

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



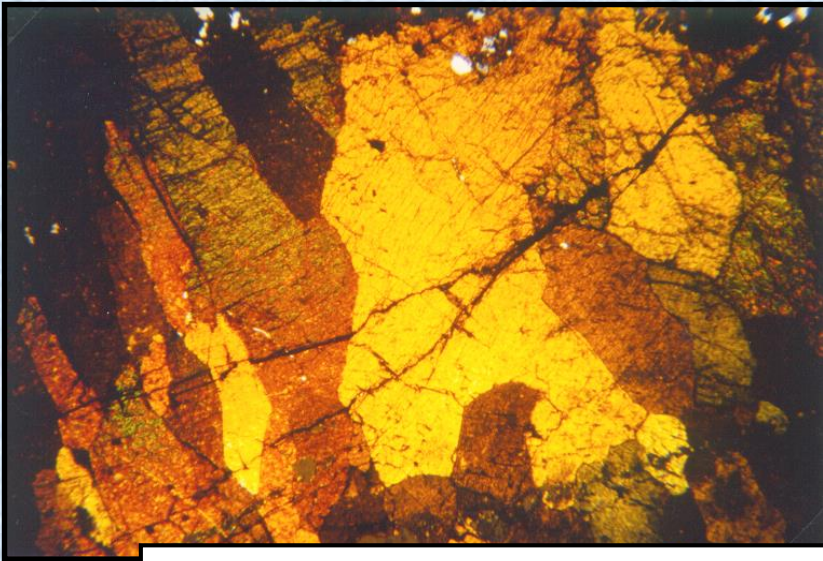
Iron-manganese phosphates with the olivine- and alluaudite-type structures: Crystal chemistry and applications

Frédéric Hatert

MAAMII, Kirovsk, July 21st, 2010

Occurrence

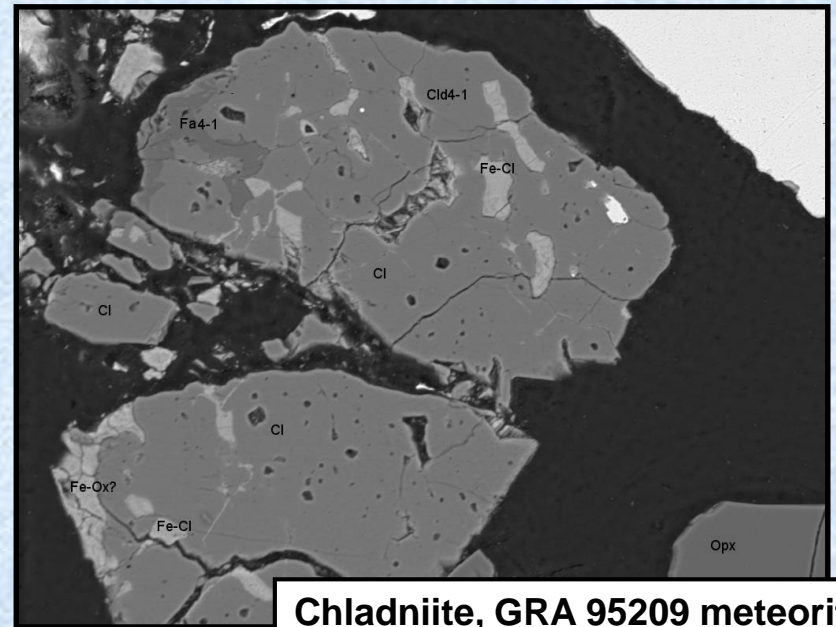
- Granitic pegmatites
- Metamorphic rocks
- Meteorites



