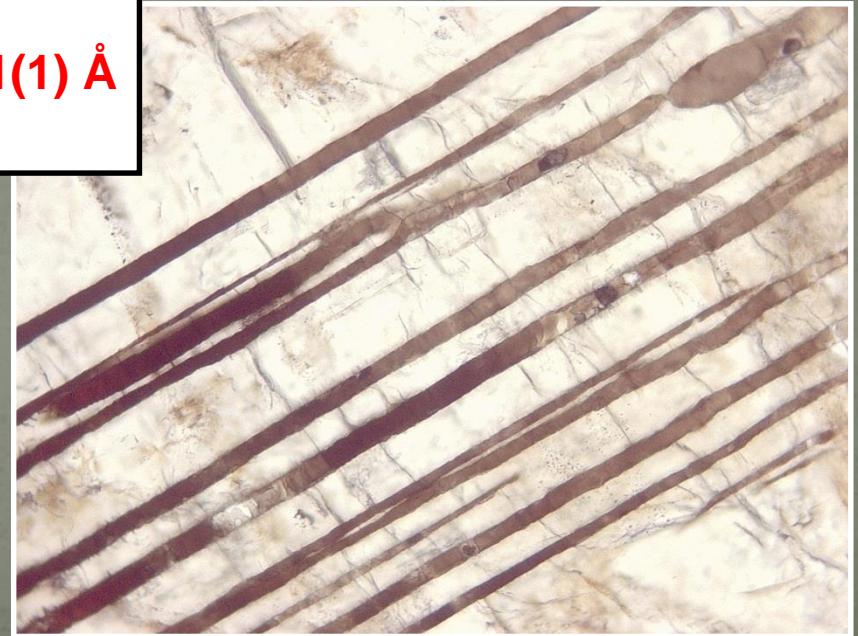
PIETRO VIGNOLA,¹ FRÉDÉRIC HATERT,^{2,*} ANDRÉ-MATHIEU FRANSOLET,² OLAF MEDENBACH,³ VALERIA DIELLA,¹ AND SERGIO ANDÒ⁴



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

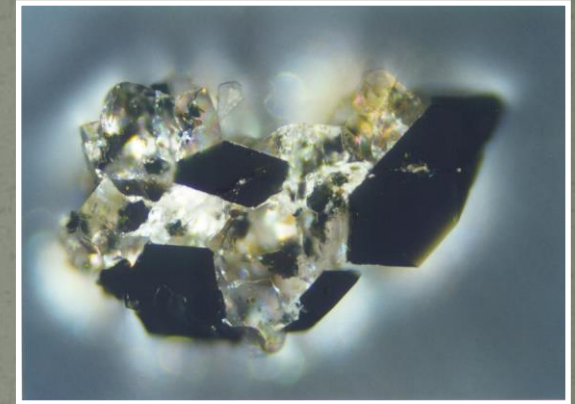
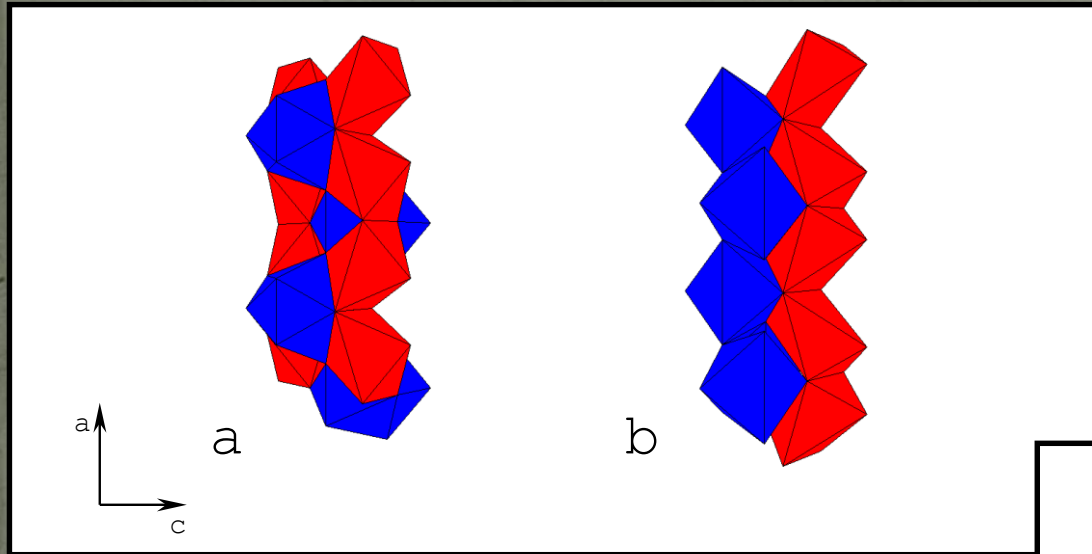


Karen Louise Webber

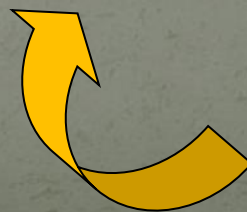
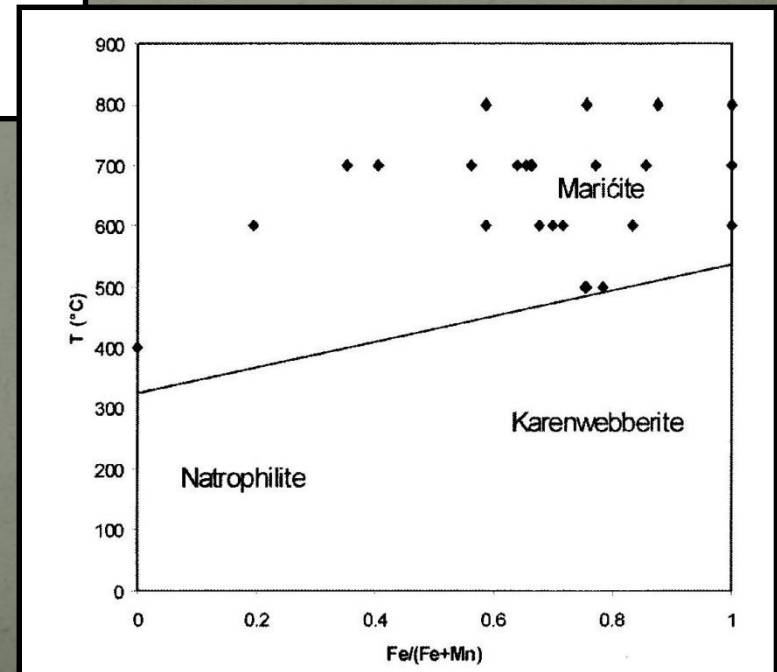


Malpensata pegmatite, Italy

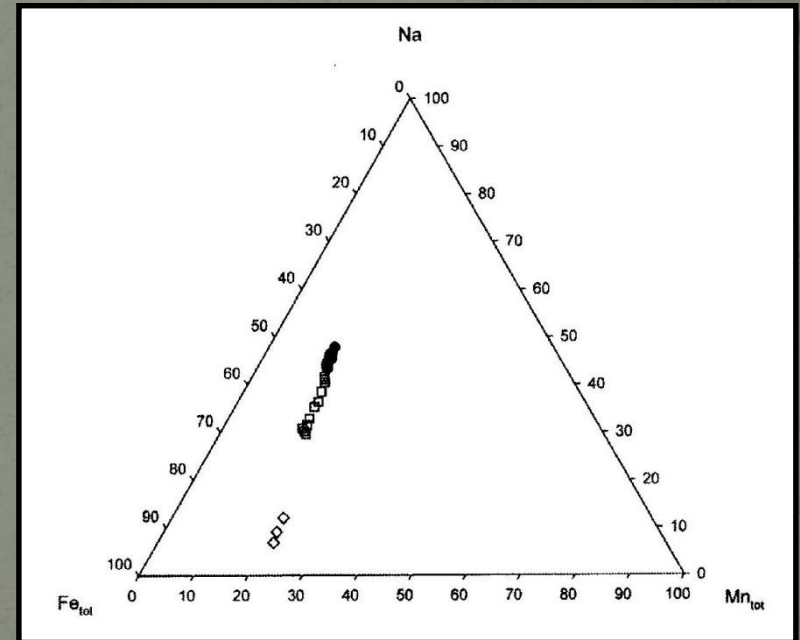
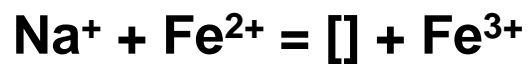
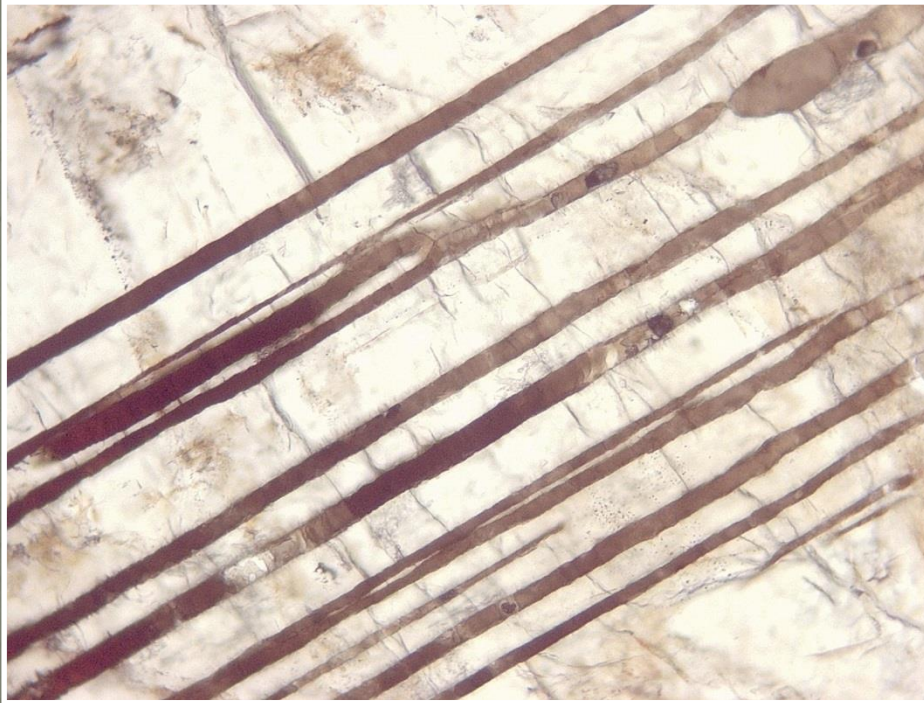
C. The stability of karenwebberite



- Maričite is the high temperature polymorph of karenwebberite
- Transition temperature $\sim 500^{\circ}\text{C}$

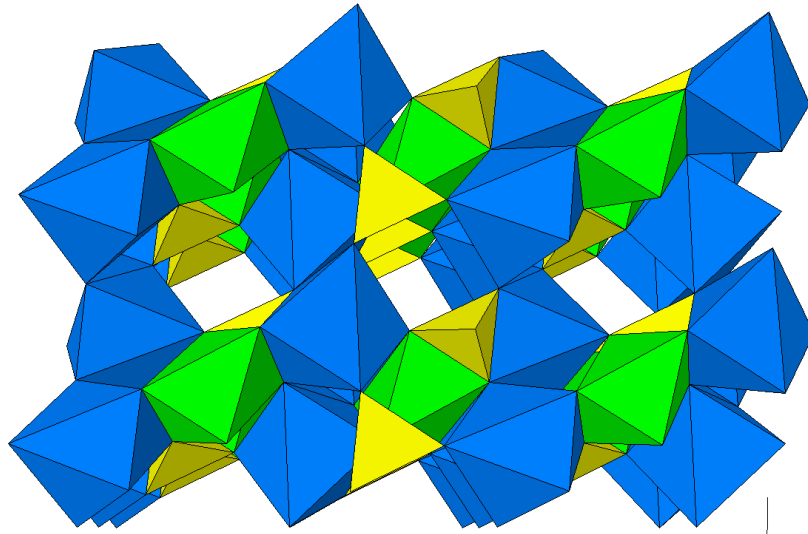


C. The oxidation of karenwebberite



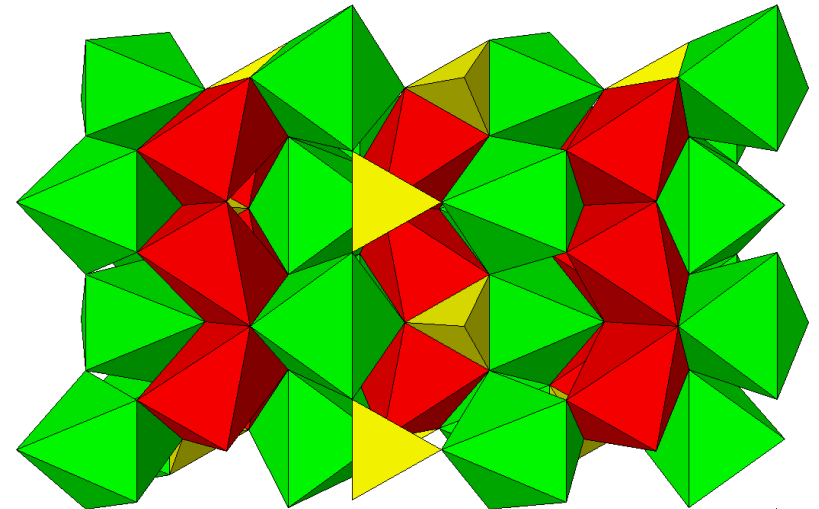
Progressive oxidation towards Na-bearing ferrisicklerite!

