

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



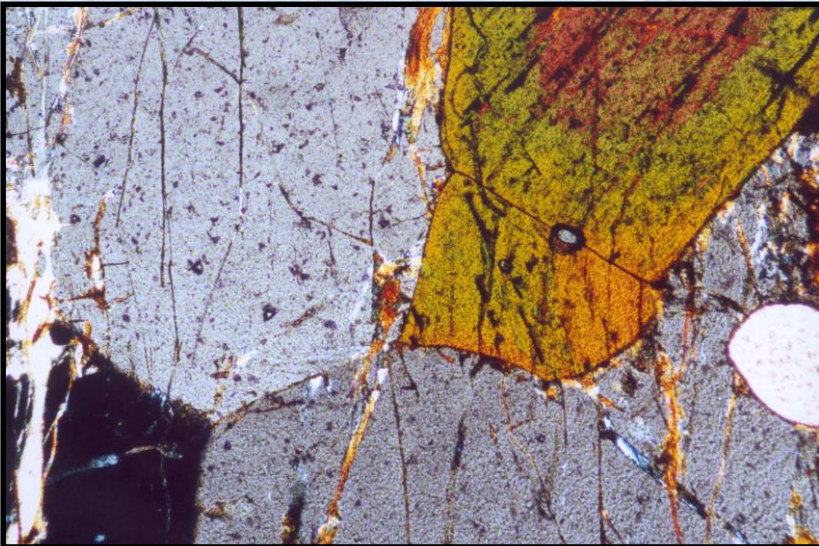
# The iron-manganese phosphates: Geological applications and development of new materials

Frédéric Hatert

Bilbao, May 17th, 2010

# Occurrence

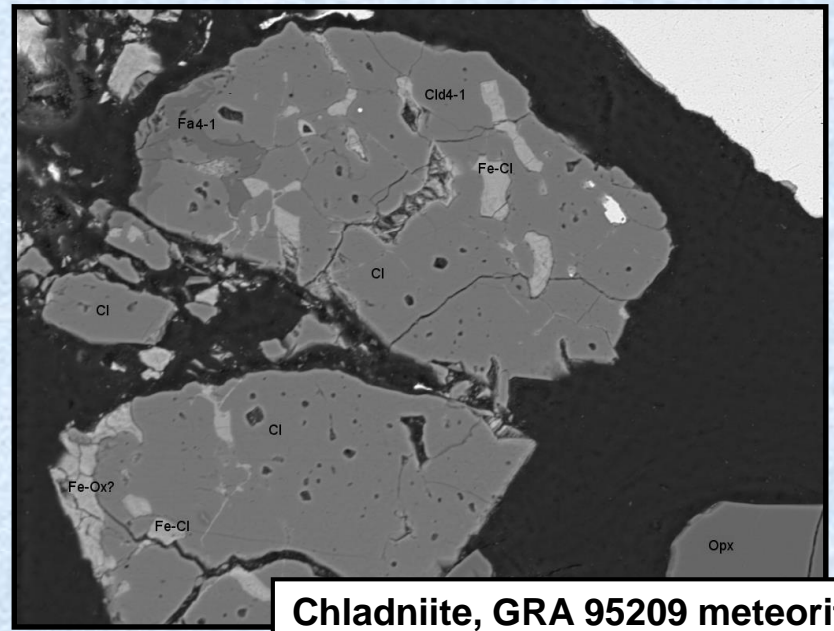
- Granitic pegmatites
- Metamorphic rocks
- Meteorites



Fillowite + alluaudite, Kabira pegmatite, Uganda



Johnsomervilleite, Loch Quoich, Scotland



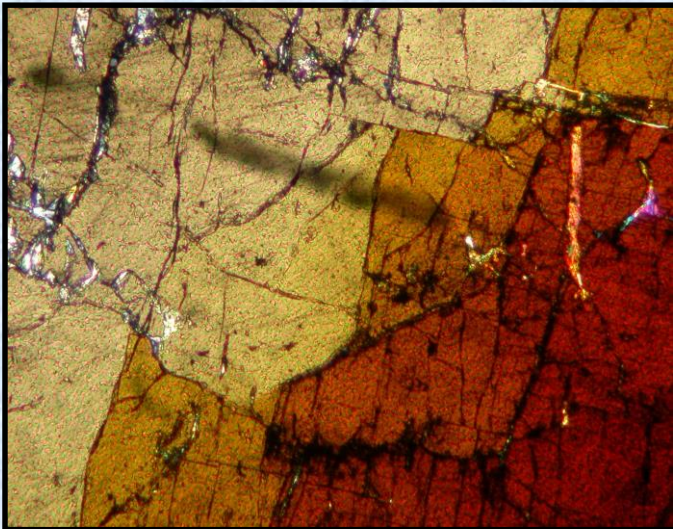
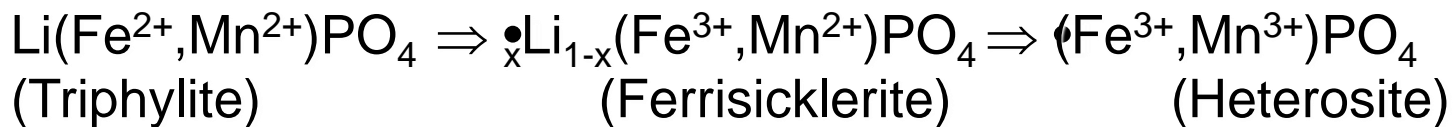
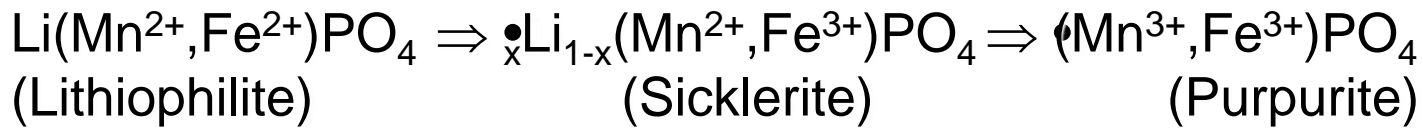
Chladniite, GRA 95209 meteorite

# Fe-Mn phosphates in pegmatites

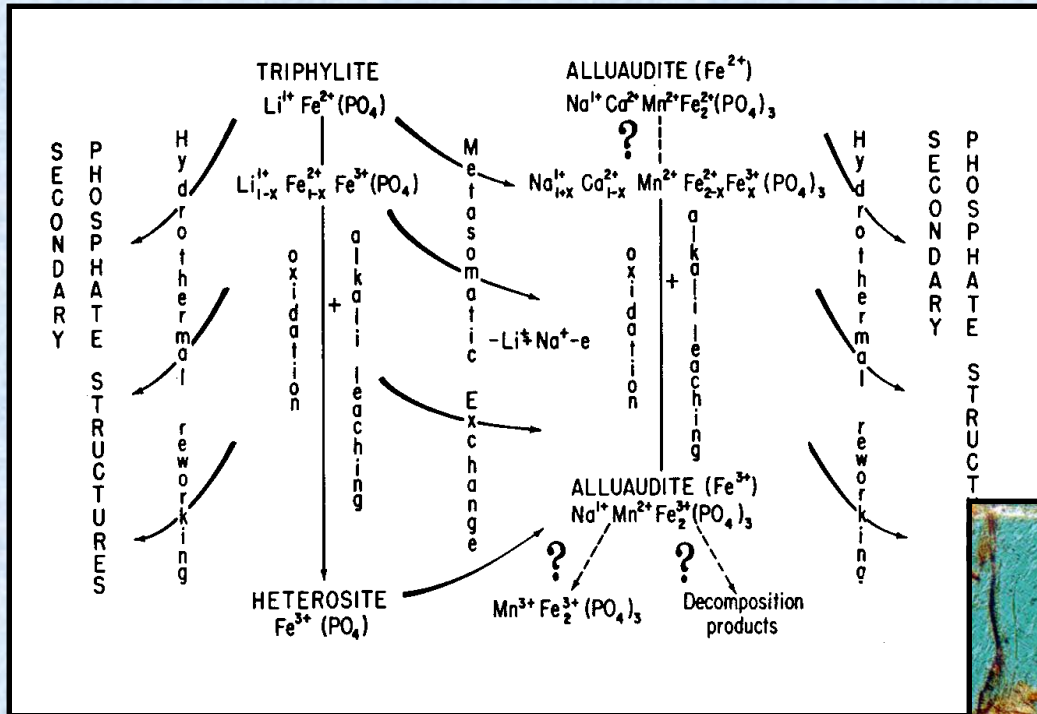


Buranga pegmatite, Rwanda

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

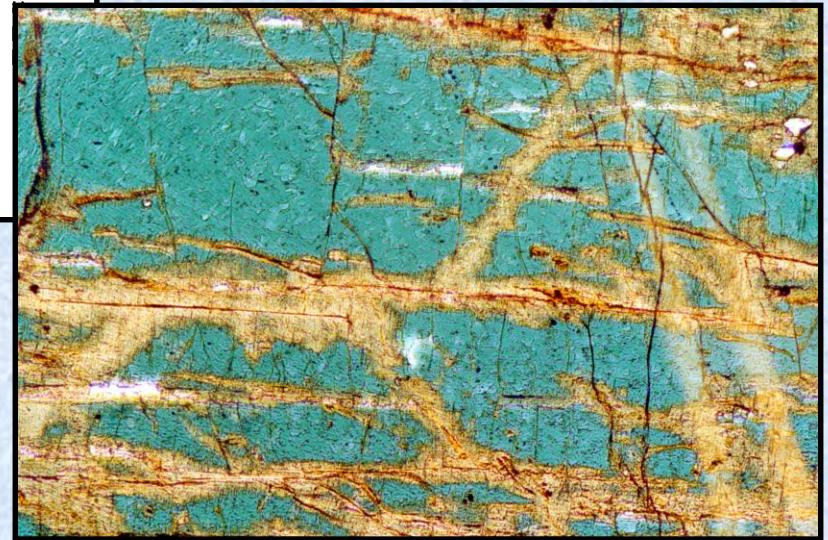
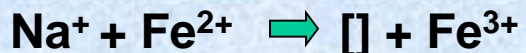
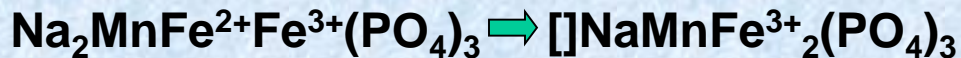