Alluaudite, Buranga pegmatite, Rwanda



Johnsomervilleite, Loch Quoich, Scotland



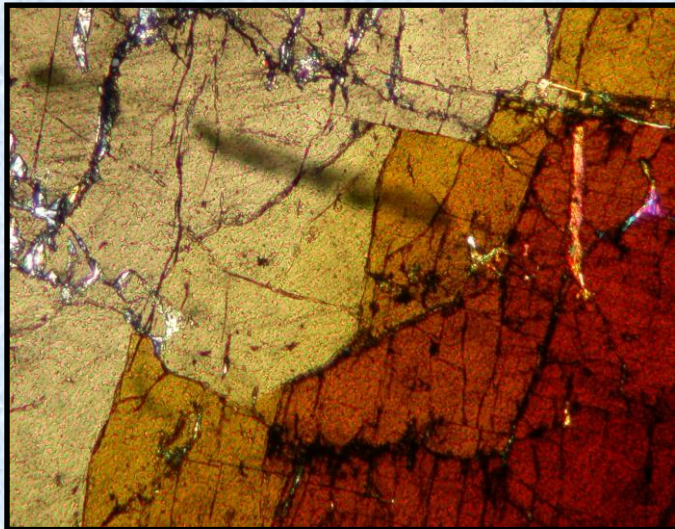
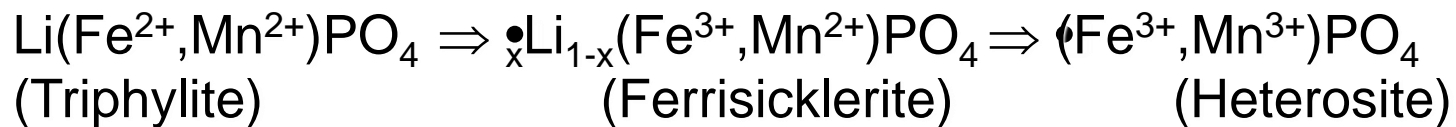
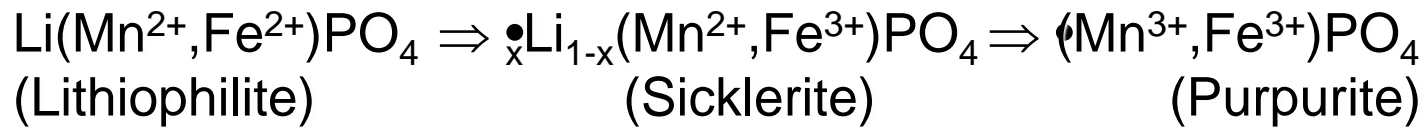
Chladniite, GRA 95209 meteorite