The sarcopside structure



Sarcopside
 $a = 6.088(1) \text{ \AA}$
 $b = 4.814(1) \text{ \AA}$
 $c = 10.484(2) \text{ \AA}$
 $\beta = 89.42(3)^\circ$
 S.G. $P2_1/c$

Triphylite
 $a = 5.987 \text{ \AA}$
 $b = 10.286 \text{ \AA}$
 $c = 4.690 \text{ \AA}$
 S.G. $Pmnb$



- Topologically identical crystal structures
- 50 % of M(1) positions are vacant in sarcopside

The triphylite + sarcopside assemblage

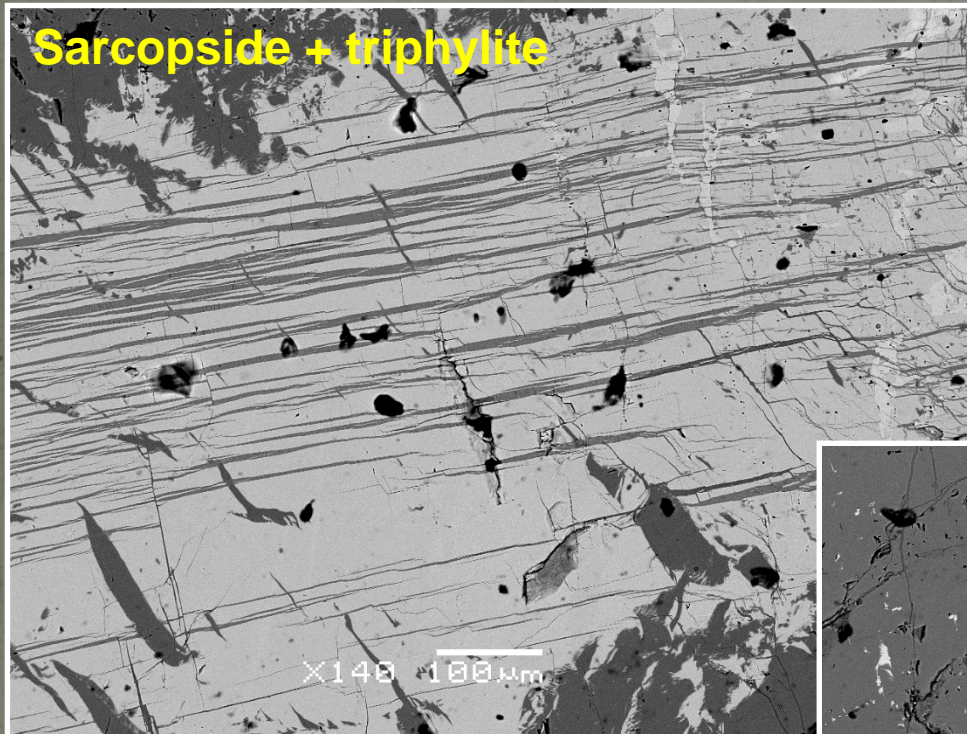
Intercroissances et inclusions dans les associations graffonite-sarcopside-triphylite

par ANDRÉ-MATHIEU FRANSOLET,
Institut de Minéralogie, Université de Liège (1).

Fransolet, 1977



The triphylite + sarcopside assemblage



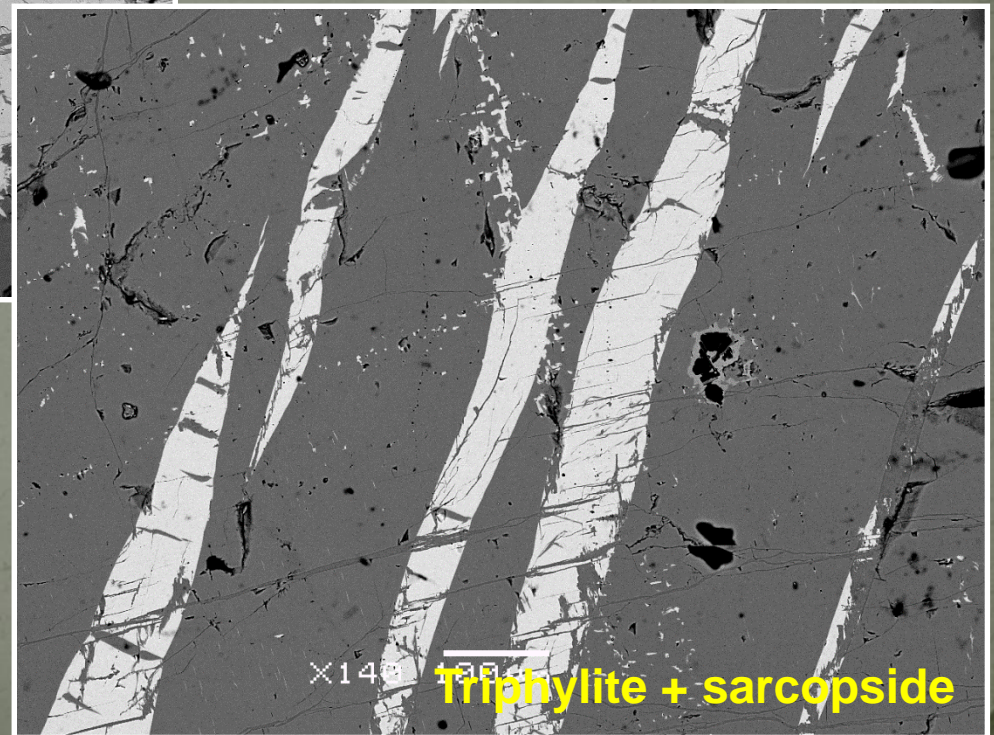
Cañada pegmatite,
Spain

Lamellar textures



EXSOLUTIONS!!

Sarcopside $(\text{Fe,Mn})_3(\text{PO}_4)_2$



Pictures: E. Roda Robles

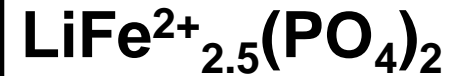
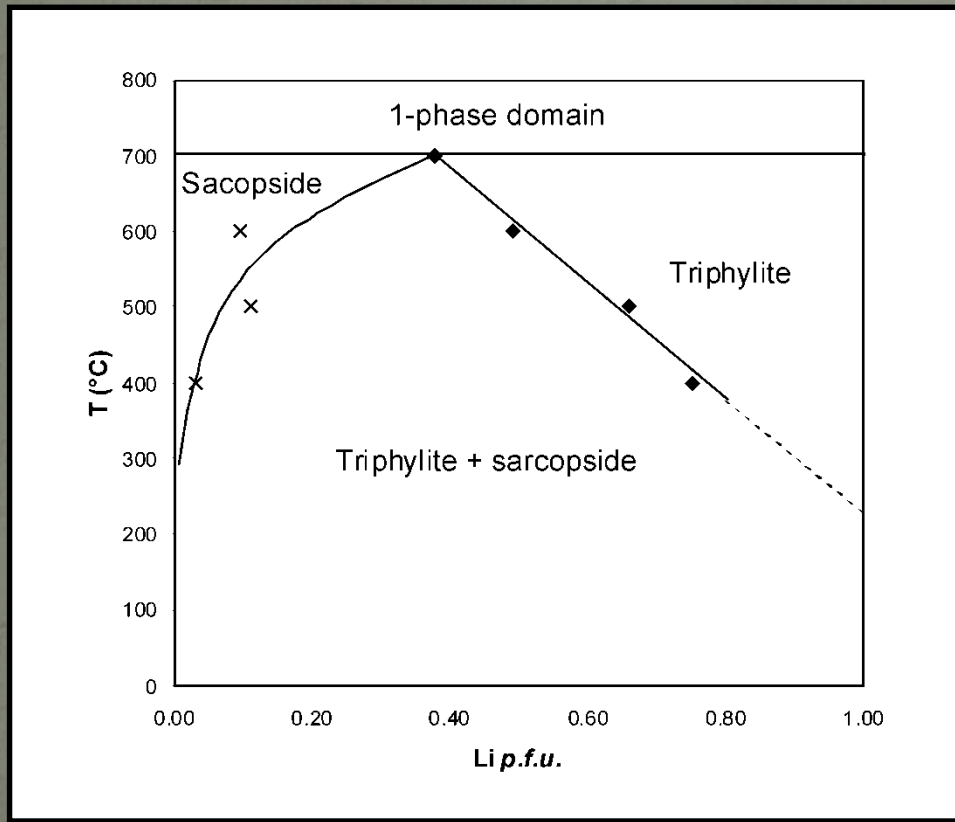
Stability of the triphylite + sarcopside assemblage



- Hydrothermal synthesis
- Tuttle-type cold-seal bombs
- $T = 400-700 \text{ }^{\circ}\text{C}$
- $P = 1 \text{ kbar}$

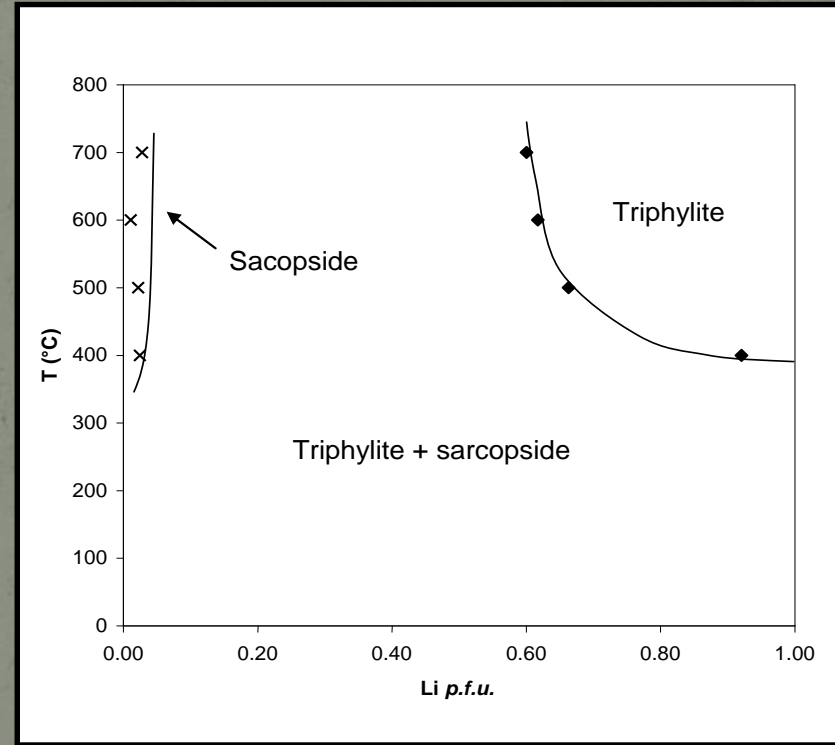
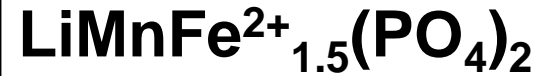
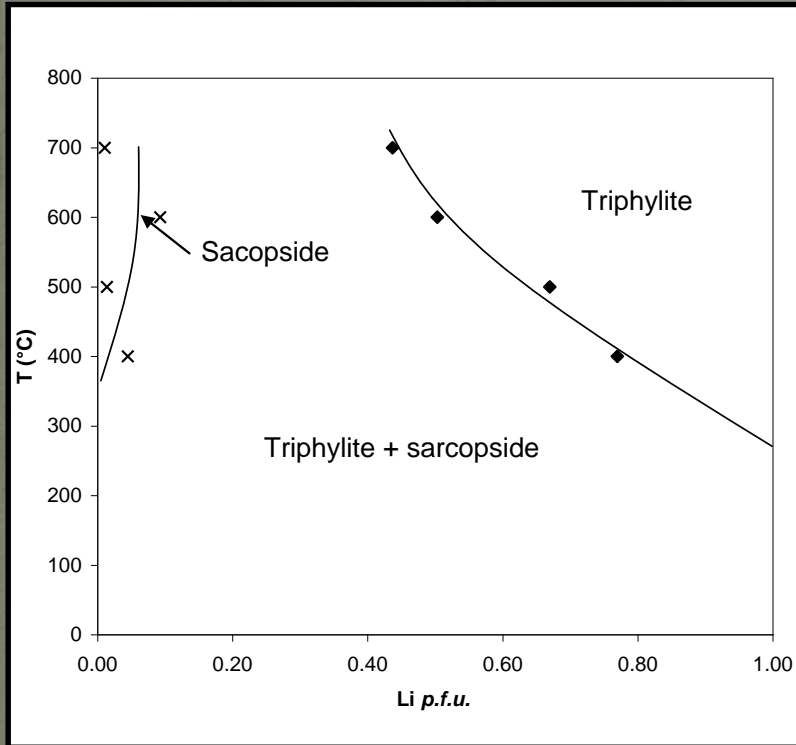
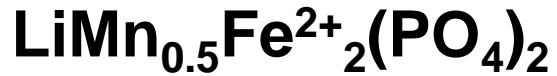