# The alluaudite group of minerals



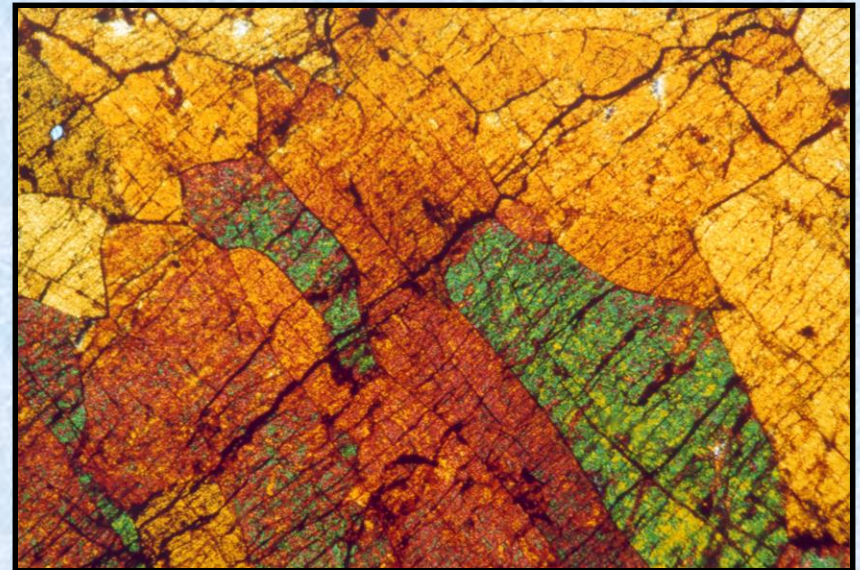
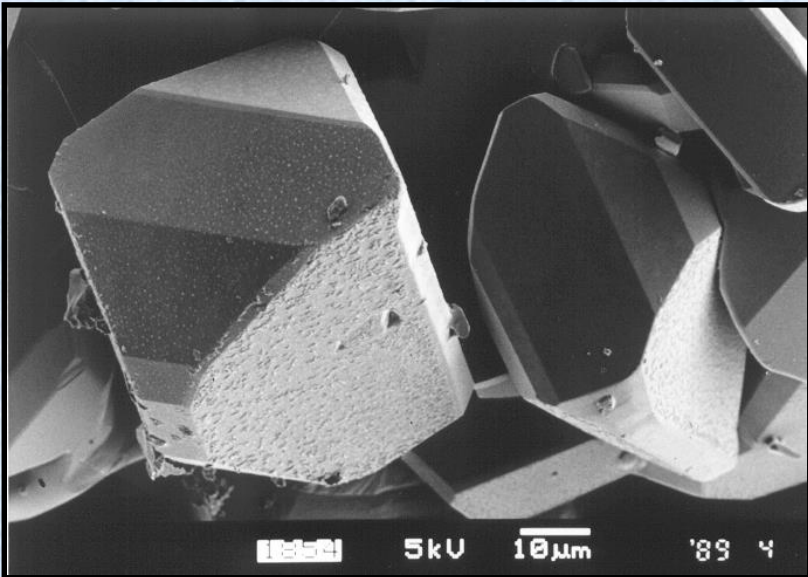
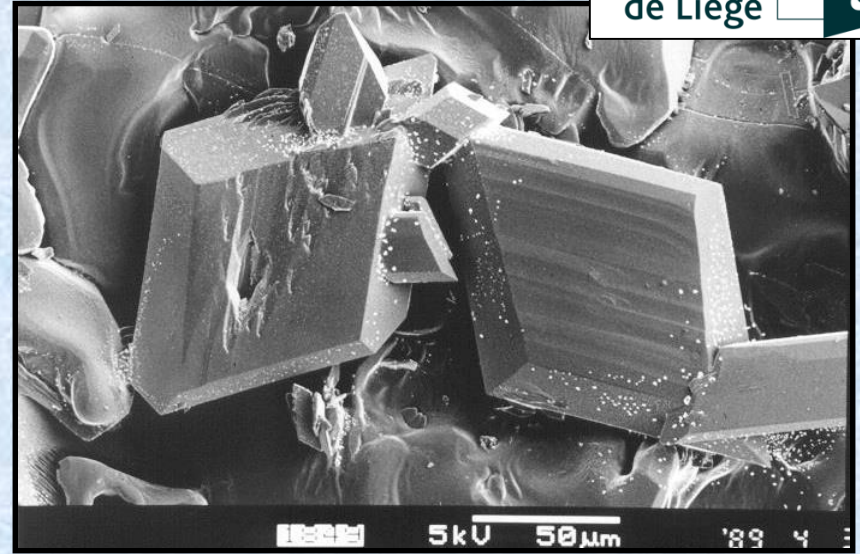
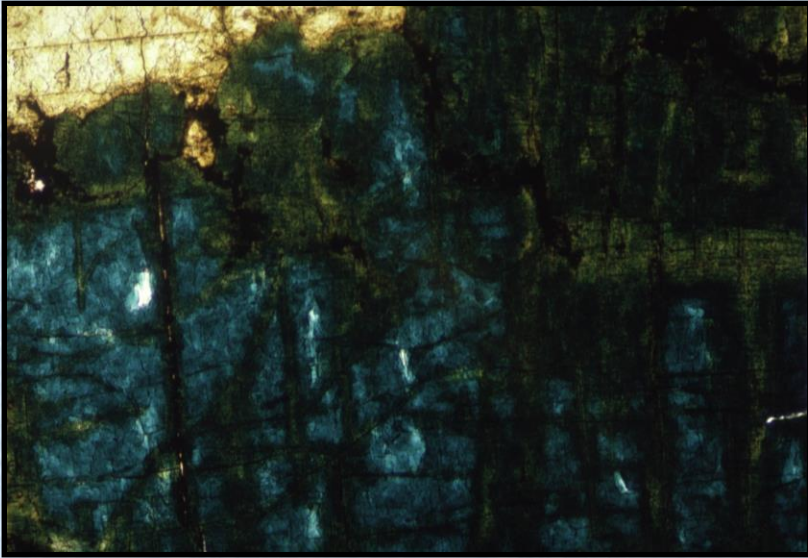
- Secondary origin
- Primary origin

## Oxidation mechanism



Alluaudite, Kibingo pegmatite, Rwanda

# The alluaudite group of minerals



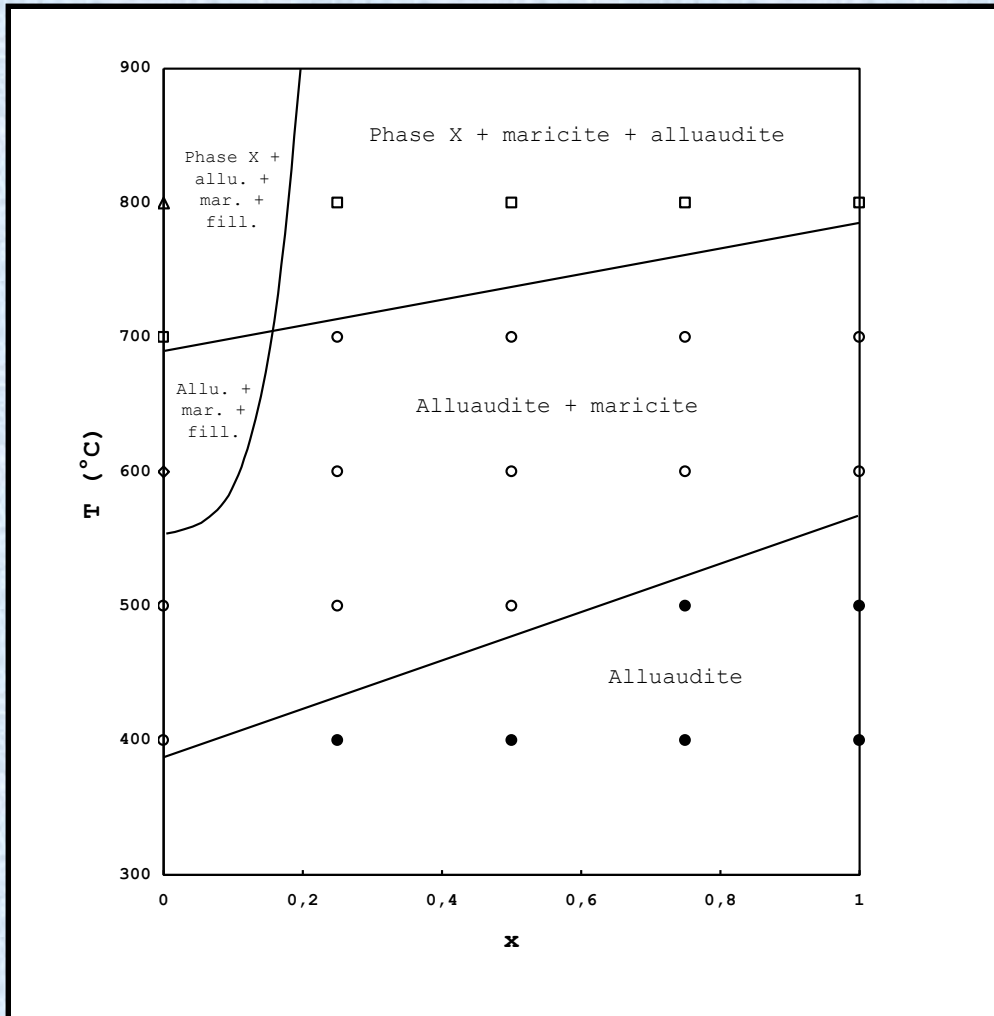
# Hydrothermal synthesis



- Tuttle-type cold-seal bombs
- $T = 400-800\text{ }^{\circ}\text{C}$
- $P = 1\text{ kbar}$
- Double capsule method (Au 4 mm,  $\text{Ag}_{70}\text{Pd}_{30}$  2 mm)
- Oxygen fugacity: Ni/NiO (NNO) buffer



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

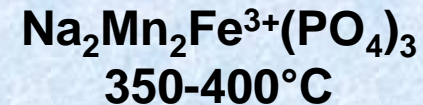


- Low T  $\Rightarrow$  alluaudite
- High T  $\Rightarrow$  "X-phase"
- Mn  $\Rightarrow$  fillowite [ $\text{NaMn}_4(\text{PO}_4)_3$ ]

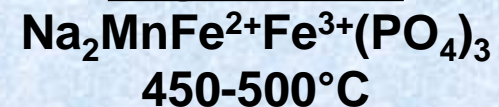
No maricite [ $\text{NaFePO}_4$ ] in  
pegmatites



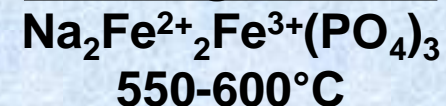
Varulite



Hagendorfite



Ferrohagendorfite



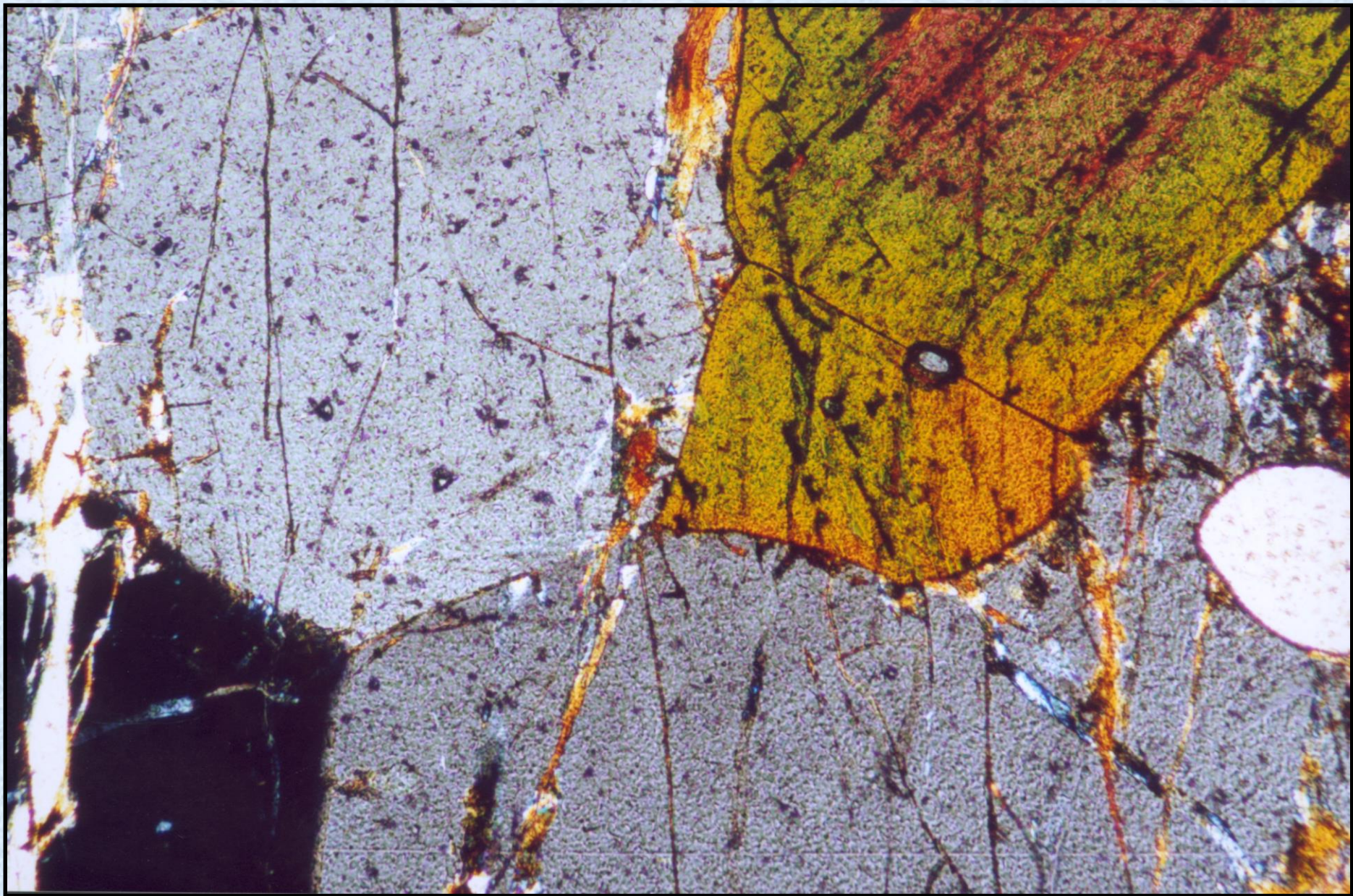


Intro.