Fe-Mn phosphates in pegmatites

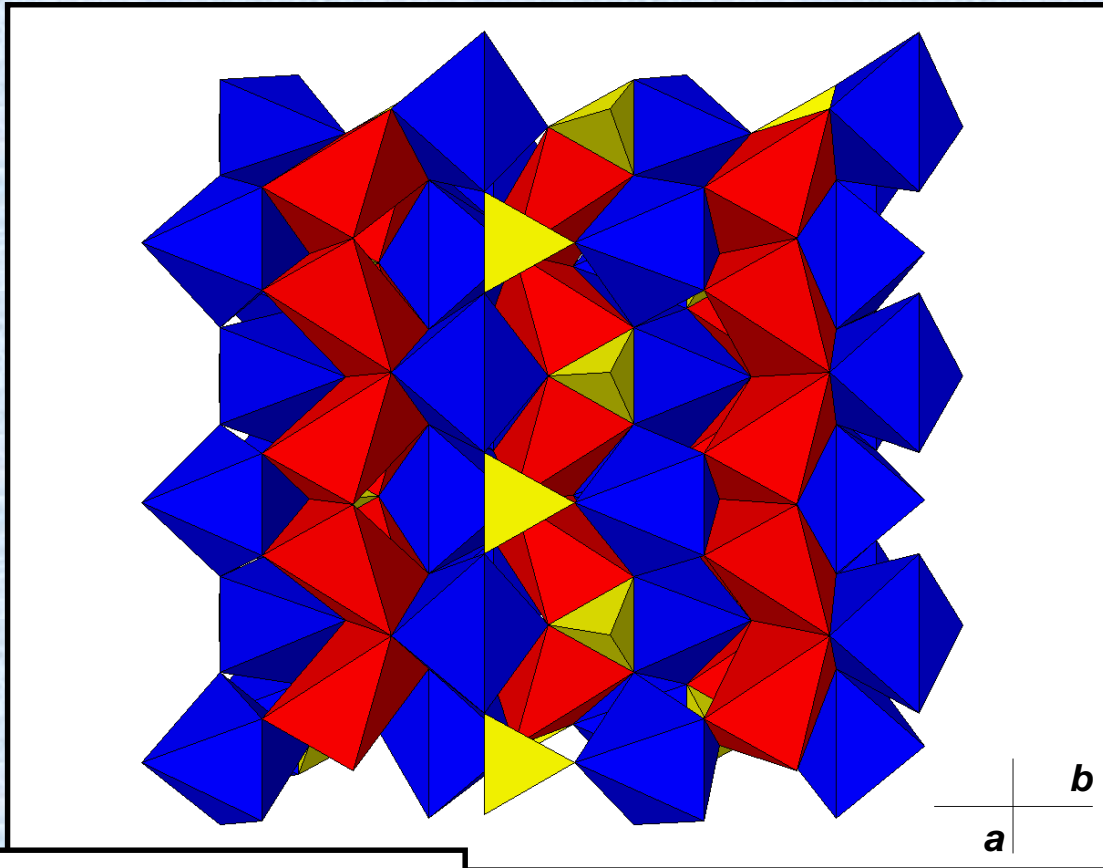


Buranga pegmatite, Rwanda

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



The triphylite structure



Red octahedra: M1
Blue octahedra: M2