Stability of the triphylite + sarcopside assemblage



- 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
- Increase of the Li-content of sarcopside, from 0.01 *a.p.f.u.* at 400°C, to 0.05 *a.p.f.u.* at 600°C
- 1-phase domain above 700°C

Triphylite-sarcopside phase diagrams

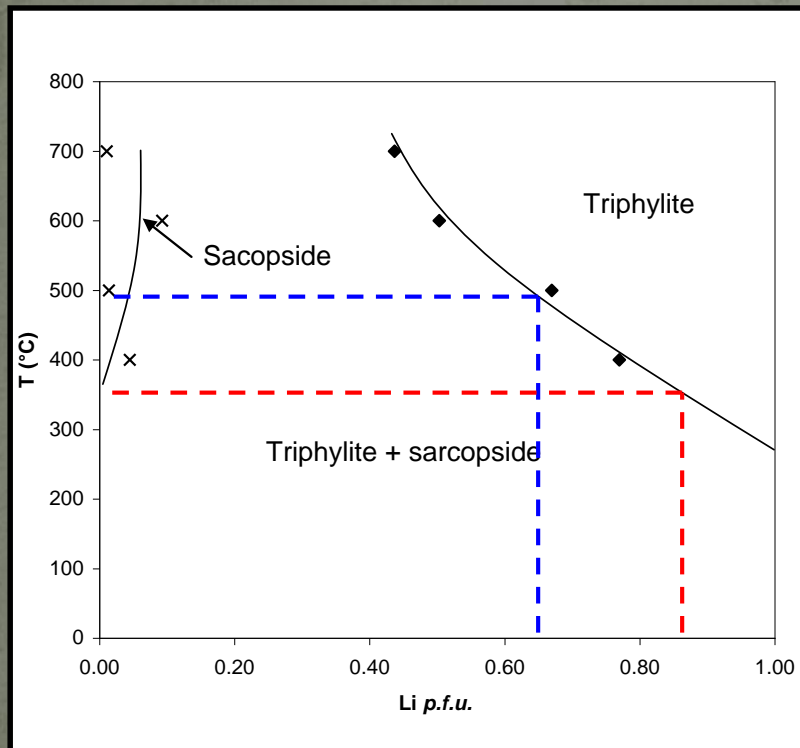


The Li-content of triphylite decreases with temperature



Geothermometer!

Calculation of crystallisation temperatures for natural assemblages



Fe/(Fe+Mn) ratio of natural triphylites and sarcopsides close to 0.800



Phase diagram for the $\text{LiMn}_{0.5}\text{Fe}^{2+}_2(\text{PO}_4)_3$ starting composition

Cañada

35 % sarcopside and 65 % triphylite
T ~ 500°C

Tsoabismund

15 % sarcopside and 85 % triphylite
T ~ 350°C

Zavalíaite, a new mineral...

ZAVALÍAITE, $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg})_3(\text{PO}_4)_2$, A NEW MEMBER OF THE SARCOPSIDE GROUP FROM THE LA EMPLEADA PEGMATITE, SAN LUIS PROVINCE, ARGENTINA

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ENCARNACIÓN RODA-ROBLES

Departamento de Mineralogía y Petrología, Universidad del País Vasco/EHU, Apdo. 644, E-48080 Bilbao, Spain

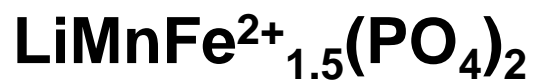
$a = 6.088(1) \text{ \AA}$
 $b = 4.814(1) \text{ \AA}$
 $c = 10.484(2) \text{ \AA}$
 $\beta = 89.42(3)^\circ$
 S.G. $P2_1/c$



Florencia Márquez Zavalía



The stability of zavaliaite?

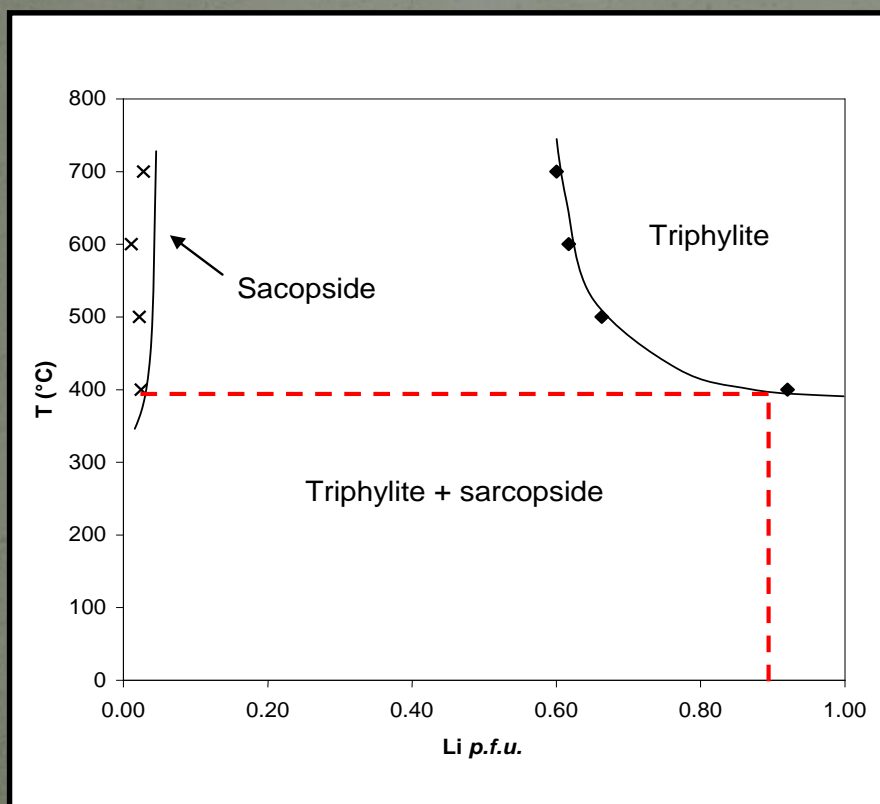


Fe/(Fe+Mn) ratio of lithiophilite
and associated zavaliaite close
to 0.43-0.48

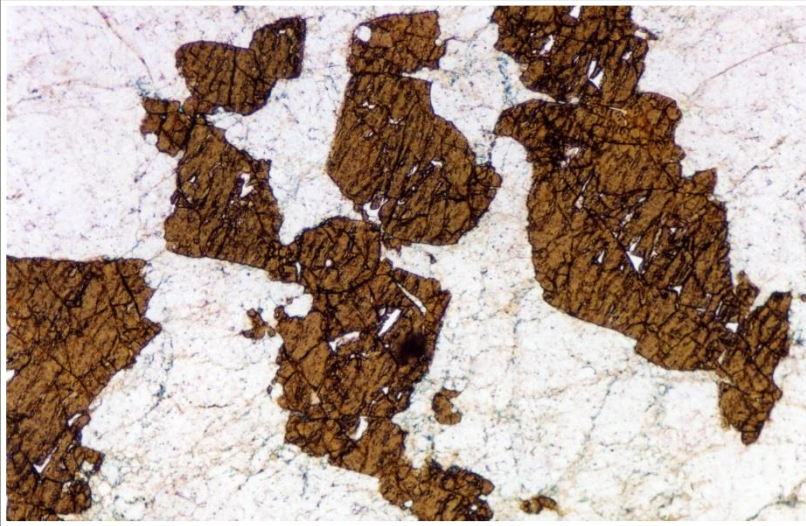
Phase diagram for the
 $\text{LiMnFe}^{2+}_{1.5}(\text{PO}_4)_3$ starting
composition

10 % zavaliaite and 90 %
lithiophilite

$T < 400^\circ\text{C}$



The alluaudite supergroup



Ferrorosemaryite, Rubindi, Rwanda

Wyllieite group ($P2_1/n$)

Wyllieite: $\text{Na}_2\text{MnFe}^{2+}\text{Al}(\text{PO}_4)_3$

Rosemaryite: $[\text{NaMnFe}^{3+}\text{Al}(\text{PO}_4)_3]$

Ferrowyllieite: $\text{Na}_2\text{Fe}^{2+}_2\text{Al}(\text{PO}_4)_3$

Ferrorosemaryite: $[\text{NaFe}^{2+}\text{Fe}^{3+}\text{Al}(\text{PO}_4)_3]$

Qingheiite: $\text{Na}_2\text{MnMgAl}(\text{PO}_4)_3$

Qingheiite-(Fe^{2+}): $\text{Na}_2\text{Fe}^{2+}\text{MgAl}(\text{PO}_4)_3$

Alluaudite group ($C2/c$)

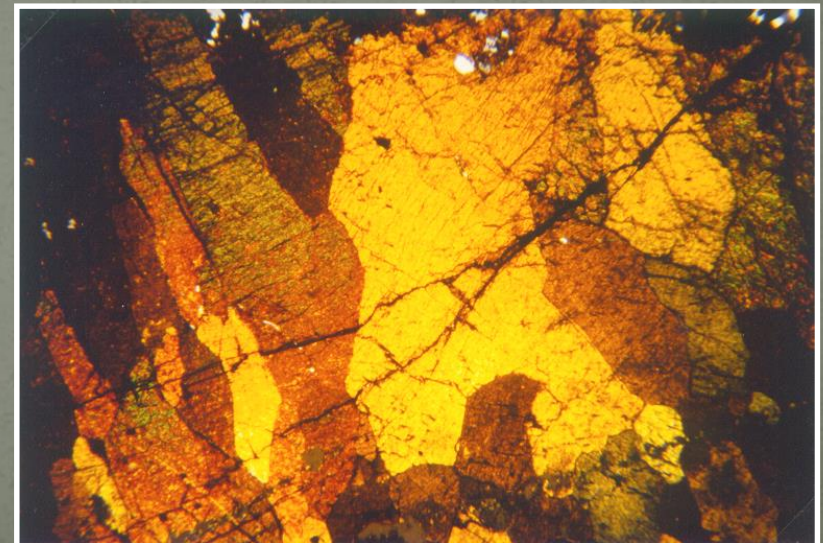
Alluaudite: $[\text{NaMnFe}^{3+}_2(\text{PO}_4)_3]$

Ferroalluaudite: $[\text{NaFe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_3]$

Hagendorfite: $\text{Na}_2\text{MnFe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$