**Stability**

Applicat.

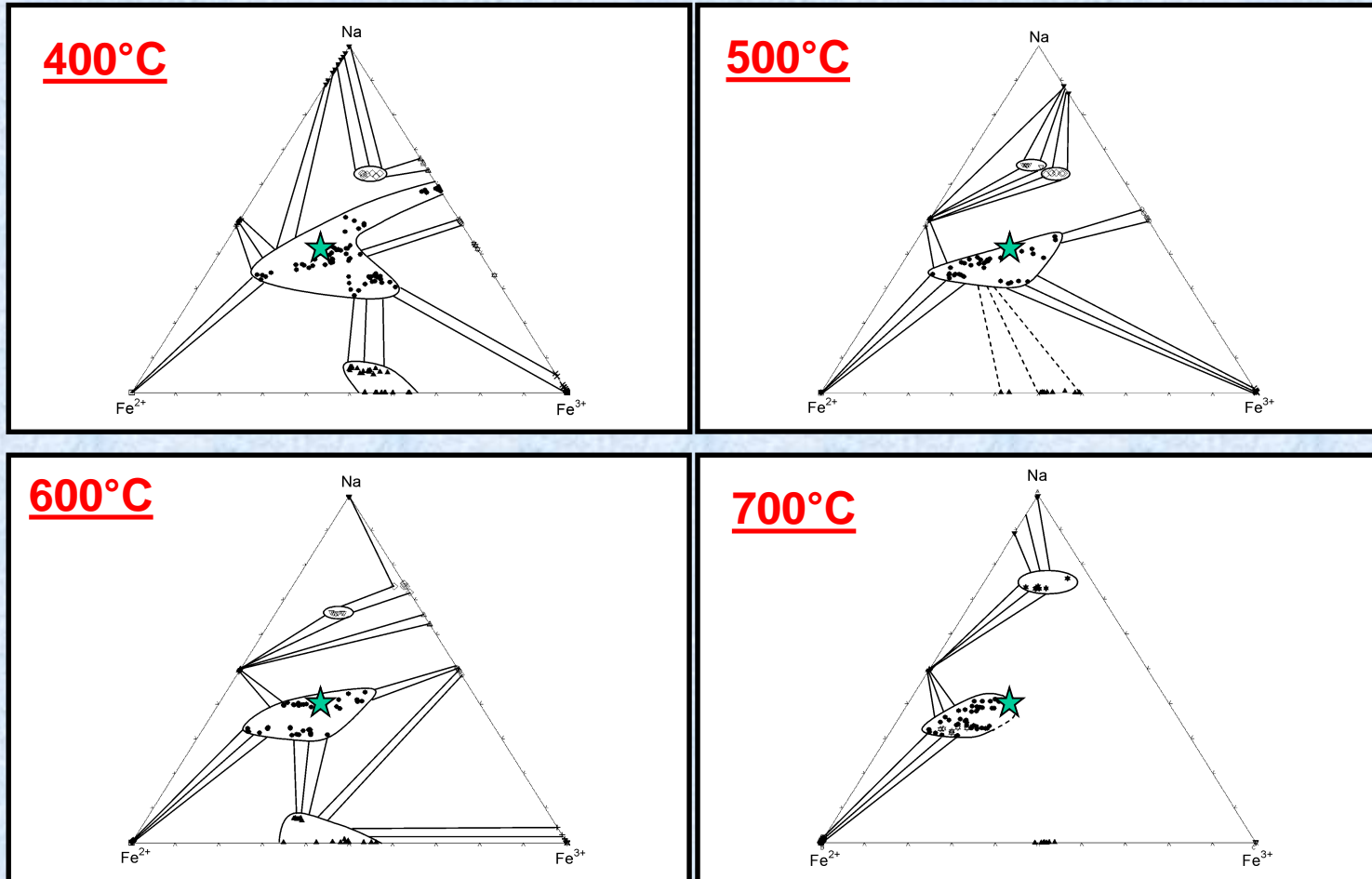
Conclus.



**Alluaudite + fillowite, Kabira, Uganda**

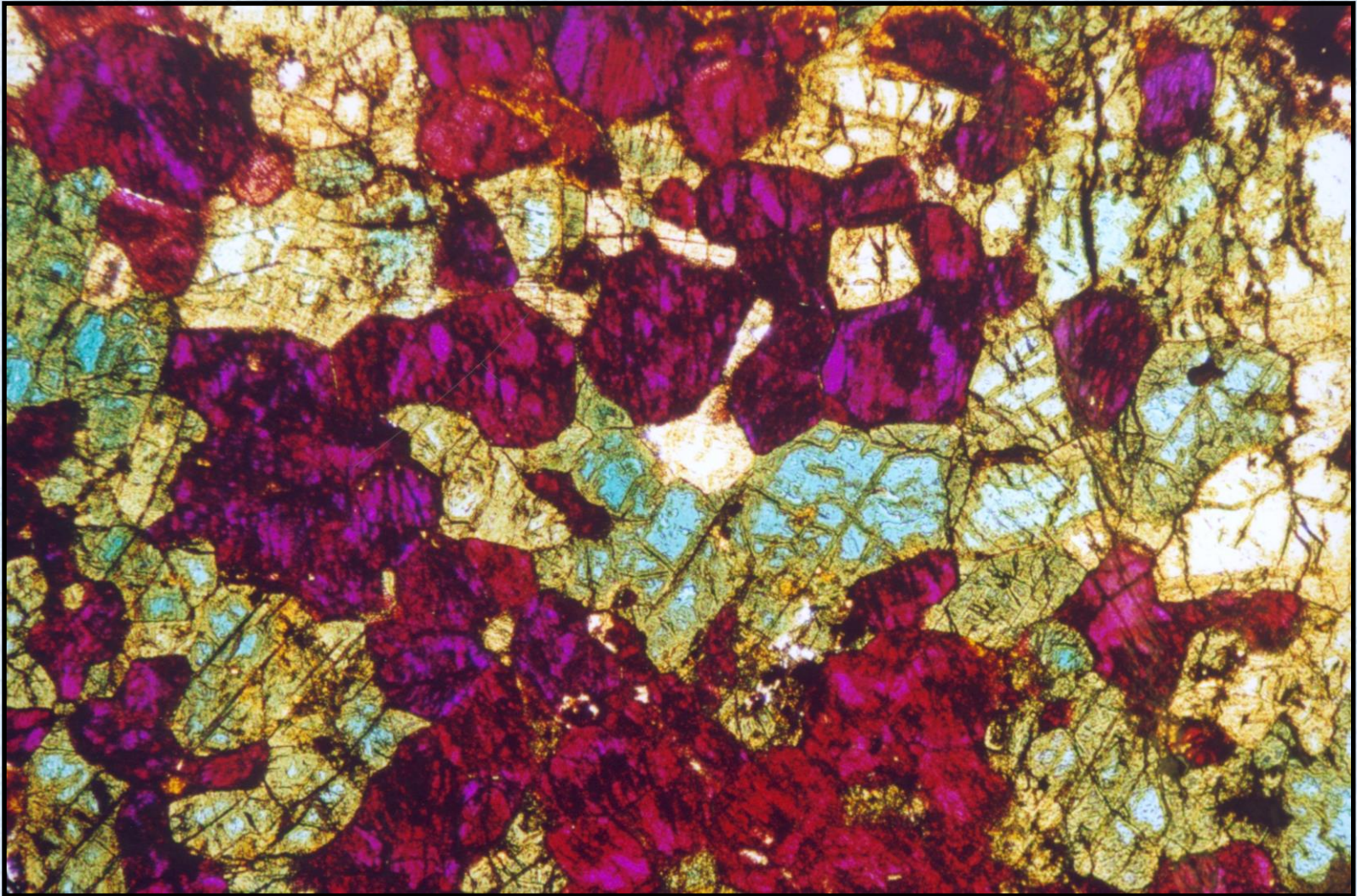
# B. The Na-Fe<sup>2+</sup>-Fe<sup>3+</sup> (+ PO<sub>4</sub>) system

★ = Ferroalluaudite from Angarf-sud, Morocco



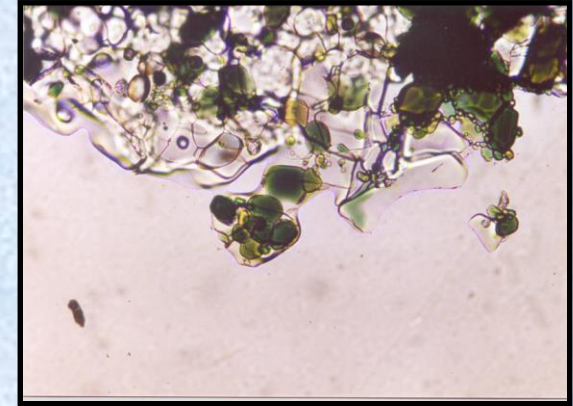
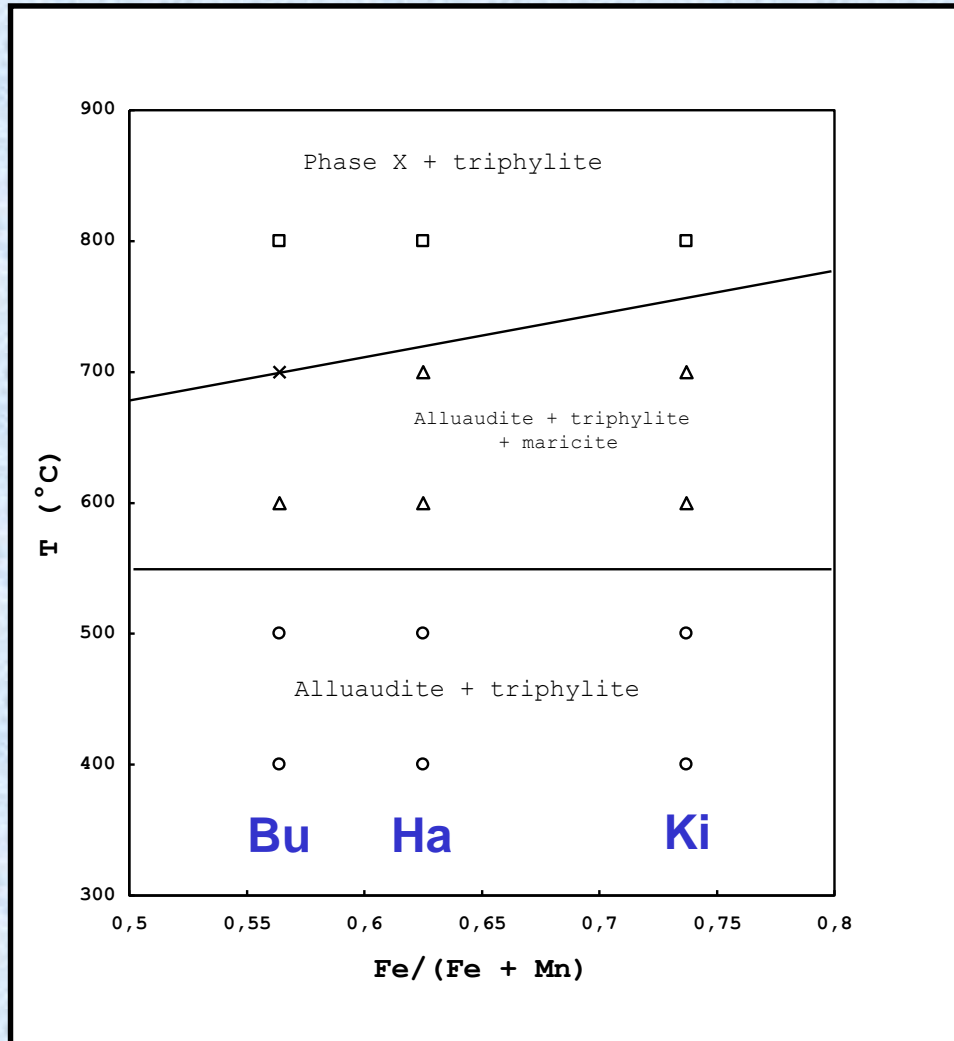
**Cristallisation between 400 and 600°C → primary origin**