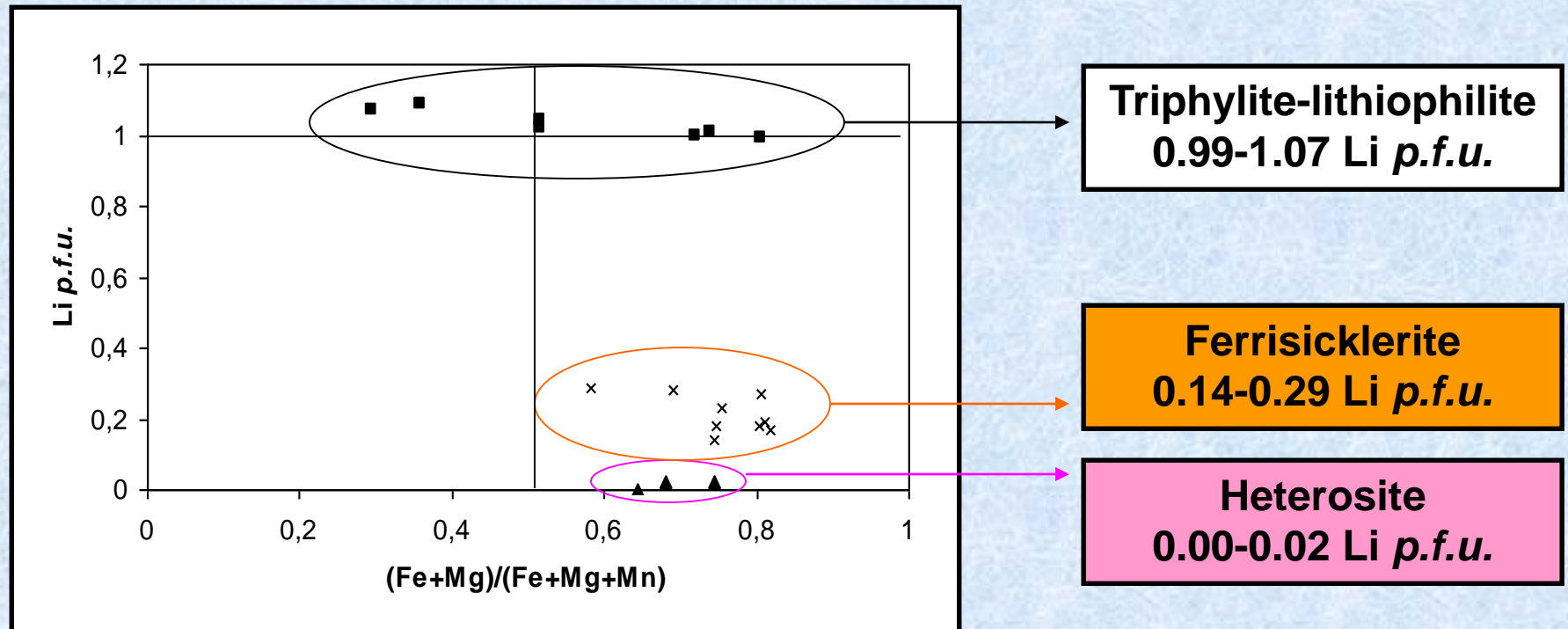
S.G. $Pmnb$

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

- M1: Li, []
- M2: Fe²⁺, Mn, Mg

Crystal chemistry of natural olivine-type phosphates

SIMS and crystal-structure analysis of 19 samples