Ferrohagendorfite: $\text{Na}_2\text{Fe}^{2+}_2\text{Fe}^{3+}(\text{PO}_4)_3$

Varulite: $\text{Na}_2\text{Mn}_2\text{Fe}^{3+}(\text{PO}_4)_3$



Alluaudite, Buranga, Rwanda

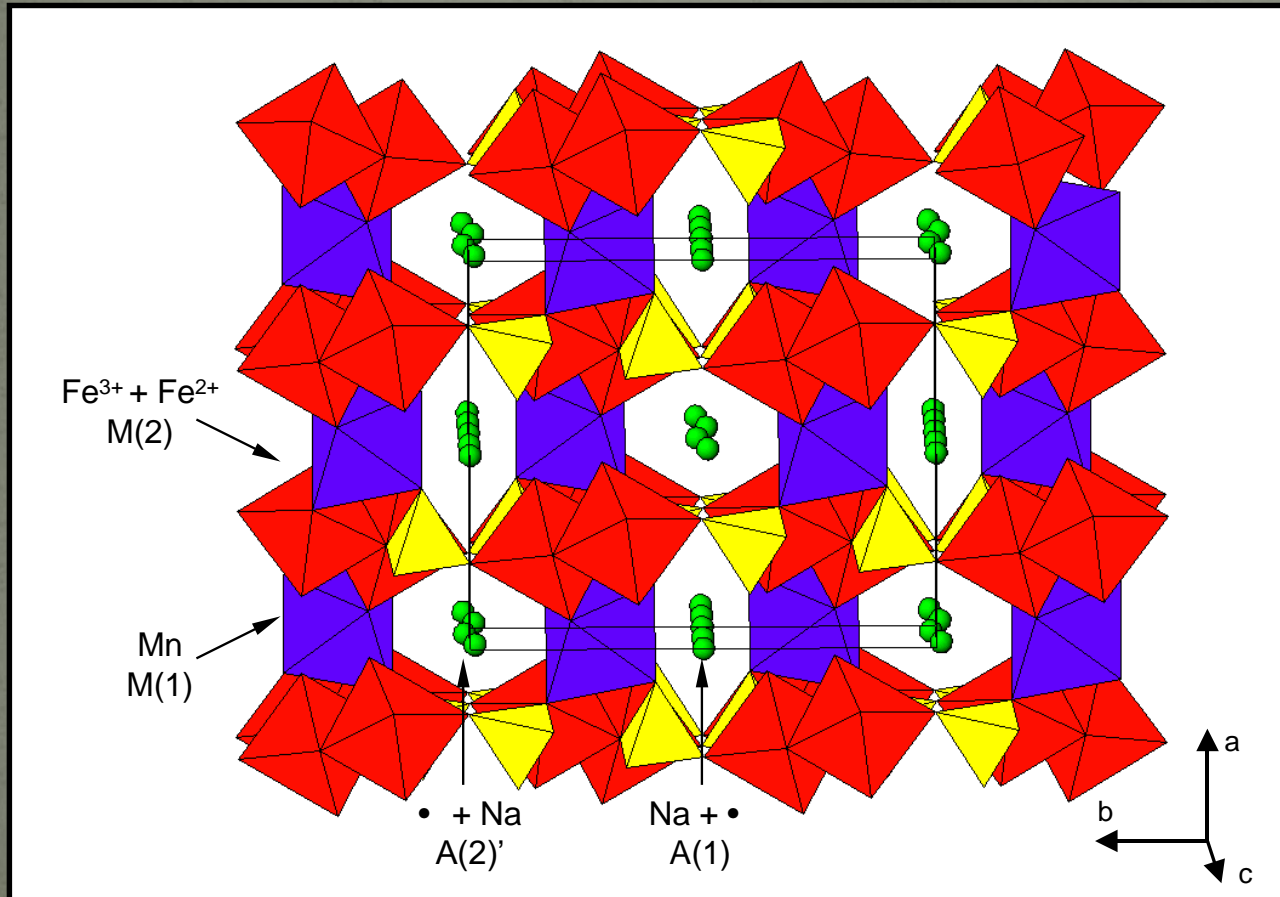
The alluaudite structure

A(2)': gable disphenoid

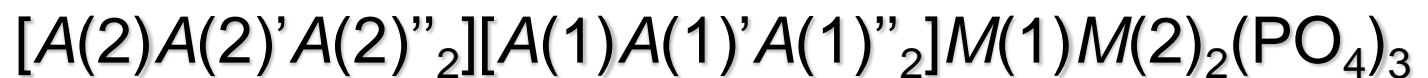
A(1): distorted cube

M(1): very distorted octahedron

M(2): distorted octahedron

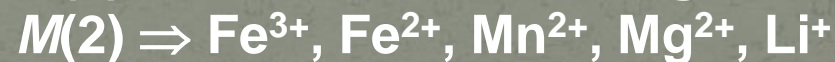
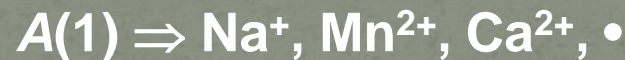


$C2/c, Z = 4$



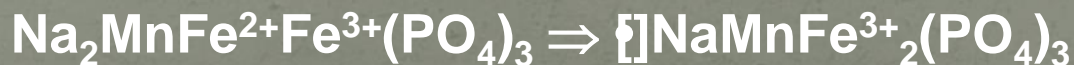
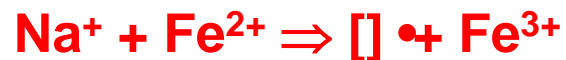
Crystal chemistry of natural alluaudites

- Moore & Ito (1979)



- Fransolet *et al.* (1985, 1986, 2004)

Oxidation mechanism:



Crystal chemistry of synthetic alluaudite-type compounds

- Solid state synthesis in air
- T = 800-950 °C
- P = 1 bar

Na-Mn-Fe³⁺ (+ PO₄) system

Role of Li⁺

Role of Cd²⁺ and Zn²⁺

Role of In³⁺ and Ga³⁺

Experimental

- Hydrothermal synthesis
- Tuttle-type cold-seal bombs
- T = 400-800 °C
- P = 1-5 kbar

Na-Mn-Fe²⁺-Fe³⁺ (+ PO₄) system

American Mineralogist, Volume 90, pages 653-662, 2005

Crystal chemistry of the hydrothermally synthesized Na₂(Mn_{1-x}Fe_x²⁺)₂Fe³⁺(PO₄)₃ alluaudite-type solid solution

FRÉDÉRIC HATERT,^{1,2,*} LEILA REBBOUH,³ RAPHAËL P. HERMANN,³ ANDRÉ-MATHIEU FRANSOLET,¹
GARY J. LONG,⁴ AND FERNANDE GRANDJEAN³

Cationic distribution

Cation	Ionic radius (Å)		Site			
	[VI]	[VIII]	A(2)'	A(1)	M(1)	M(2)
Ag ⁺	1.15	1.28	X	X		
Na ⁺	1.02	1.18	X	X	X	
Cu ⁺	0.77	-	p	p		
Li ⁺	0.76	0.92	p	p		
Ca ²⁺	1.00	1.12	p	p	p	
Cd ²⁺	0.95	1.10		p	X	p
Mn ²⁺	0.830	0.96	p	p	X	X
Fe ²⁺	0.780	0.92			X	X
Co ²⁺	0.745	0.90			X	X
Zn ²⁺	0.740	0.90			X	P
Cu ²⁺	0.73	-		p		
Mg ²⁺	0.720	0.89			X	X
In ³⁺	0.800	0.92			p	X
Fe ³⁺	0.645	0.78		p		X
Ga ³⁺	0.620	-				p
Cr ³⁺	0.615	-				p
Al ³⁺	0.535	-				p

Solid-state synthesis
and hydrothermal
experiments



X-ray structure
refinements

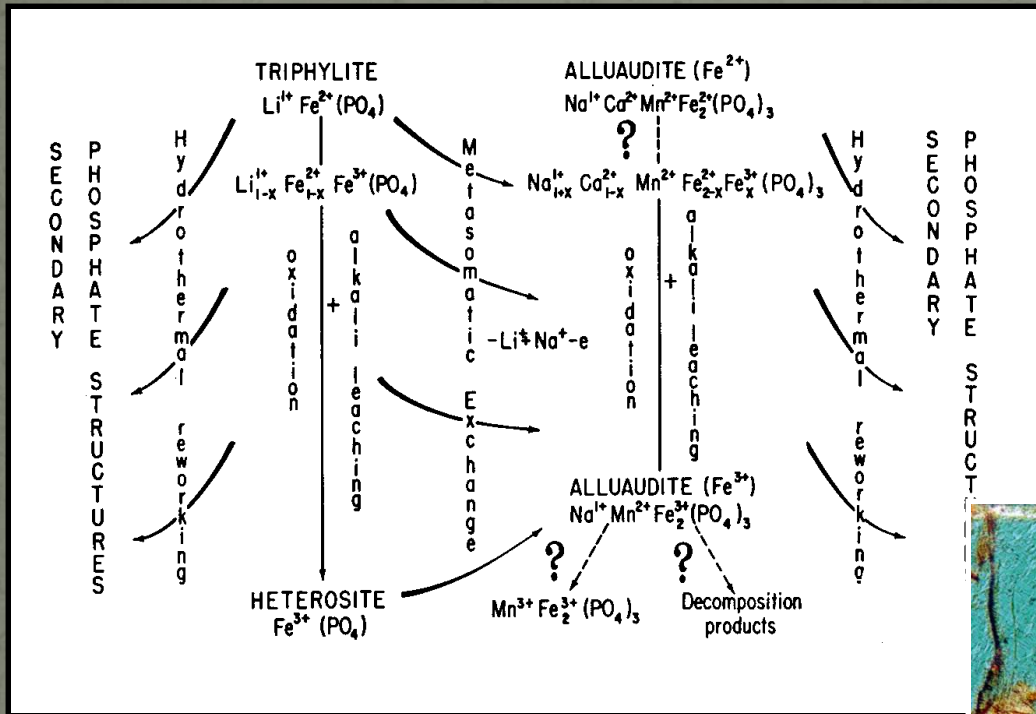
X : Complete occupancy of the site
p : Partial occupancy of the site

Crystal chemistry of the divalent cation in alluaudite-type phosphates:
A structural and infrared spectral study of the $\text{Na}_{1.5}(\text{Mn}_{1-x}\text{M}^{2+}_x)_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$
solid solutions ($x = 0$ to 1 , $\text{M}^{2+} = \text{Cd}^{2+}, \text{Zn}^{2+}$)

Frédéric Hatert*

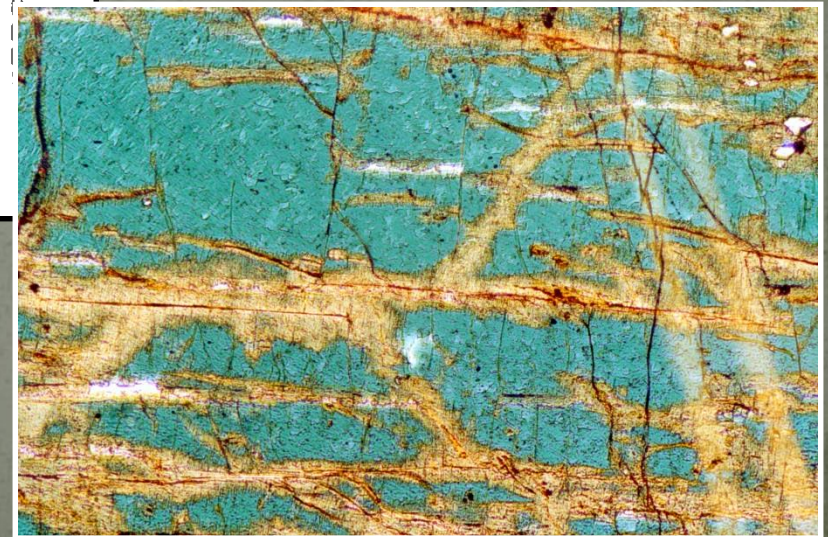
Laboratoire de Minéralogie, Université de Liège, Bâtiment B18, B-4000 Liège, Belgium

The stability of alluaudites?



- Secondary origin
- Primary origin

Oxidation mechanism



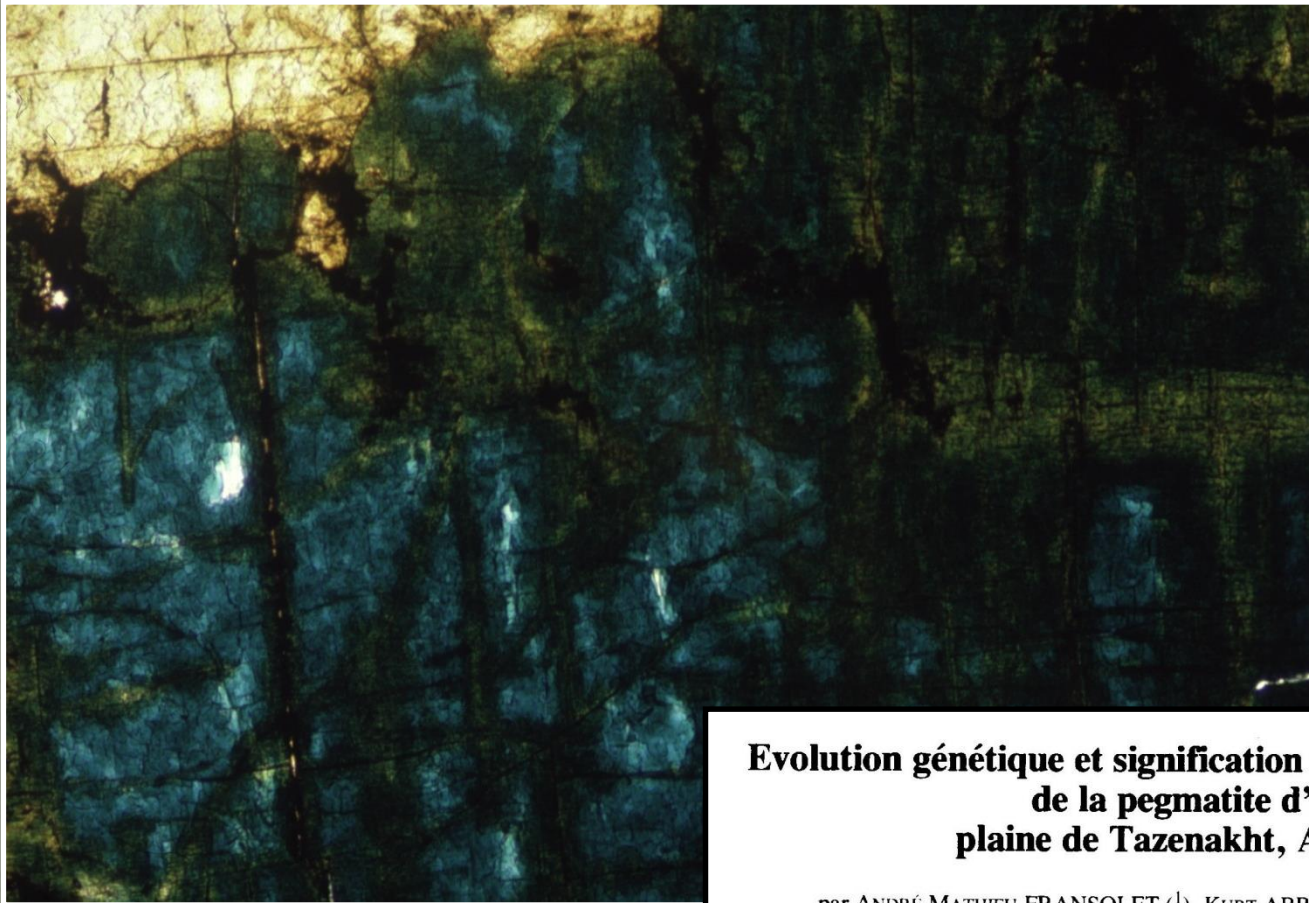
Alluaudite, Kibingo pegmatite, Rwanda

Questions

- ➔ A. Stability of Fe-bearing alluaudites?
- ➔ B. Stability of Fe-Mn-bearing alluaudites ?
- ➔ C. Stability of the alluaudite + triphylite assemblage ?
- ➔ D. Stability of wyllieites?