## C. The triphylite + alluaudite assemblage



Hagendorfite, alluaudite, and heterosite, Kibingo pegmatite, Rwanda

# Stability of the triphylite + alluaudite assemblage



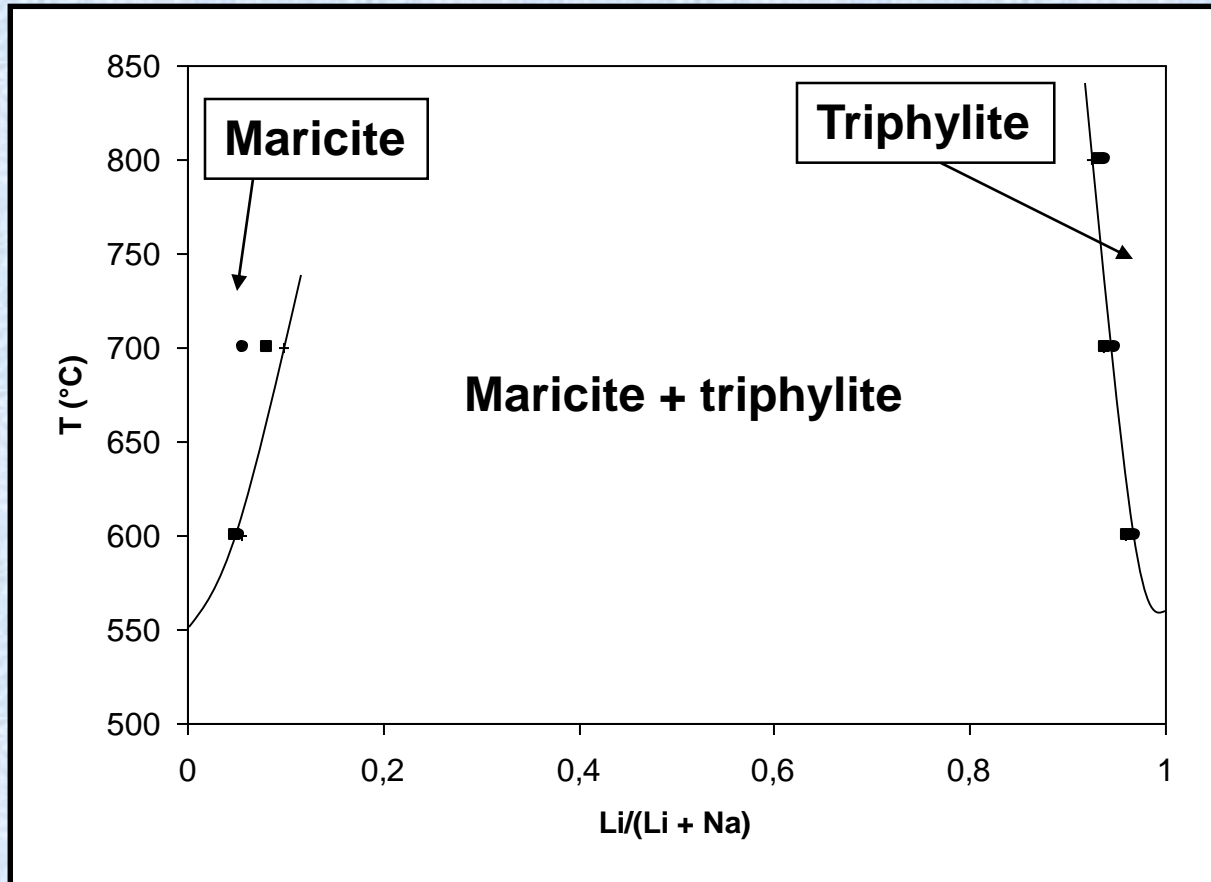
**No maricite in pegmatites**



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

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

# The Na-in-triphyllite geothermometer



**Geothermometer!**

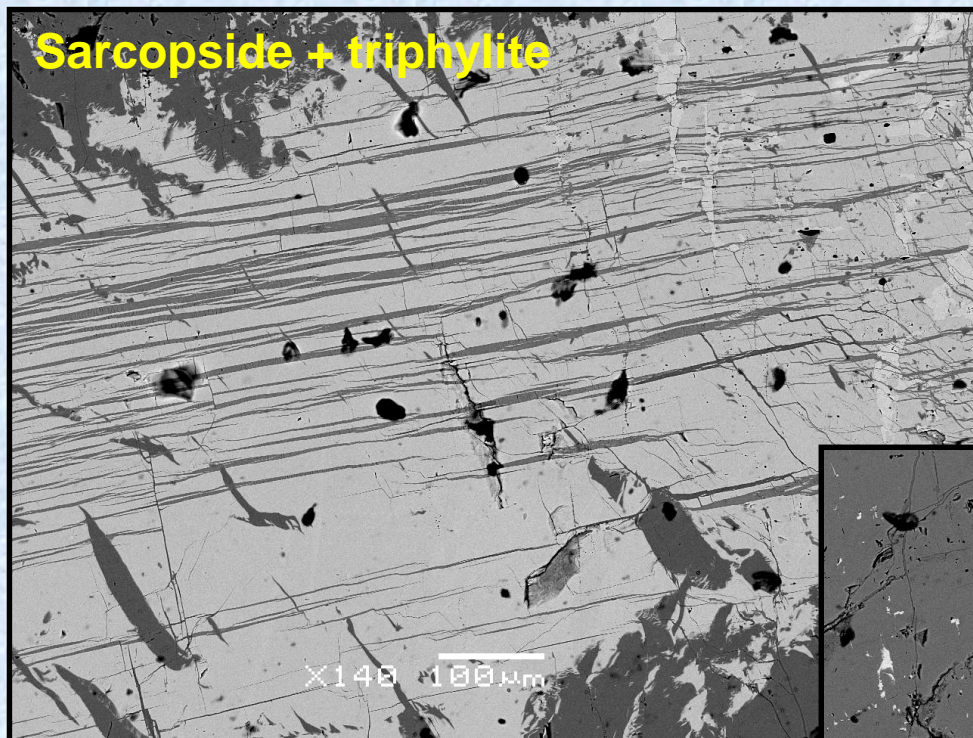


• In triphyllite, Na can reach 0.08 *a.p.u.f.* at 800°C

• In maricite, Li can reach 0.10 *a.p.u.f.* at 700°C

• No partitioning below ca. 550°C

## D. The triphylite + sarcopside assemblage

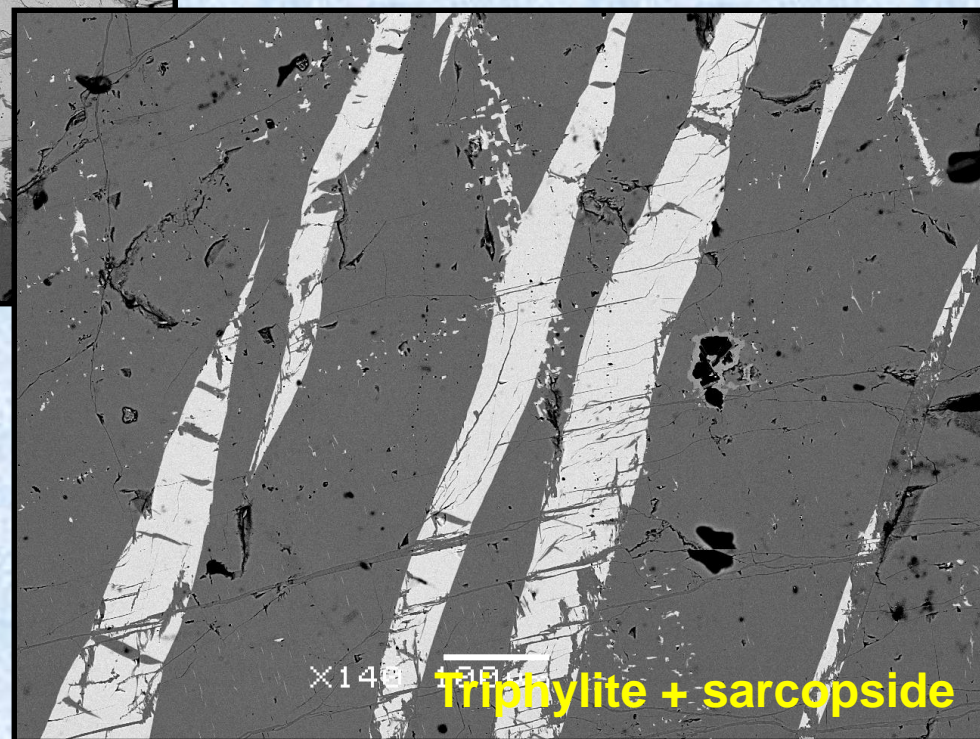


**Cañada pegmatite,  
Spain**

**Lamellar textures**



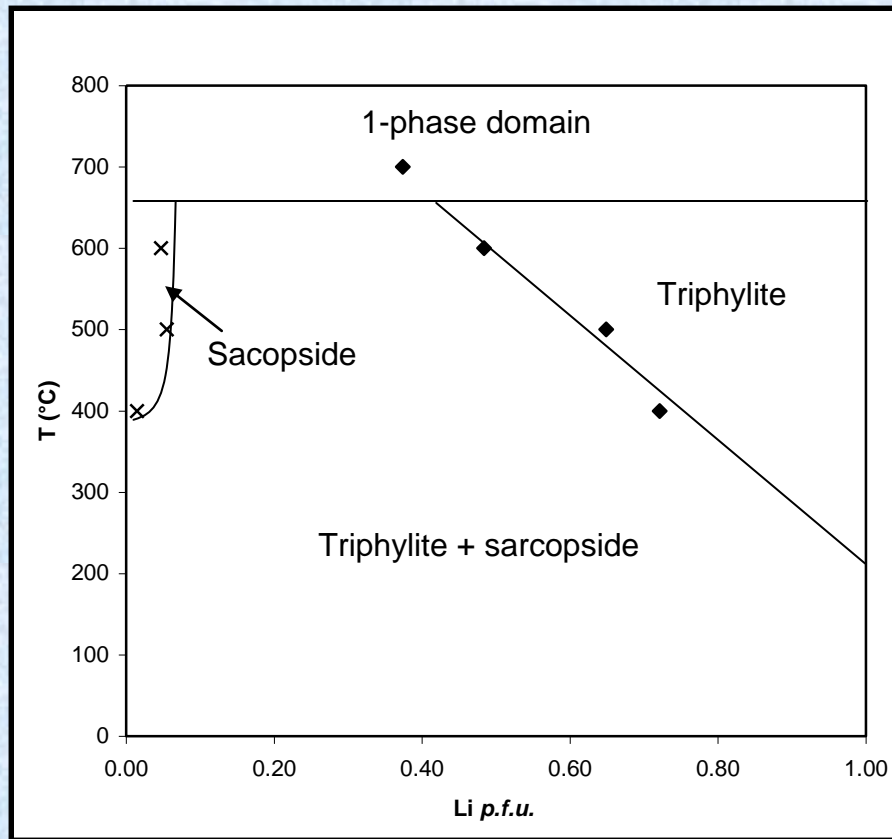