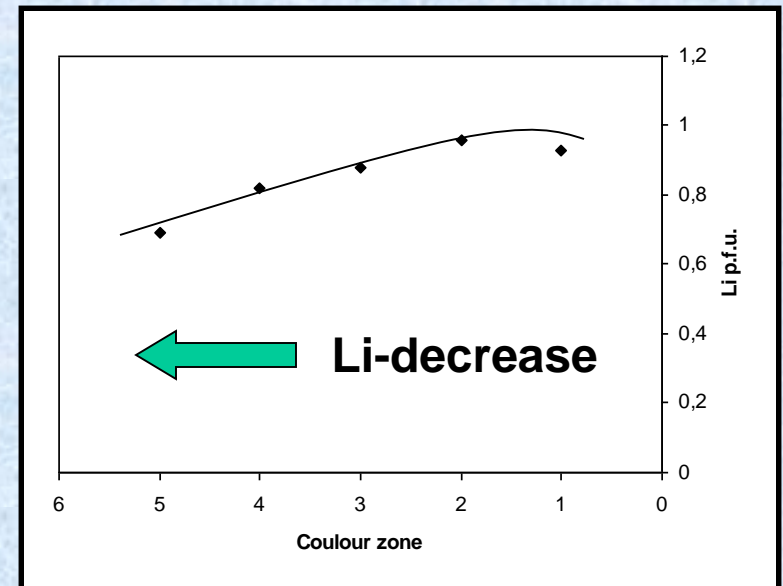
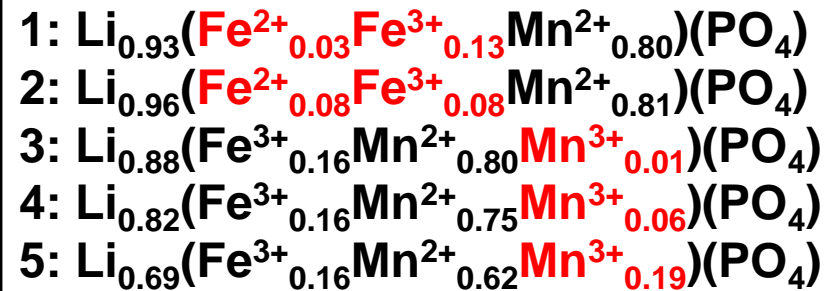
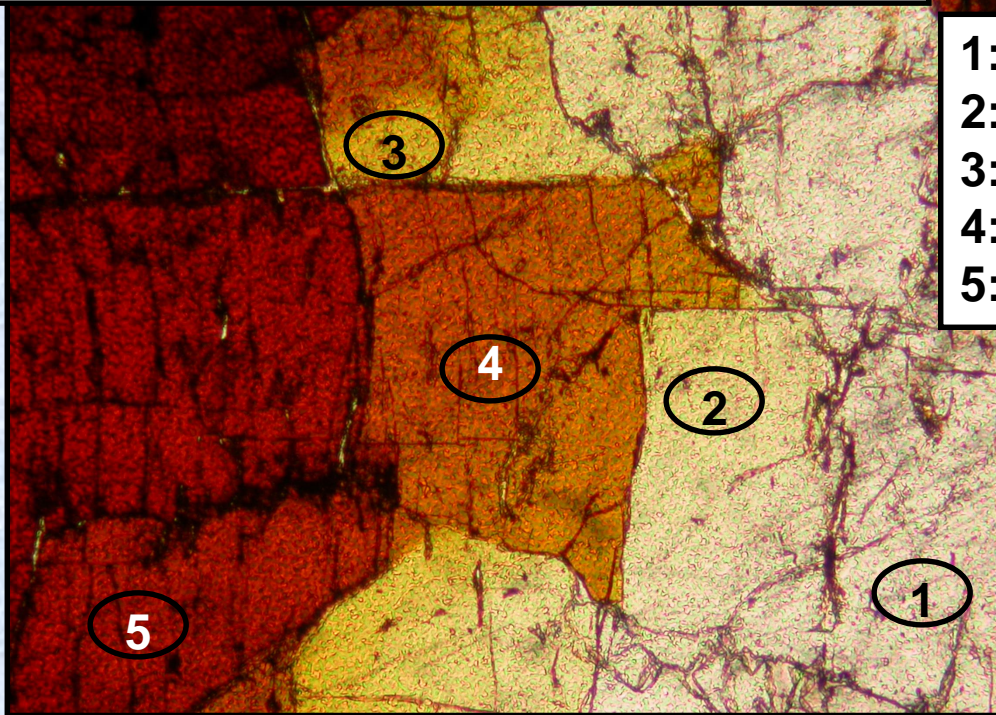
Heterosite may contain up to 0.21 wt. % Li_2O , and ferrisicklerite may show a low Li-content of 1.31 wt. % Li_2O