A. Fe-rich alluaudites

Ferroalluaudite, $\text{NaFe}^{2+}\text{Fe}^{3+}_2(\text{PO}_4)_3$, Angarf-sud, Morocco



Evolution génétique et signification des associations de phosphates de la pegmatite d'Angarf-Sud, plaine de Tazenakht, Anti-Atlas, Maroc

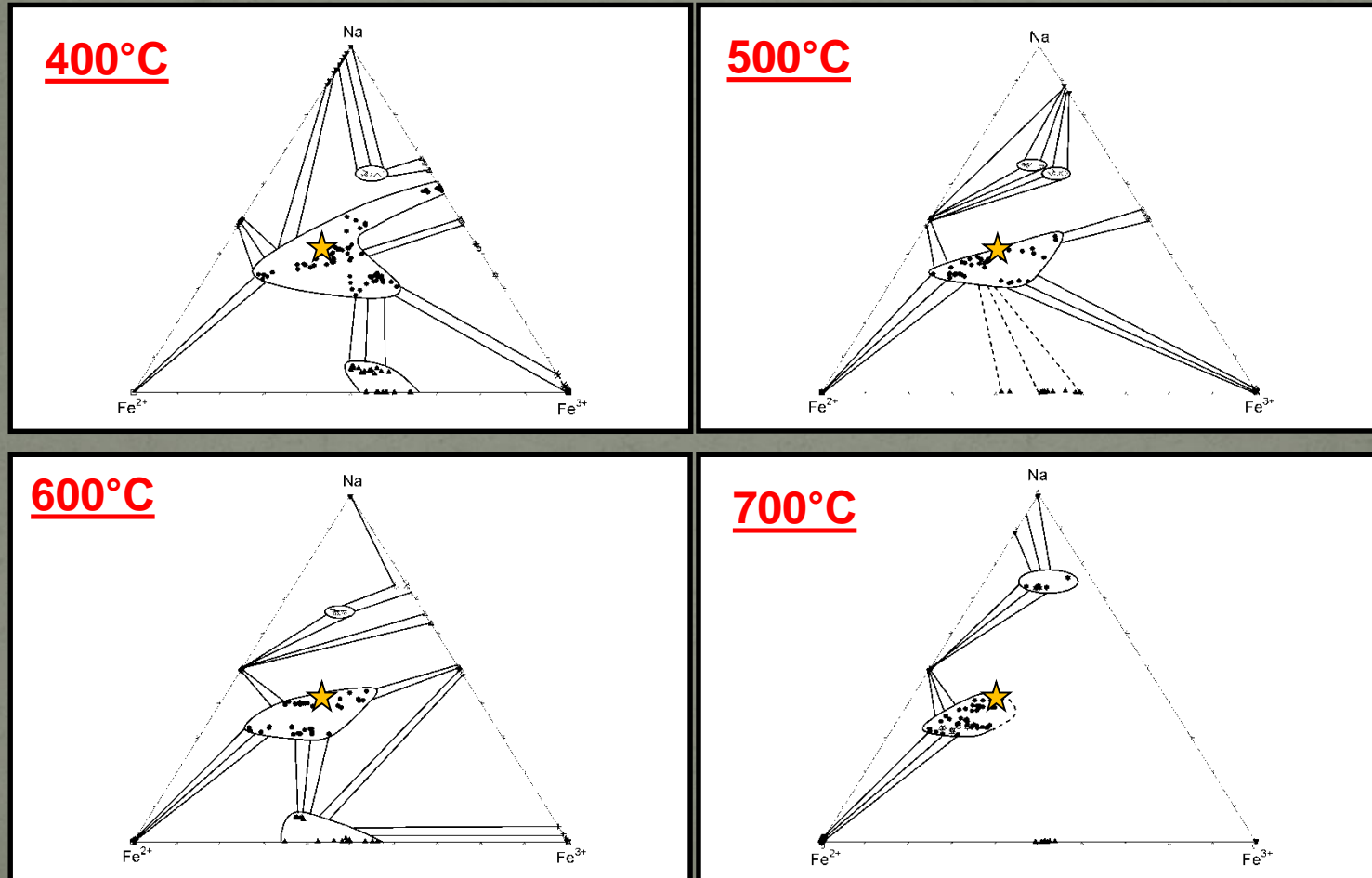
par ANDRÉ-MATHIEU FRANSOLET ⁽¹⁾, KURT ABRAHAM ⁽²⁾ et JEAN-MARIE SPEETJENS ⁽¹⁾

⁽¹⁾ Institut de Minéralogie, Université de Liège, Place du Vingt-Août, 9, B-4000 Liège (Belgique).

⁽²⁾ Institut für Mineralogie, Ruhr-Universität Bochum,
Universitätsstrasse 150, Postfach 10 21 48, D-4630 Bochum-1 (Westdeutschland).

A. The Na-Fe²⁺-Fe³⁺ (+ PO₄) system

★ = Ferroalluaudite from Angarf-sud, Morocco



Cristallisation between 400 and 700°C → primary origin

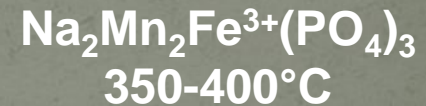
B. The $\text{Na}_2(\text{Mn}_{1-x}\text{Fe}^{2+}_x)_2\text{Fe}^{3+}(\text{PO}_4)_3$ solid solution

- Low T \Rightarrow alluaudite
- High T \Rightarrow "X-phase"
- Mn \Rightarrow fillowite $[\text{NaMn}_4(\text{PO}_4)_3]$

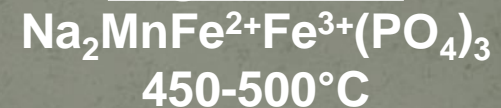
No maricite $[\text{NaFePO}_4]$ in
pegmatites



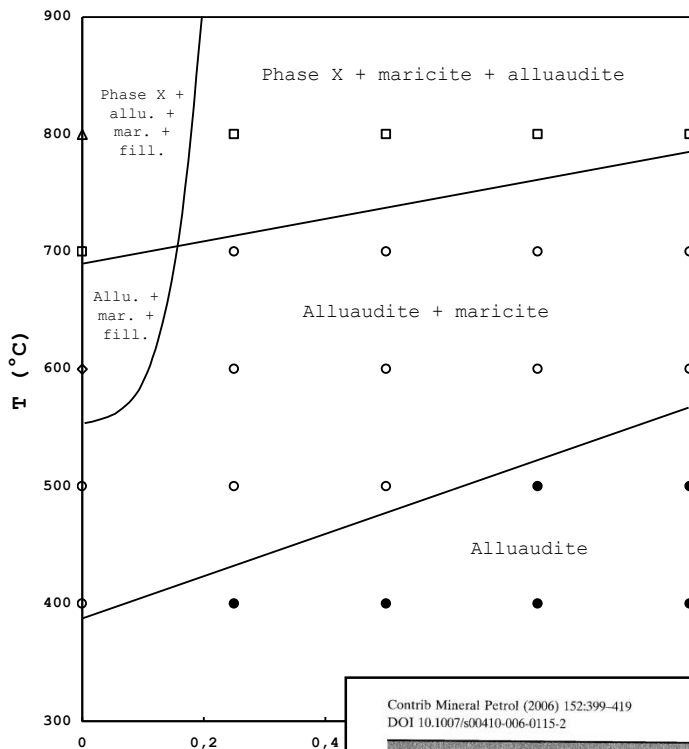
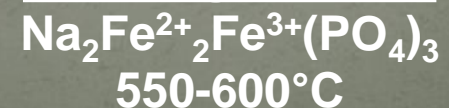
Varulite



Hagendorfite



Ferrohagendorfite



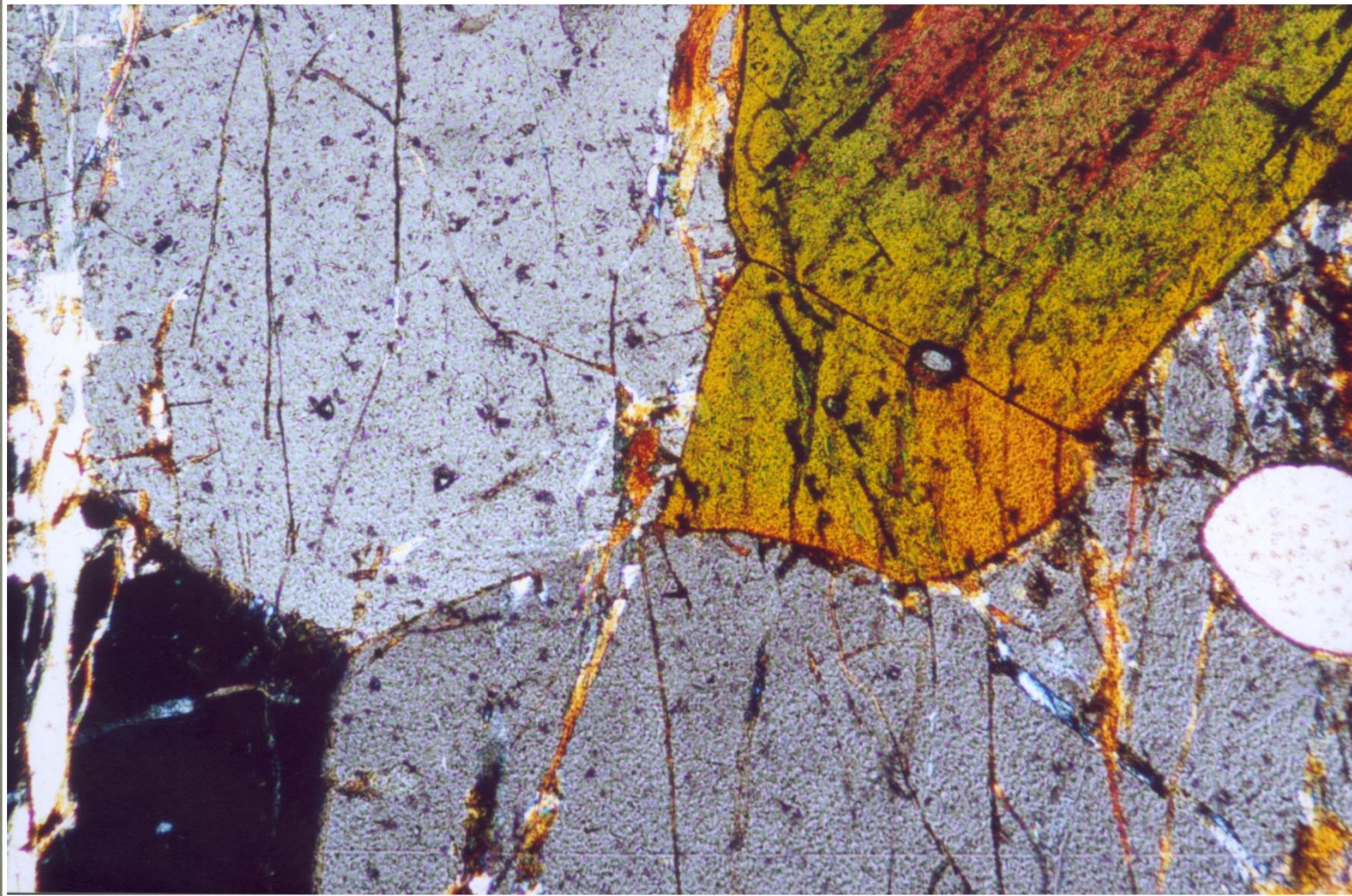
Contrib Mineral Petrol (2006) 152:399–419
DOI 10.1007/s00410-006-0115-2