**EXSOLUTIONS!!**



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

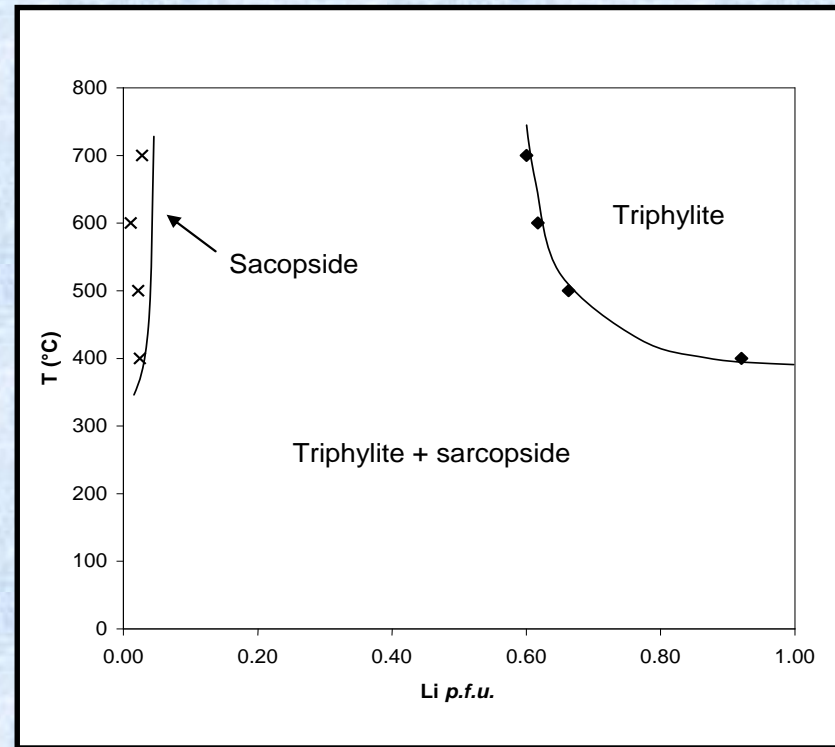
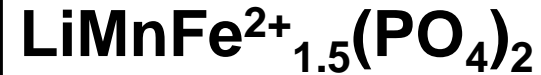
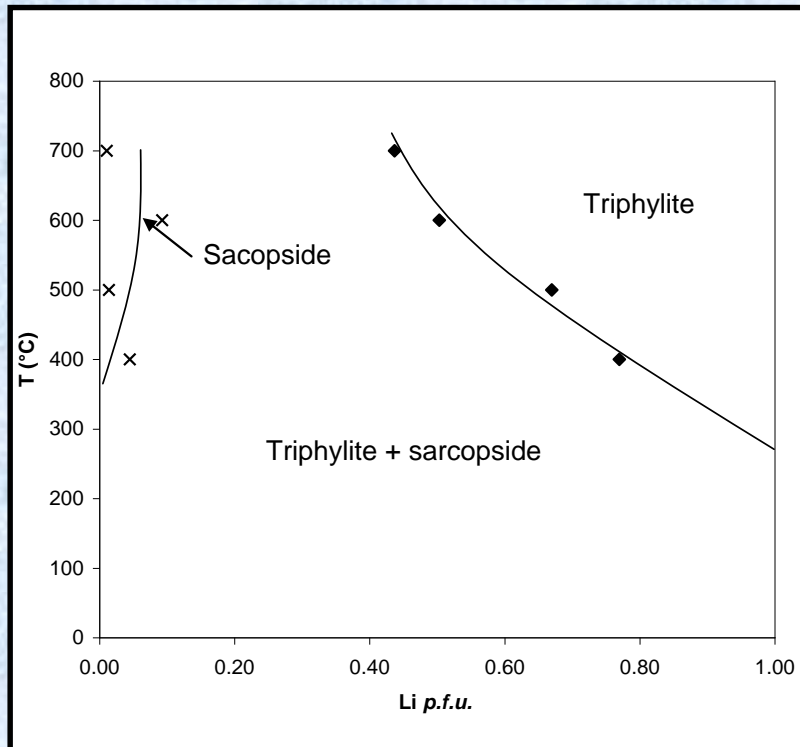
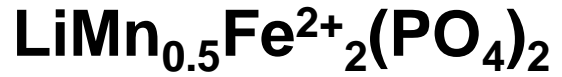
**Pictures: E. Roda Robles**

# Stability of the triphylite + sarcopside assemblage

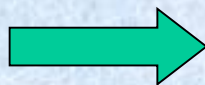


- **Decrease of the Li-content of triphylite, from 0.72 *a.p.f.u.* at 400°C, to 0.48 *a.p.f.u.* at 600°C**
- **Increase of the Li-content of sarcopside, from 0.01 *a.p.f.u.* at 400°C, to 0.05 *a.p.f.u.* at 600°C**
- **1-phase domain above 650°C**

# Triphylite-sarcopside phase diagrams



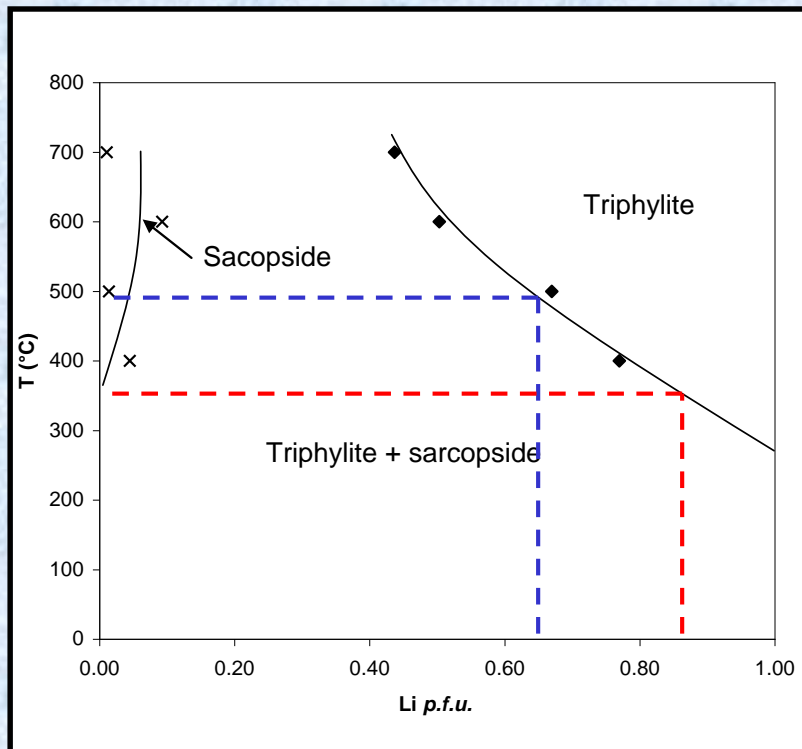
The Li-content of triphylite decreases with temperature



**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

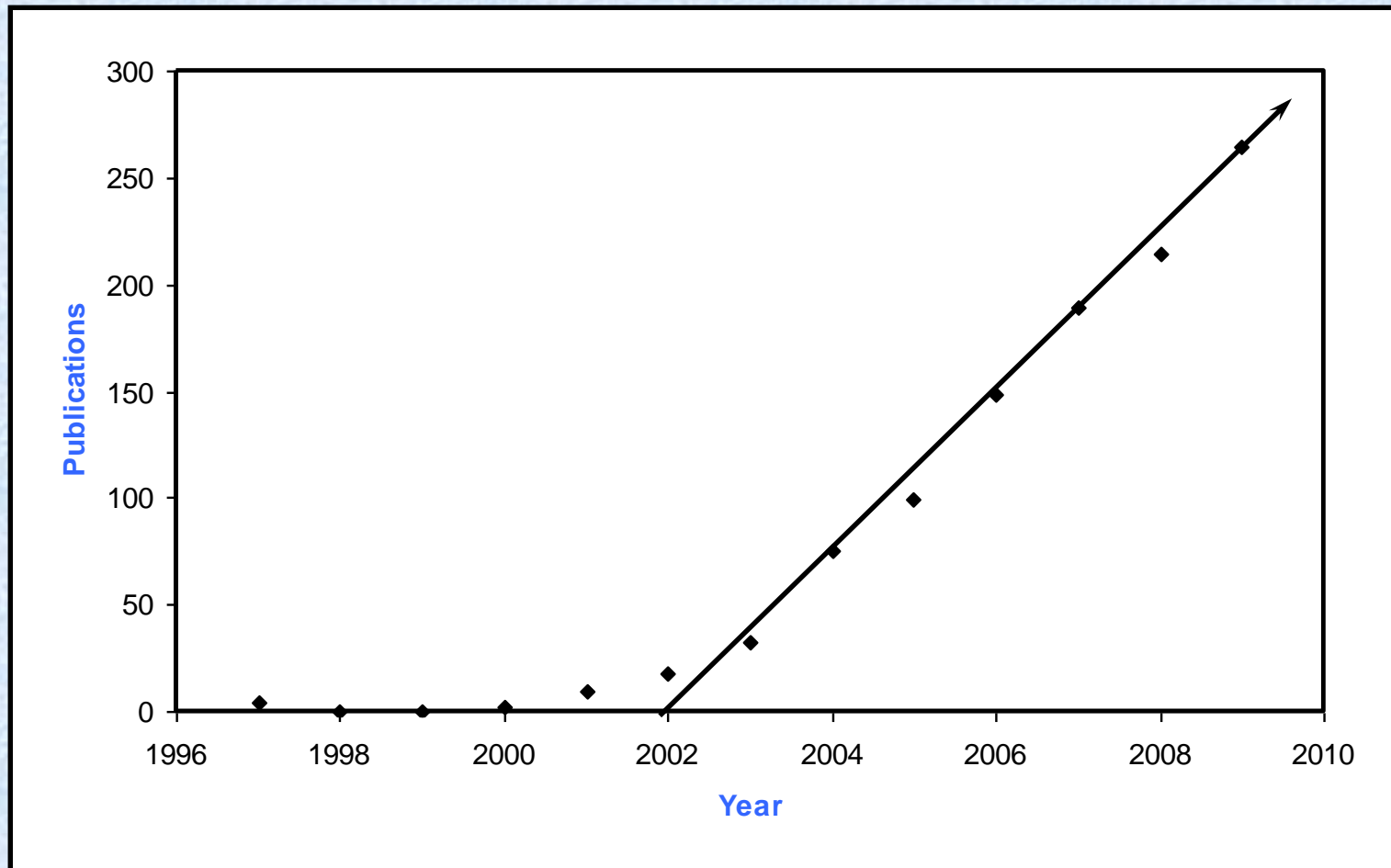
T ~ 350°C

# Li-ion batteries

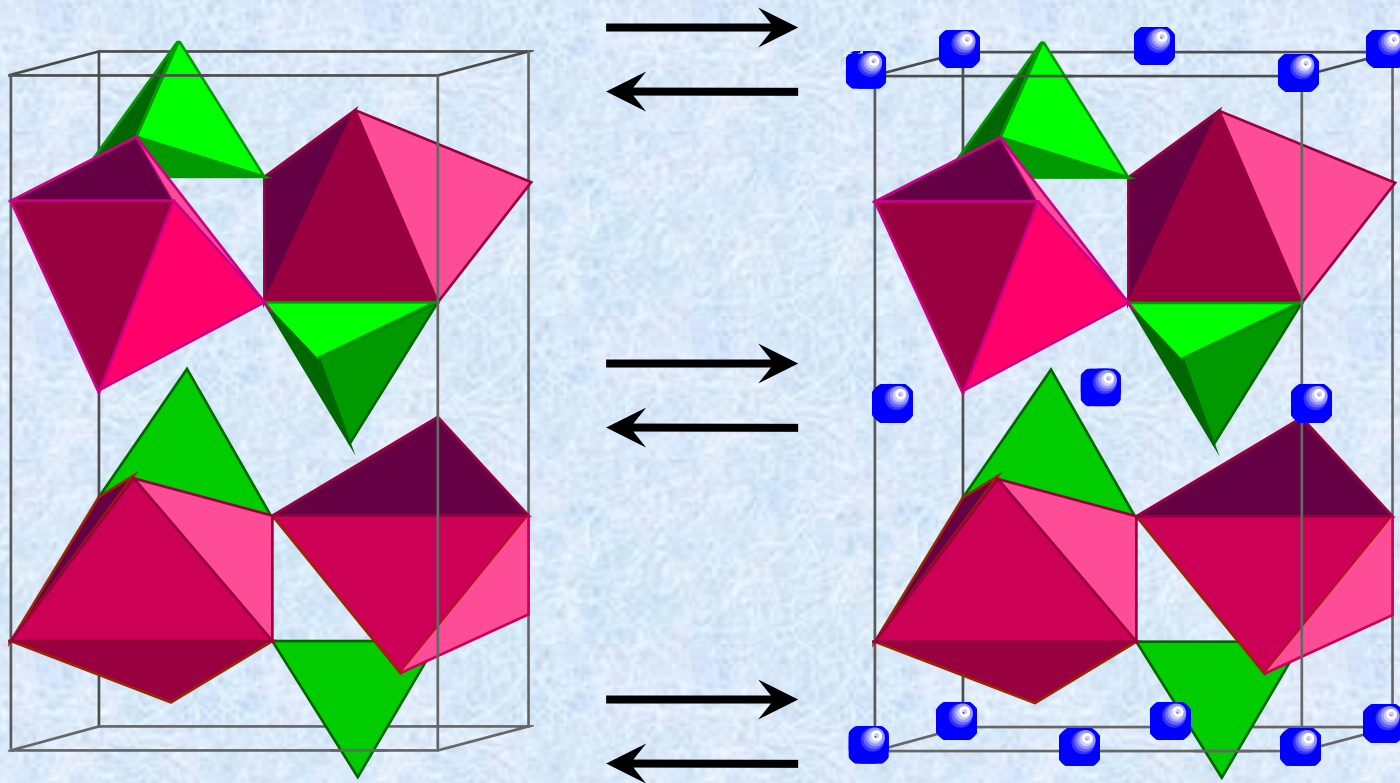
	Layered struct.		Spinel	Triphylite
	LiCoO <sub>2</sub>	LiNiCoO <sub>2</sub>	LiMn <sub>2</sub> O <sub>4</sub>	LiFePO <sub>4</sub>
Capacity (mAh/g)	140-150	170-180	110-120	160-170
Potential (V)	3,9	3,8	4,0	3,4
Resistance to cycling	Poor	Poor	+/-	Good
Exchange speed	Good	Good	Good	Good
Electrode density	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

# $\text{LiFe}^{2+}(\text{PO}_4)$ as cathode material ?

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



# Intercalation – extraction of Li

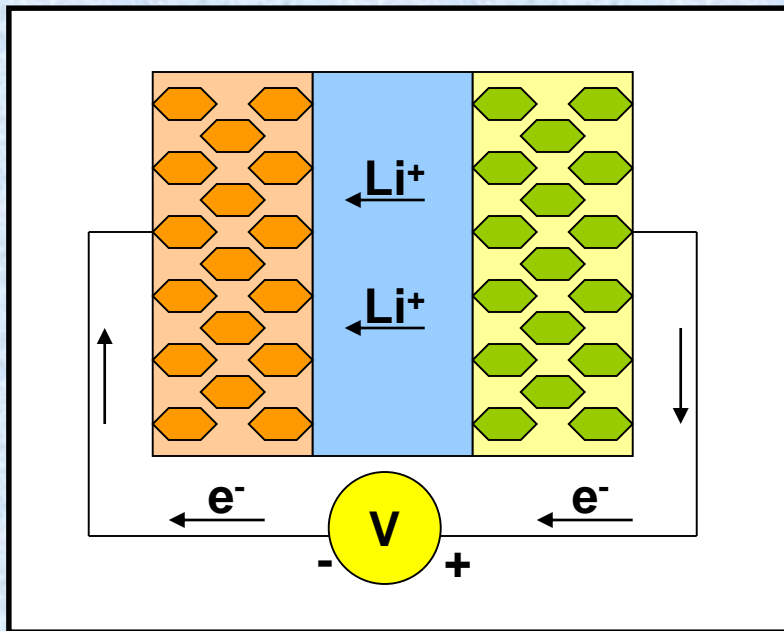


Heterosite,  $\text{Fe}^{3+}(\text{PO}_4)$

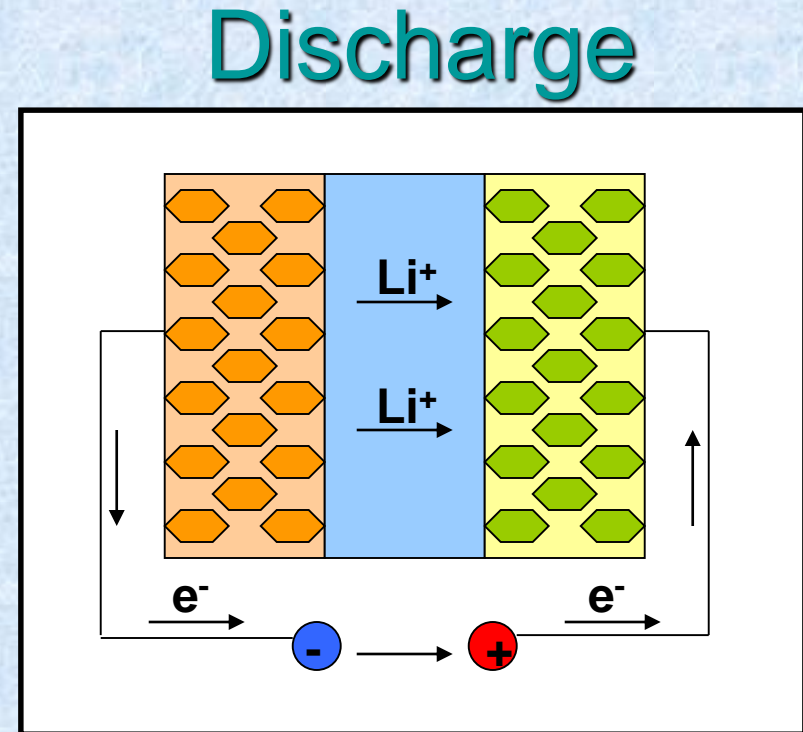
Triphylite,  $\text{LiFe}^{2+}(\text{PO}_4)$

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

# Principle of Li-ion batteries



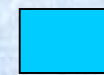
Charge



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



Metallic Li



Electrolyte

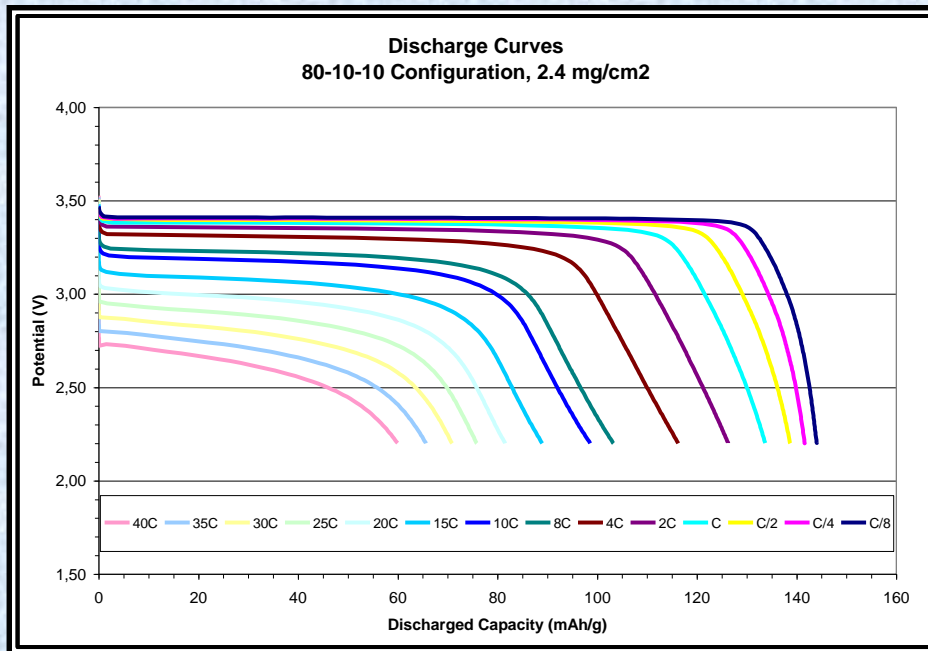
# Performance

nature

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

LETTERS

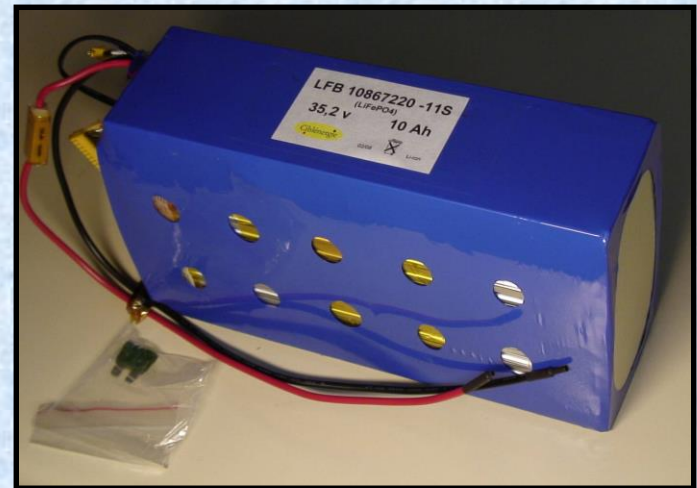
## Battery materials for ultrafast charging and discharging

Byoungwoo Kang<sup>1</sup> & Gerbrand Ceder<sup>1</sup>

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 material<sup>1-3</sup>. Here we show that batteries<sup>4,5</sup> 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 LiFePO<sub>4</sub> (ref. 6), a material with high lithium bulk mobility<sup>7,8</sup>, 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.