ORIGINAL PAPER

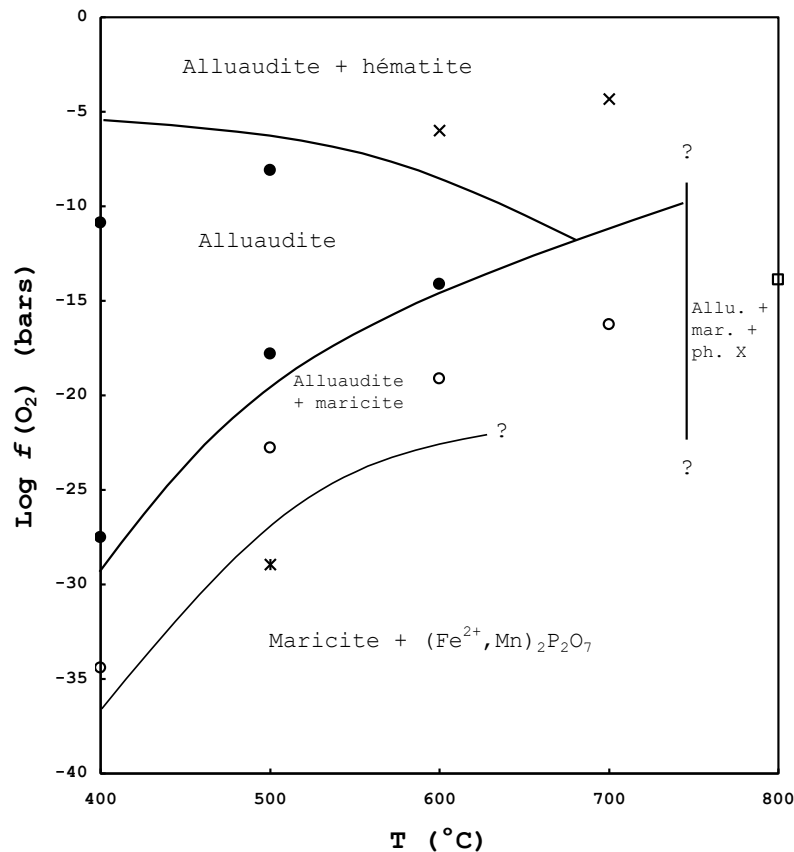
**The stability of primary alluaudites in granitic pegmatites:
an experimental investigation of the $\text{Na}_2(\text{Mn}_{2-2x}\text{Fe}_{1+2x})(\text{PO}_4)_3$
system**

Frédéric Hatert · André-Mathieu Franolet ·
Walter V. Maresch

B. The alluaudite + fillowite assemblage



B. $\text{Na}_2\text{MnFe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$



Composition of primary
alluaudite

Temperature and oxygen
fugacity can be
constrained

C. The triphylite + alluaudite assemblage

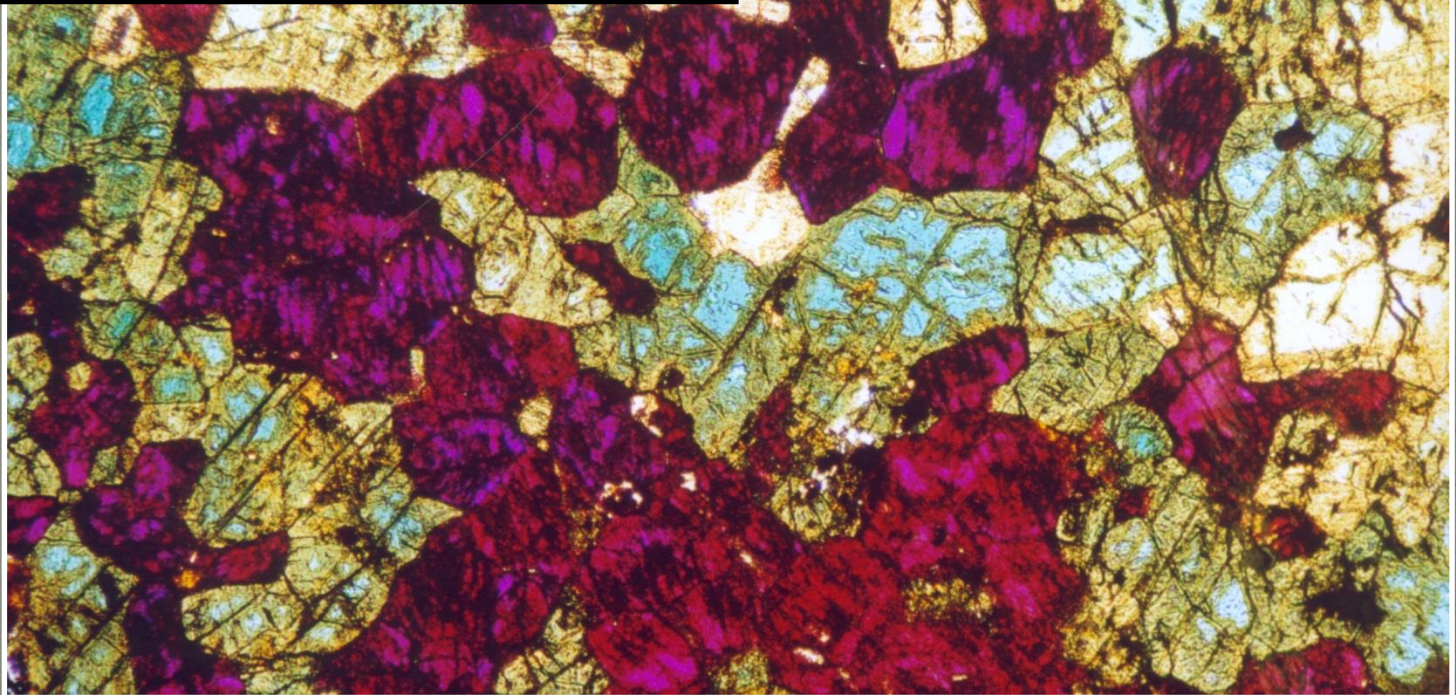
PETROGRAPHIC EVIDENCE FOR PRIMARY HAGENDORFITE IN AN UNUSUAL ASSEMBLAGE OF PHOSPHATE MINERALS, KIBINGO GRANITIC PEGMATITE, RWANDA

ANDRÉ-MATHIEU FRANSOLET AND FRÉDÉRIC HATERT

*Laboratoire de Minéralogie, Département de Géologie, Université de Liège, Bâtiment B18,
Sart Tilman, B-4000 Liège, Belgique*

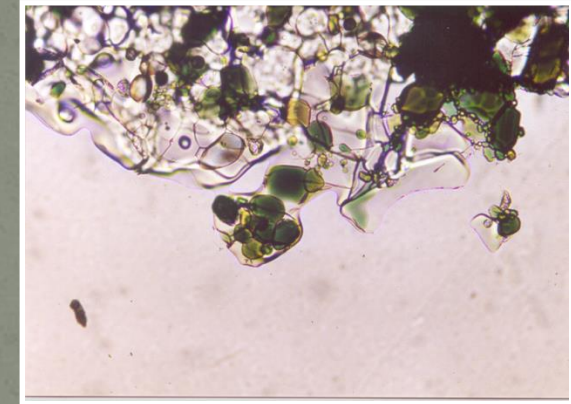
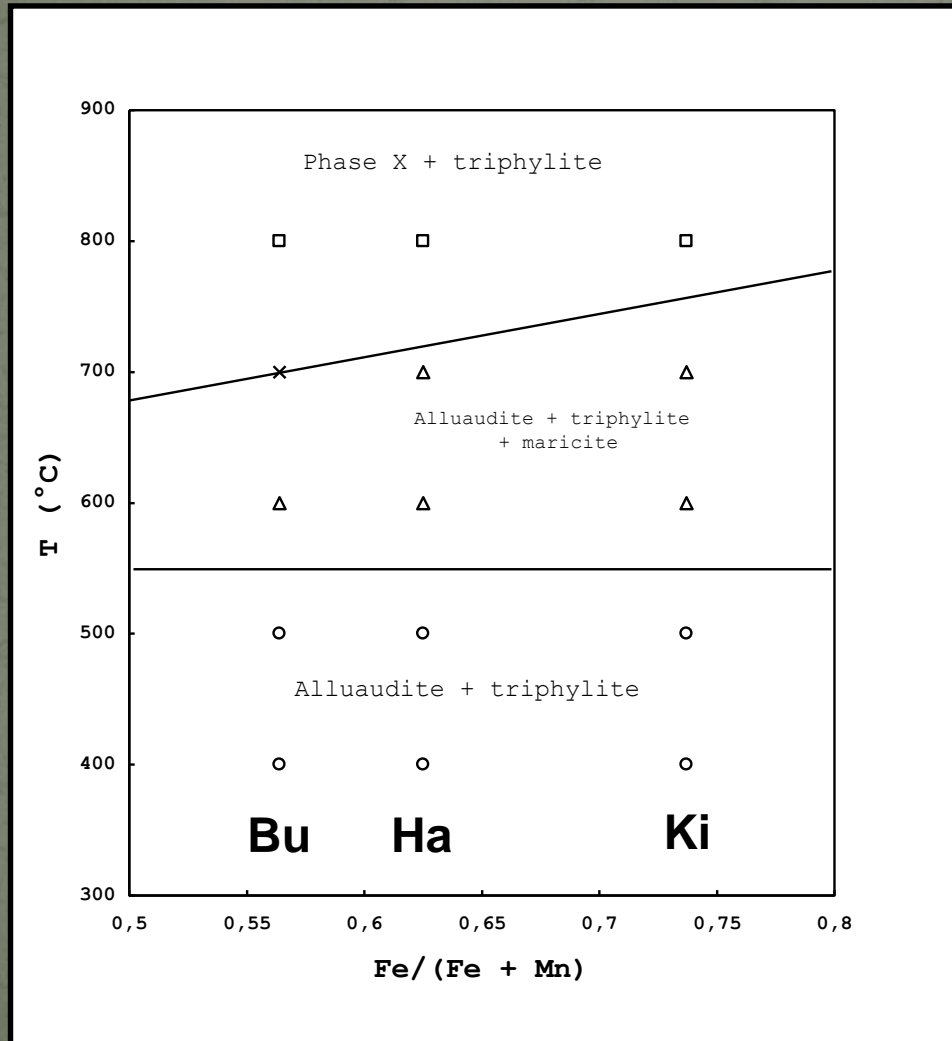
FRANÇOIS FONTAN

Laboratoire de Minéralogie, Université Paul-Sabatier de Toulouse, 39, Allées Jules-Guesde, F-31000 Toulouse, France



Hagendorfite, alluaudite, and heterosite, Kibingo pegmatite, Rwanda

C. Stability of the triphylite + alluaudite assemblage



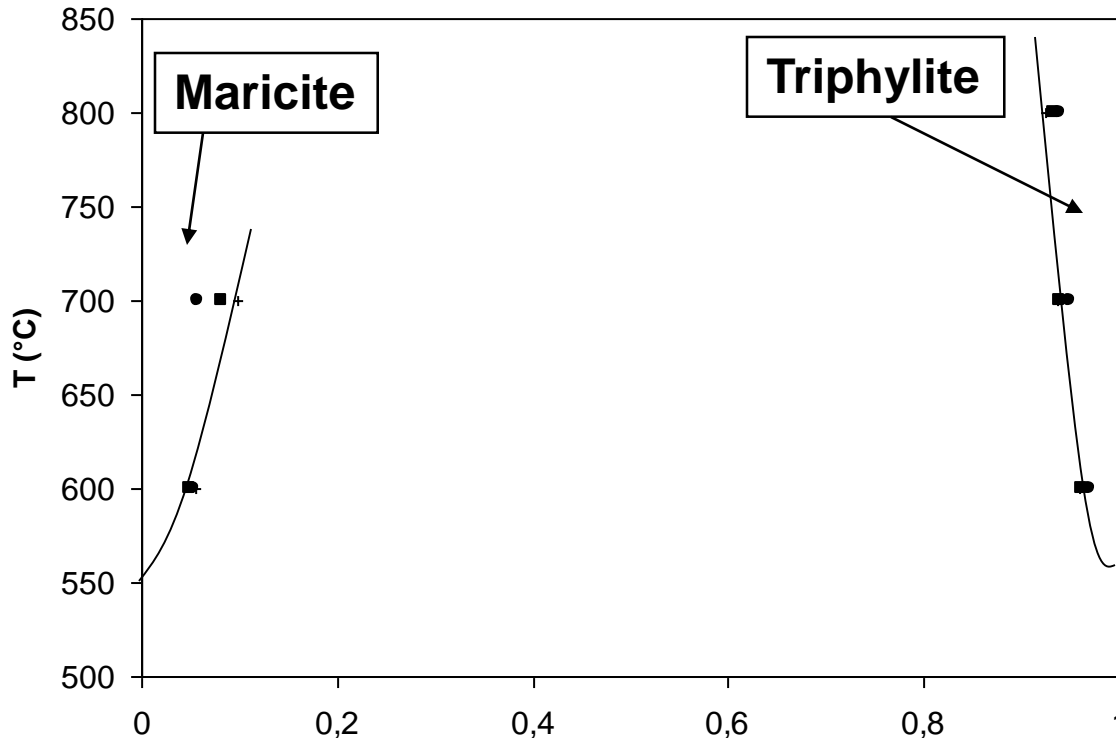
No maricite in pegmatites



Alluaudite + triphylite
assemblage stable up to
500-600°C

Bu = Buranga, Rwanda
Ha = Hagendorf-Süd, Germany
Ki = Kibingo, Rwanda

C. The Na-in-triptylite geothermometer



Experimental investigation of the alluaudite + triptylite assemblage, and development of the Na-in-triptylite geothermometer: applications to natural pegmatite phosphates