# LiFePO<sub>4</sub>-based batteries production

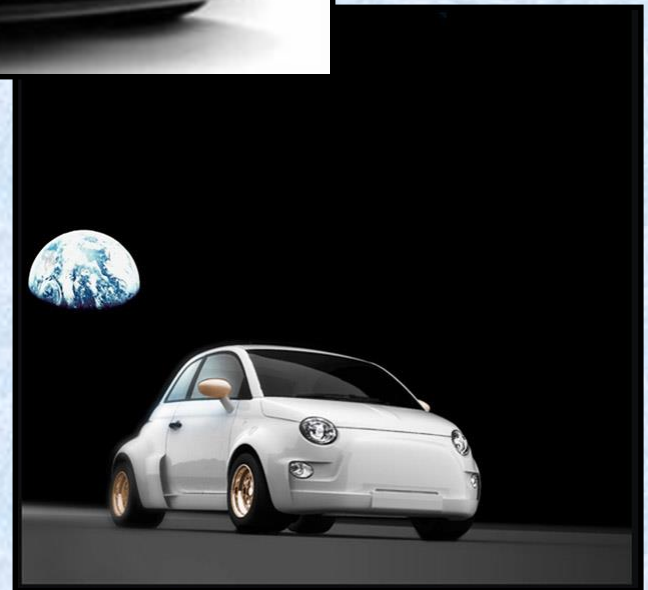
- Phostech Lithium was founded in 2001
- Based on the commercial potential of C-LiFePO<sub>4</sub> and other Phosphate-based cathode materials
- Obtained exclusive rights for the manufacture and sales of LiFePO<sub>4</sub> for Lithium-Ion battery applications with University of Texas and Hydro-Quebec
- Obtained through UDM the access to four improvement patents resulting from UDM's research for Hydro-Québec, including C additive to LiFePO<sub>4</sub> and a new synthesis way from a Fe<sup>+3</sup> precursor



# LiFePO<sub>4</sub>-based batteries applications



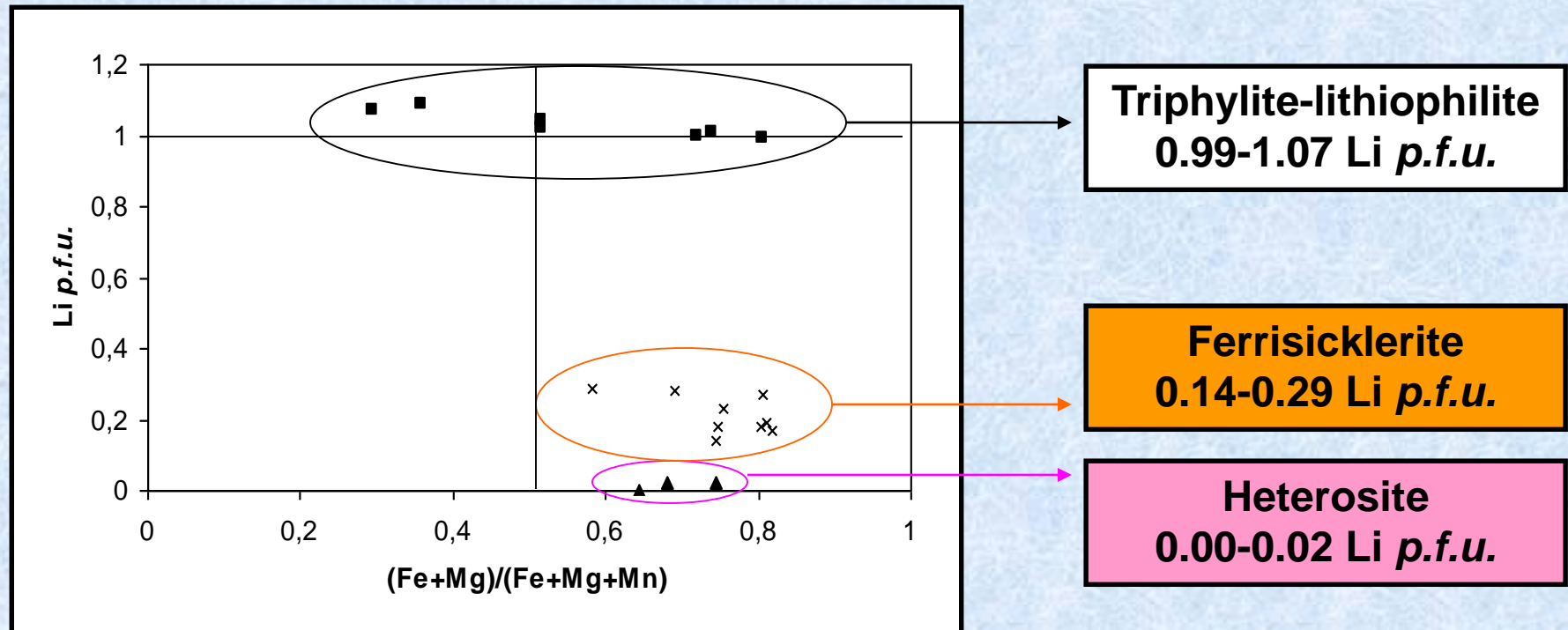
- **Cars**
- **Bicycles**
- **Motorbikes**
- **Mobile phones**
- **Laptops**
- **Storage of green energy**





# Crystal chemistry of natural olivine-type phosphates

## SIMS and crystal-structure analysis of 19 samples



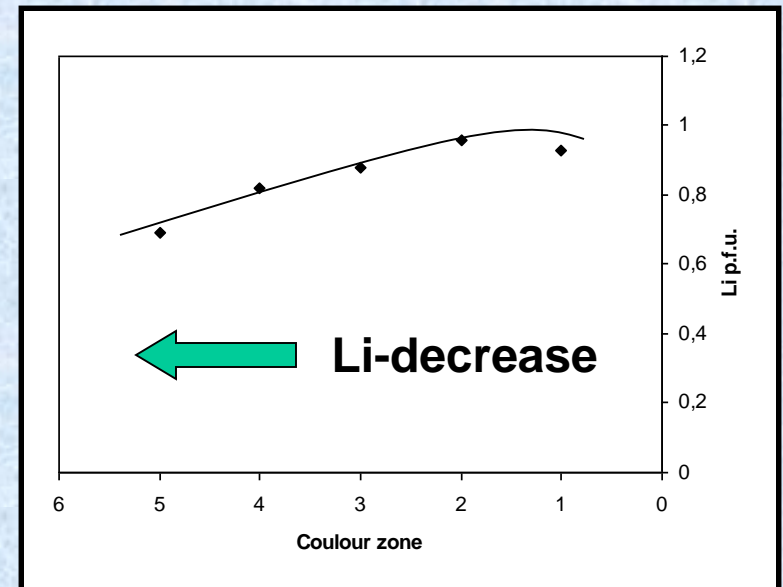
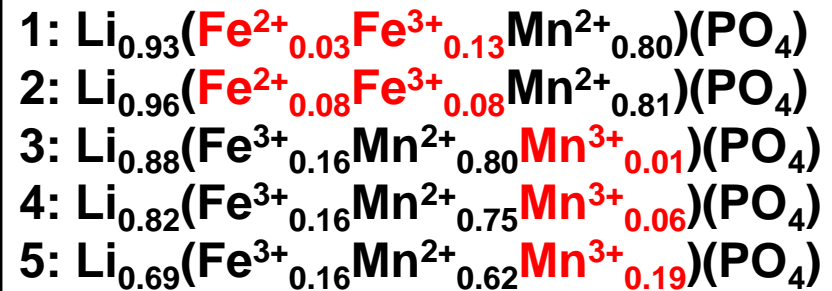
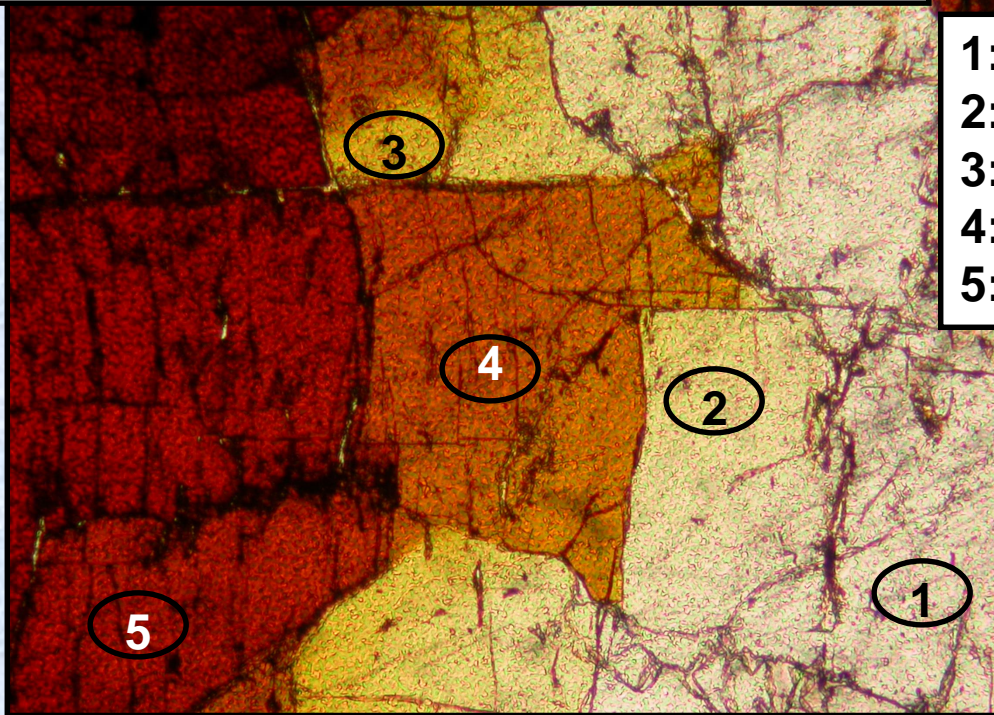
**Heterosite may contain up to 0.21 wt. % Li<sub>2</sub>O, and ferrisicklerite may show a low Li-content of 1.31 wt. % Li<sub>2</sub>O**



**Close Li-contents!**

# The progressive transition from lithiophilite to sicklerite

Sample from the Altaï Mountains, China



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

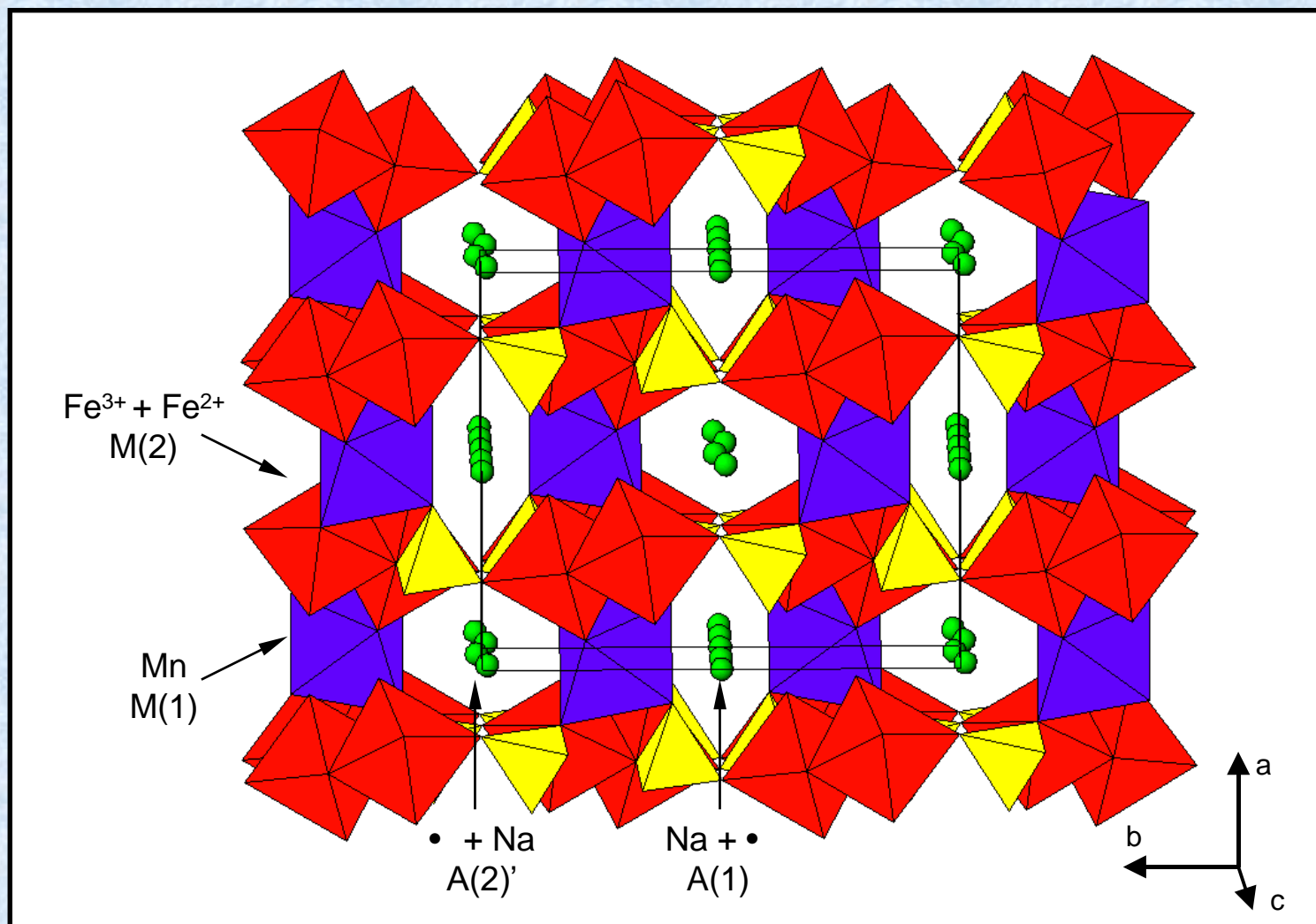
# The alluaudite structure

$A(2)'$ : gabled disphenoid

$A(1)$ : distorted cube

$M(1)$ : very distorted octahedron

$M(2)$ : distorted octahedron



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

X : Complete occupancy of the site

p : Partial occupancy of the site

Solid-state synthesis  
and hydrothermal  
experiments



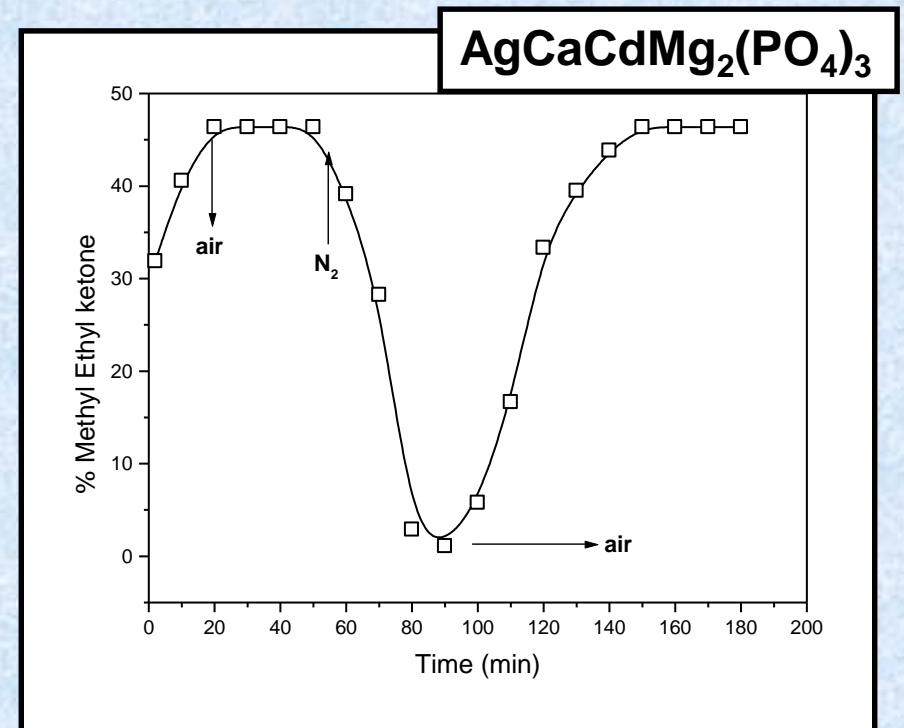
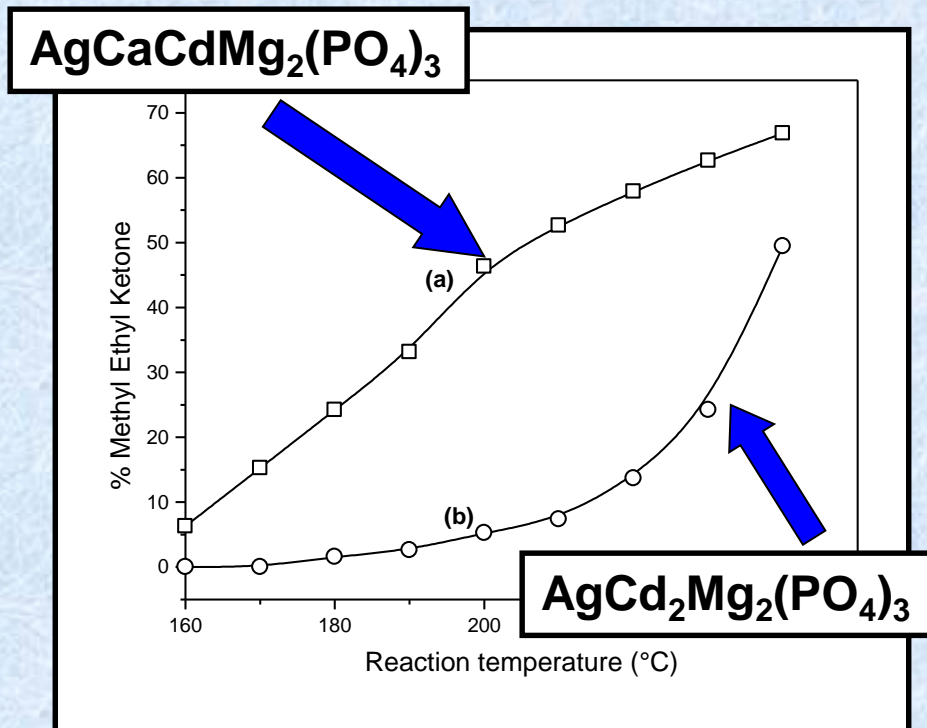
X-ray structure  
refinements



Cationic  
distribution

# Applications: catalytic properties

**Probe reaction:** Butan-2-ol  $\Rightarrow$  Methyl ethyl ketone + butenes + CO<sub>2</sub>



**$\Rightarrow$  Catalytic activity comparable to that of nasicon-type phosphates**

# The role of lithium in alluaudites



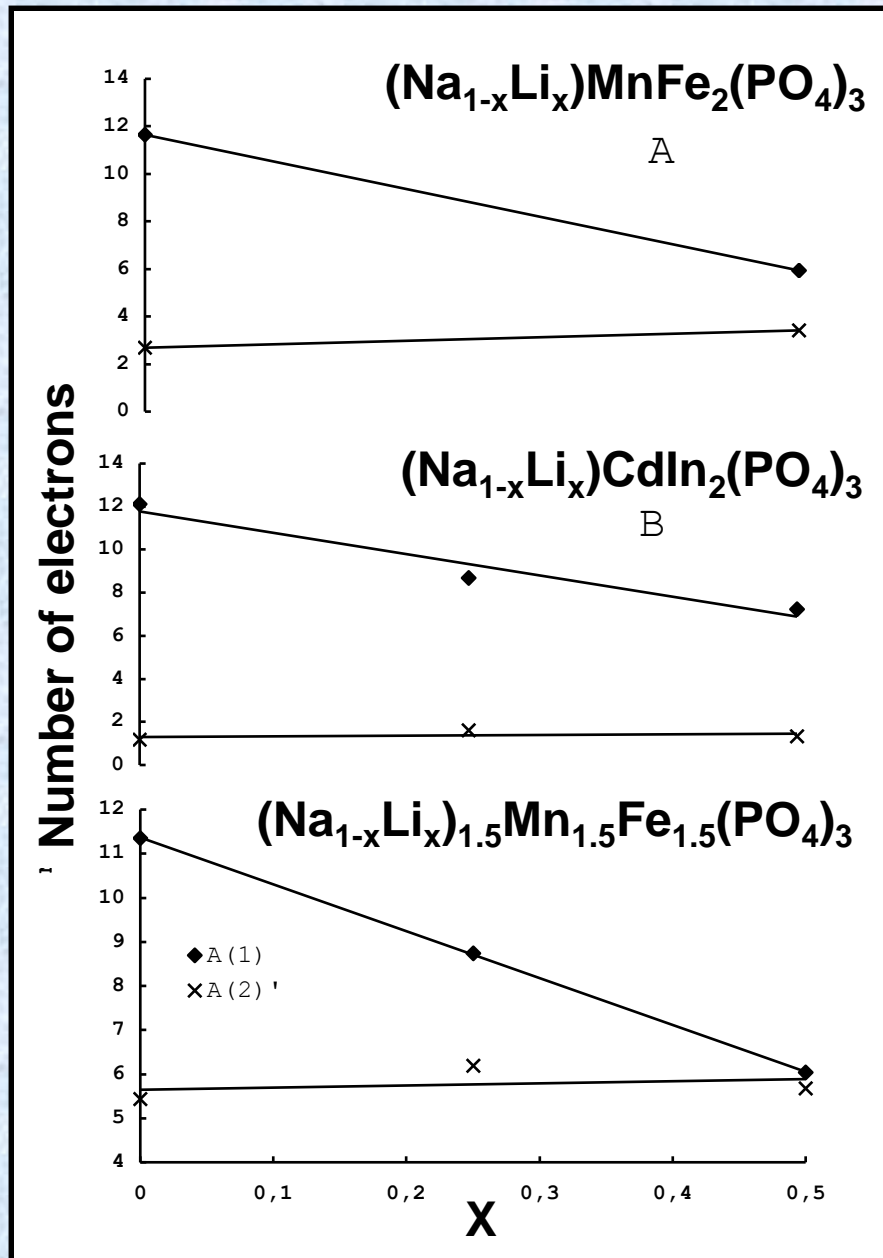
Single-crystal structure refinements  
Variations of the unit-cell parameters  
Mössbauer spectroscopy



X-ray Rietveld refinements



X-ray Rietveld refinements

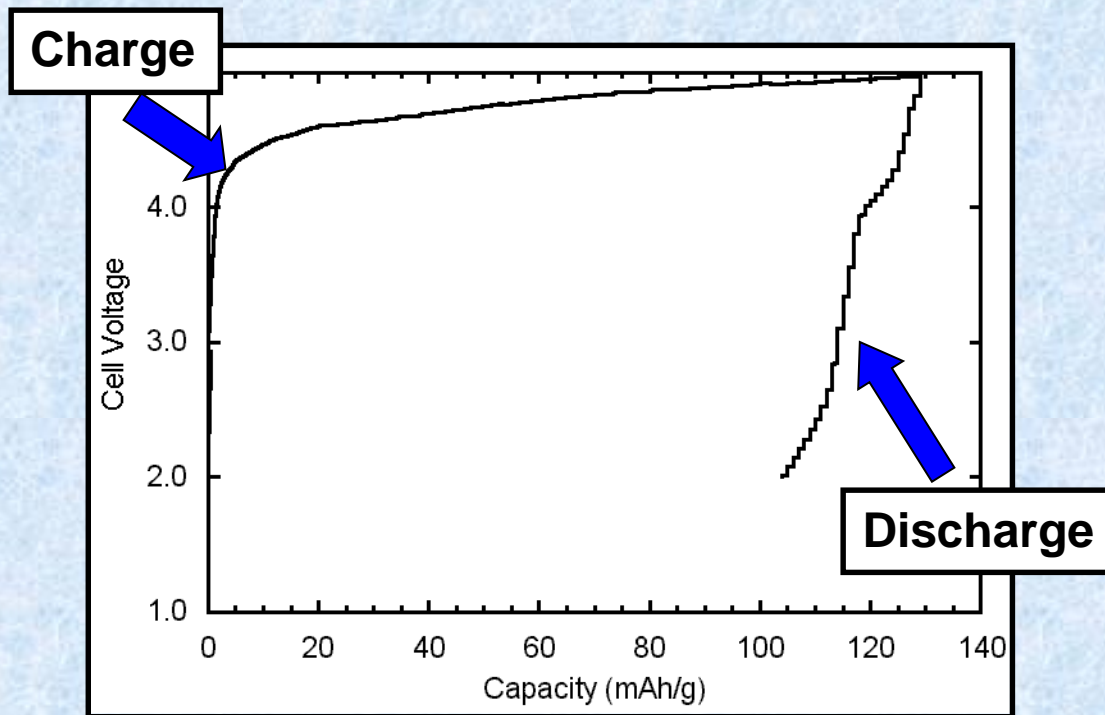
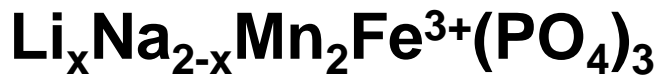


Number of electrons on A(1) and A(2)'



**Li localized on the large A(1) site**

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



**Low performance**

Investigation of other  
alluaudite-type  
phosphates necessary



# 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  $\text{LiFePO}_4$  as electrode material in Li-ion batteries.