Frederic Hatert · Luisa Ottolini ·
Peter Schmid-Beurmann

• In triptylite, 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

• No partitioning below ca. 550°C

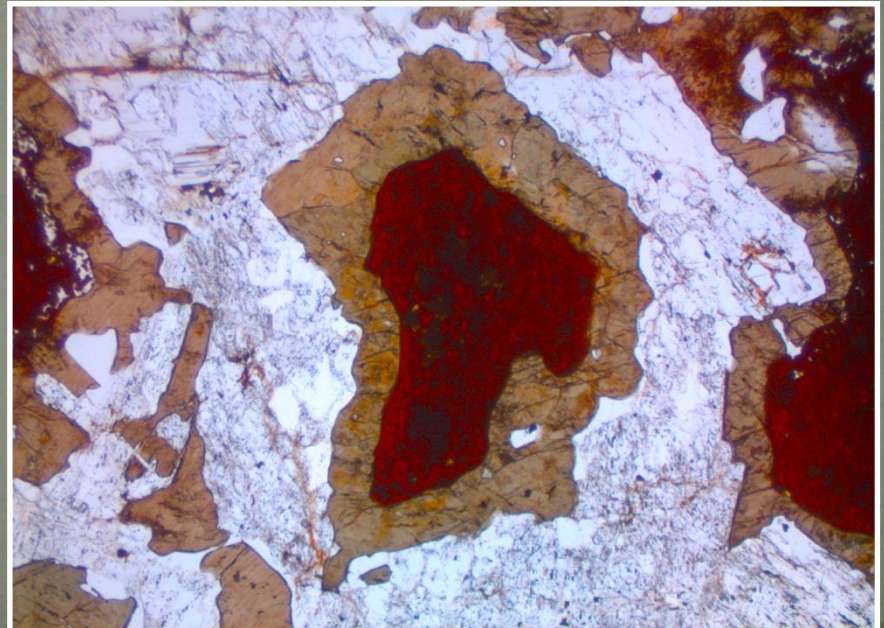
➔ **Geothermometer!**

D. Stability of wyllieites?

Qingheiite-(Fe²⁺), Na₂Fe²⁺MgAl(PO₄)₃, a new phosphate mineral from the Sebastião Cristino pegmatite, Minas Gerais, Brazil

FRÉDÉRIC HATERT^{1,*}, MAXIME BAIJOT¹, SIMON PHILIPPO² and JOHAN WOUTERS³

- Reaction between albite and triphylite
- High temperature hydrothermal transformations
- Factors governing the transition from alluaudites to wyllieites not clearly understood

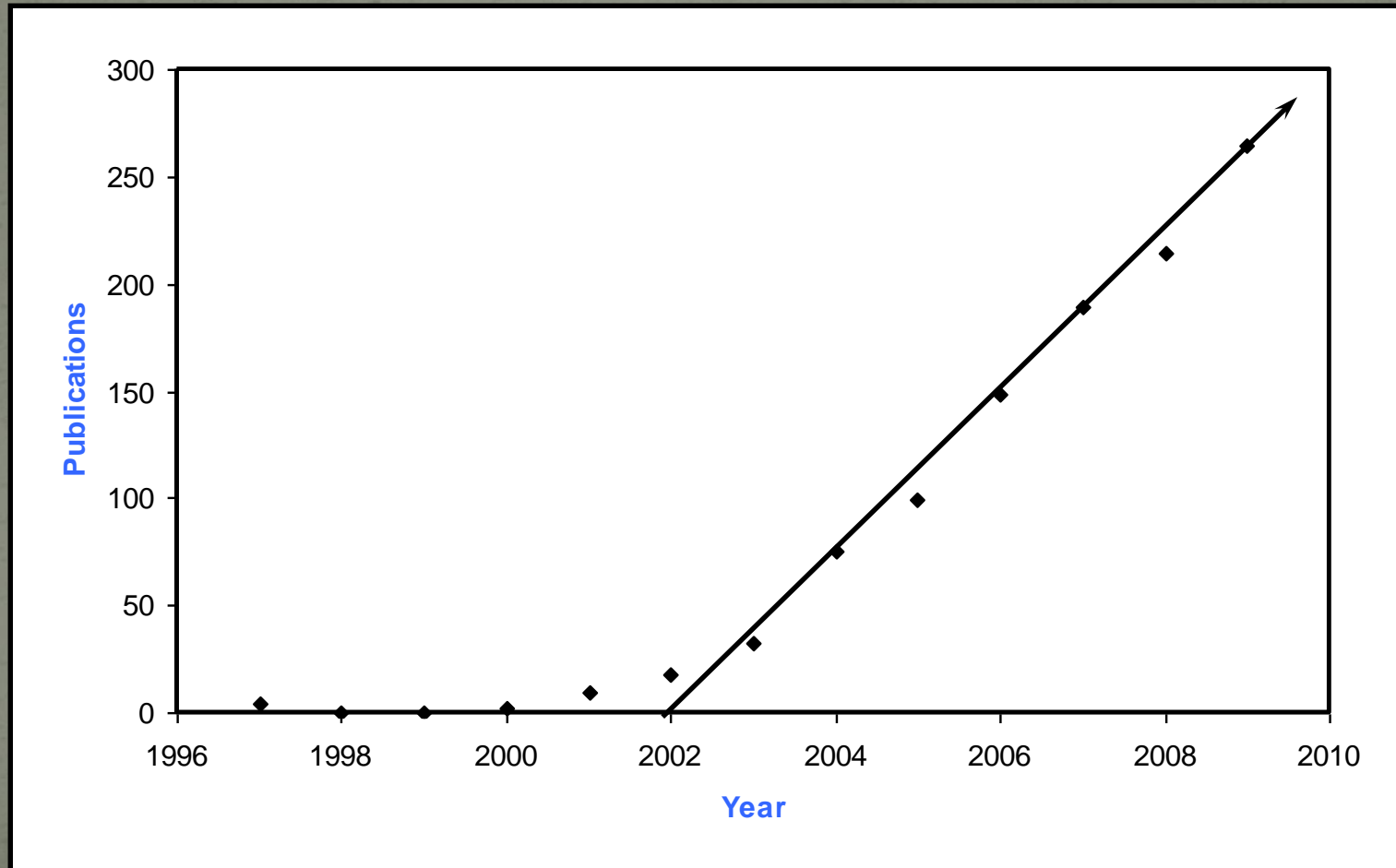


Applications: Li-ion batteries

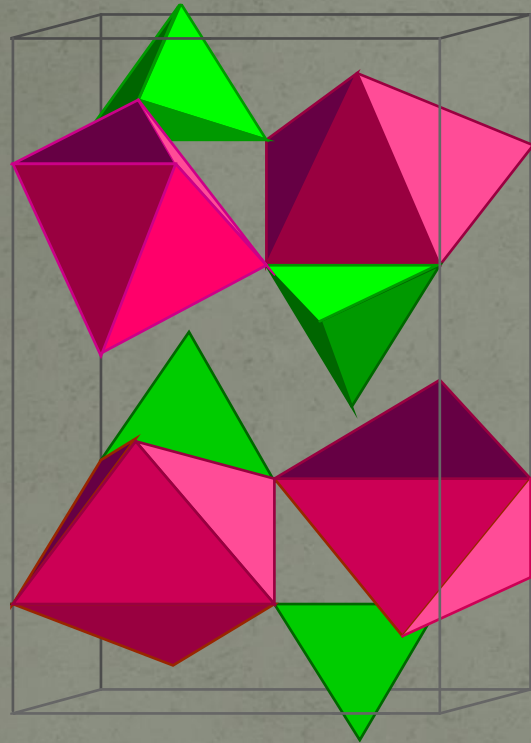
	Layered struct.		Spinel	Triphylite
	LiCoO ₂	LiNiCoO ₂	LiMn ₂ O ₄	LiFePO ₄
Capacity (mAh/g)	140-150	170-180	110-120	160-170
Potentiel (V)	3,9	3,8	4,0	3,4
Resistance to cycling	Poor	Poor	+/-	Good
Exchange speed	Good	Good	Good	Good
Electrode density	Good	+/-	+/-	Poor
Security	+/-	?	Good	Good
Cost of chemicals	High	+/-	Low	Low
Cost of synthesis	Low	High	+/-	Low
Abundance	Low	+/-	High	High
Toxicity	?	?	Low	Very low

LiFe²⁺(PO₄) as cathode material

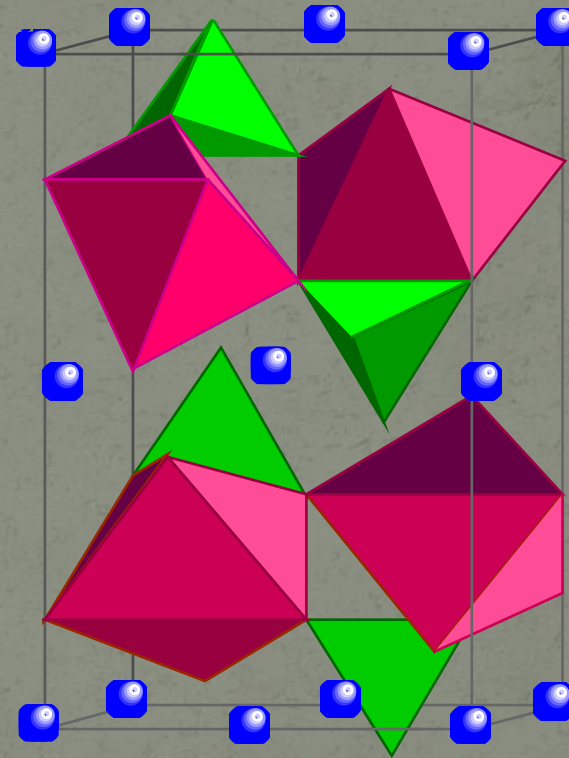
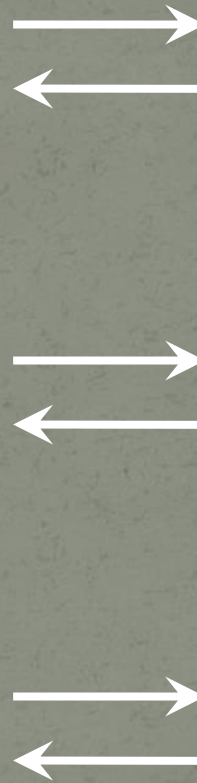
Electrochemical properties demonstrated by Padhi *et al.* (1997)



Intercalation – extraction of Li



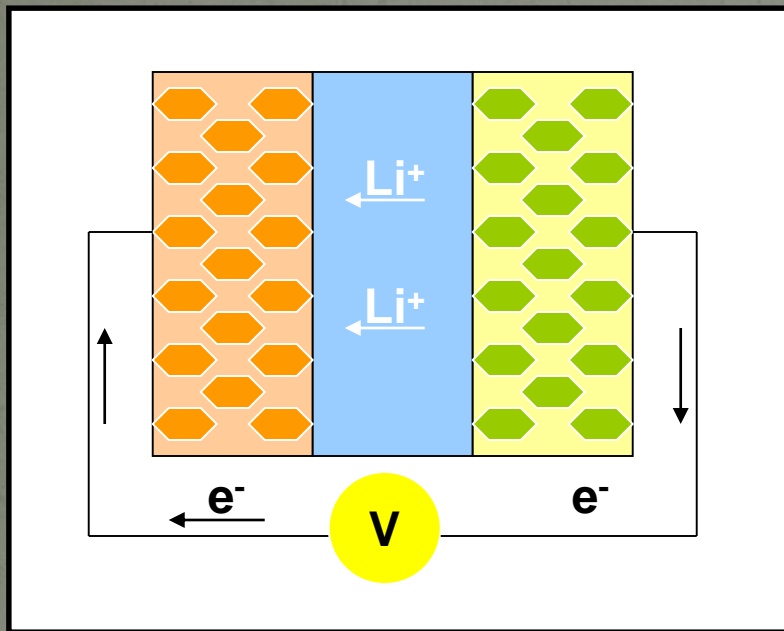
Heterosite, $\text{Fe}^{3+}(\text{PO}_4)$



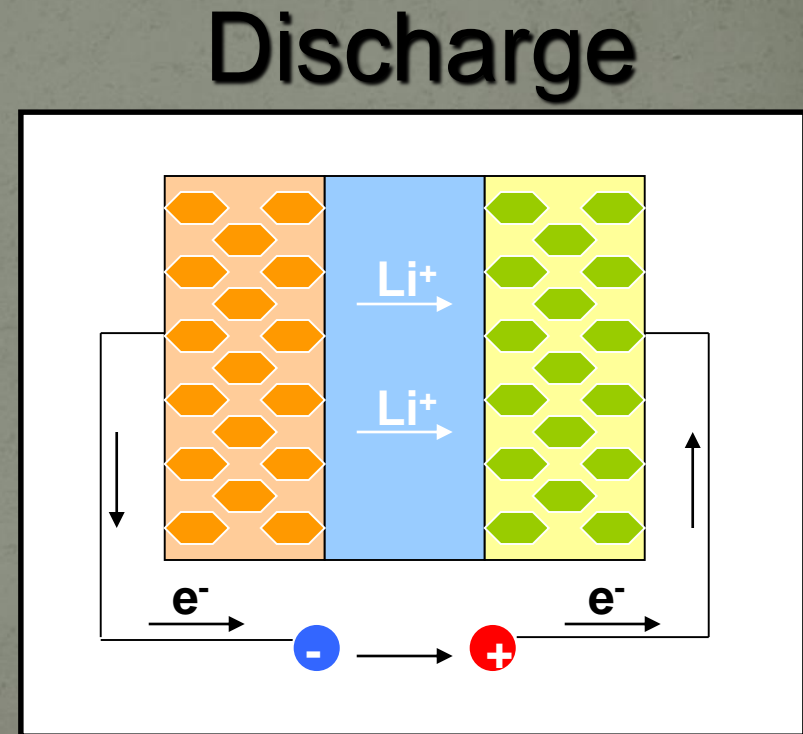
Triphylite, $\text{LiFe}^{2+}(\text{PO}_4)$

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

Principle of Li-ion batteries



Charge



$\text{LiFe}^{2+}(\text{PO}_4)$



Metallic Li



Electrolyte

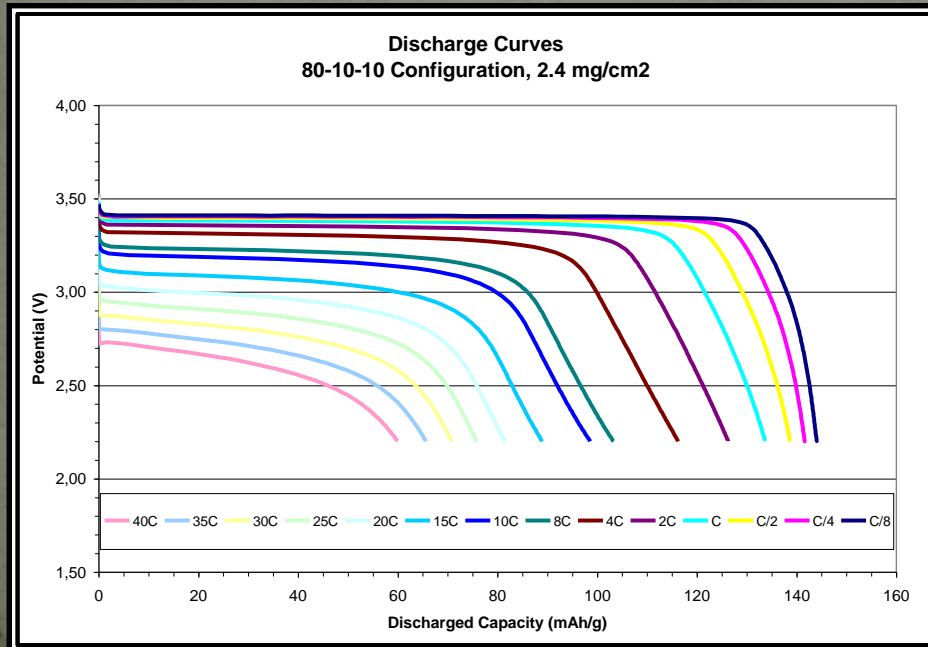
Performance

nature

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

LETTERS

Battery materials for ultrafast charging and discharging

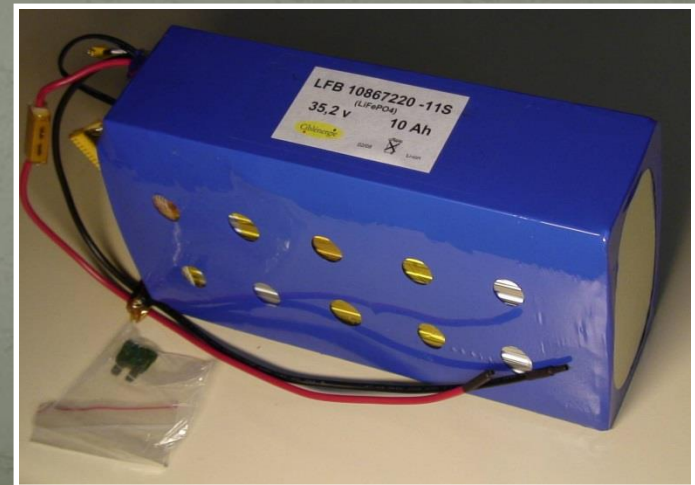
Byoungwoo Kang¹ & Gerbrand Ceder¹

The storage of electrical energy at high charge and discharge rate is an important technology in today's society, and can enable hybrid and plug-in hybrid electric vehicles and provide back-up for wind and solar energy. It is typically believed that in electrochemical systems very high power rates can only be achieved with supercapacitors, which trade high power for low energy density as they only store energy by surface adsorption reactions of charged species on an electrode material¹⁻³. Here we show that batteries^{4,5} which obtain high energy density by storing charge in the bulk of a material can also achieve ultrahigh discharge rates, comparable to those of supercapacitors. We realize this in LiFePO₄ (ref. 6), a material with high lithium bulk mobility^{7,8}, by creating a fast ion-conducting surface phase through controlled off-stoichiometry. A rate capability equivalent to full battery discharge in 10–20 s can be achieved.

LiFePO₄-based batteries production



- Phostech Lithium was founded in 2001
- Based on the commercial potential of C-LiFePO₄ and other Phosphate-based cathode materials
- Obtained exclusive rights for the manufacture and sales of LiFePO₄ for Lithium-Ion battery applications with University of Texas and Hydro-Quebec
- Obtained through UDM the access to four improvement patents resulting from UDM's research for Hydro-Québec, including C additive to LiFePO₄ and a new synthesis way from a Fe⁺³ precursor



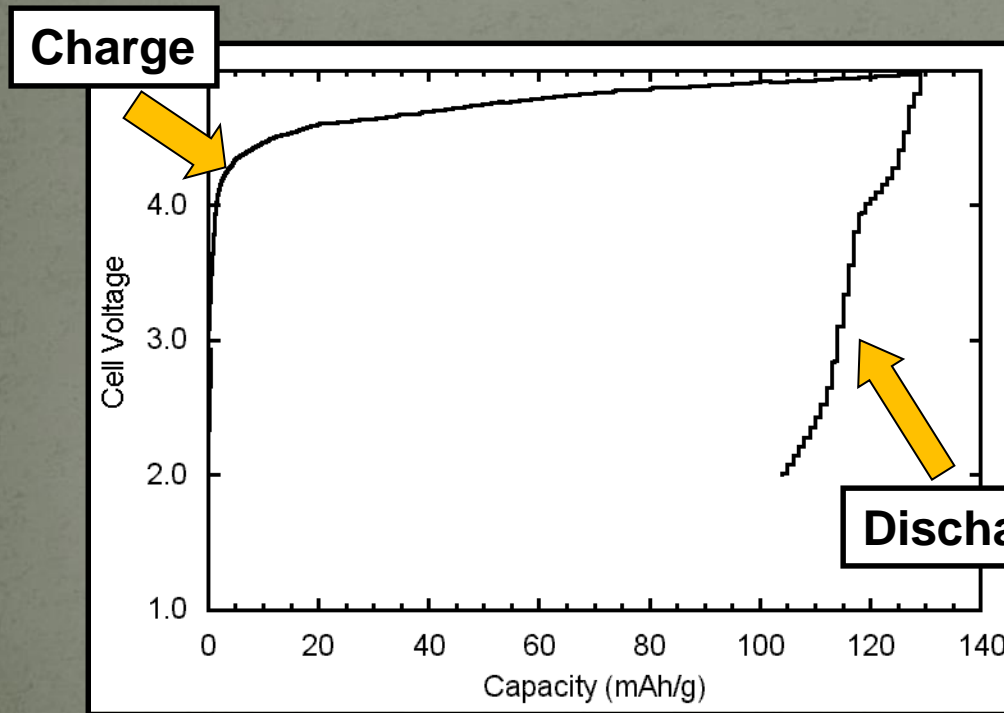
LiFePO₄-based batteries applications



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



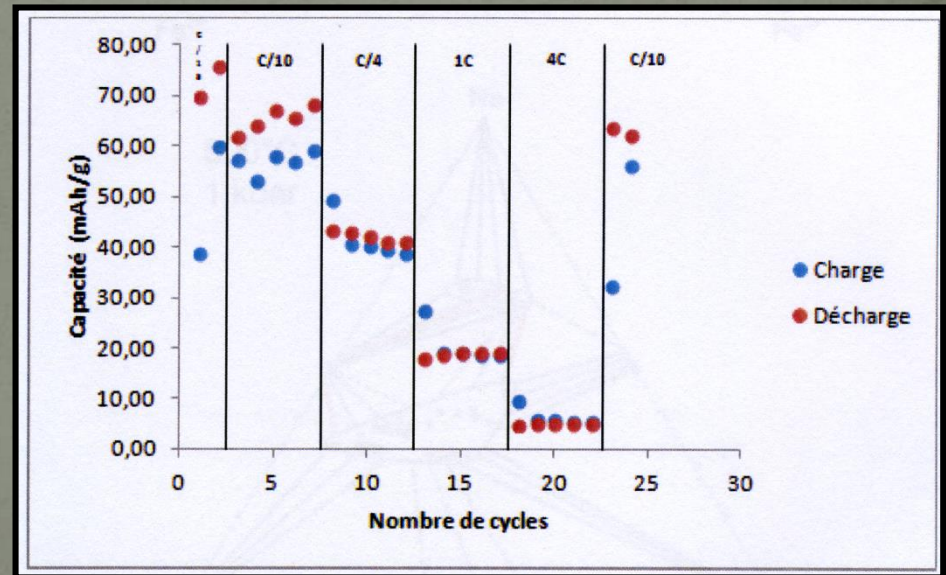
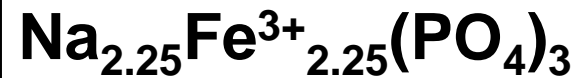
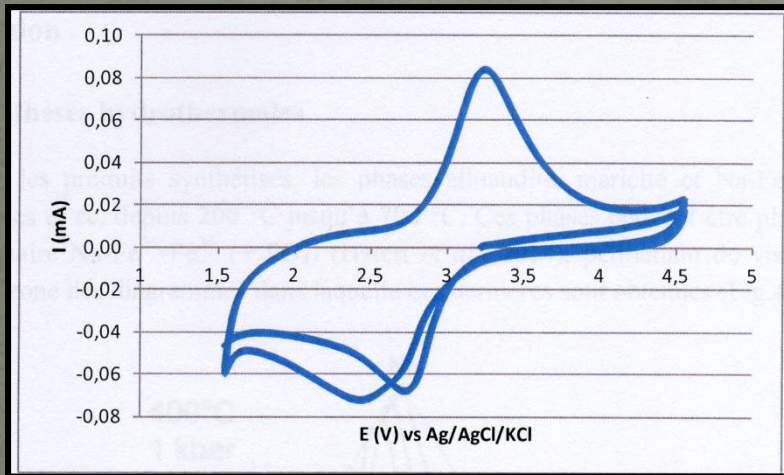
Alluaudites as a promising cathode material for Li-ion batteries?



Low performance

Investigation of other
alluaudite-type
phosphates necessary

Electrochemical investigation of new alluaudite-type phosphates



➔ Promizing properties!

Conclusions

- Iron-manganese phosphates play a crucial role in the geochemical evolution of granitic pegmatites, and are very sensitive to the variations of physico-chemical parameters
- An experimental investigation of alluaudites, and of the alluaudite + triphylite and triphylite + sarcopside assemblages, has provided tools which can be used to estimate the P, T, and oxygen fugacity conditions that prevailed in pegmatites
- Phosphates with the olivine- and alluaudite-type structures show interesting properties, related to the mobility of large cations in their crystal structures. These properties are responsible for the recent use of LiFePO_4 as electrode material in Li-ion batteries.