Close Li-contents!

The progressive transition from lithiophilite to sicklerite

Sample from the Altaï Mountains, China



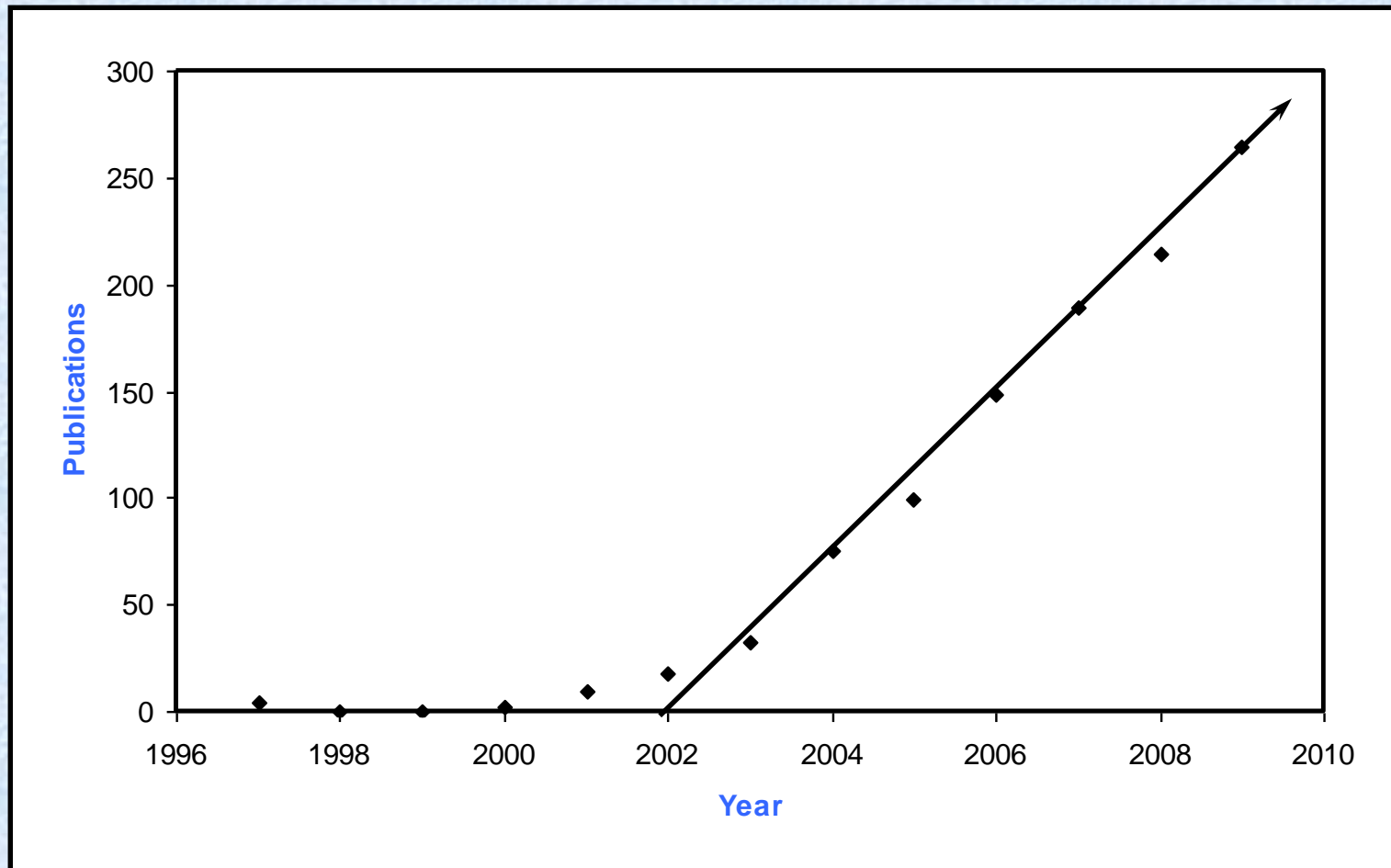
- The transition from lithiophilite to sicklerite is progressive
- The change in colour is due to the presence of Mn^{3+}

Li-ion batteries

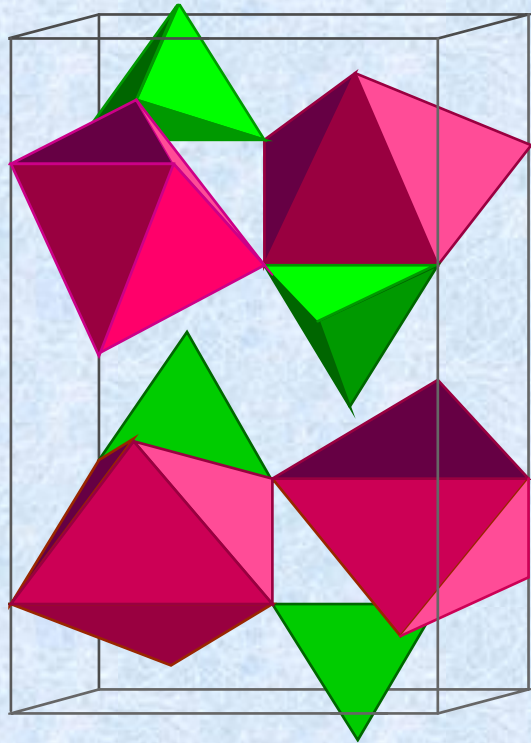
	Layered struct.		Spinel	Triphylite
	LiCoO ₂	LiNiCoO ₂	LiMn ₂ O ₄	LiFePO ₄
Capacity (mAh/g)	140-150	170-180	110-120	160-170
Potential (V)	3,9	3,8	4,0	3,4
Resistance to cycling	Poor	Poor	+/-	Good
Exchange speed	Good	Good	Good	Good
Electrode density	Good	+/-	+/-	Poor
Security	+/-	?	Good	Good
Cost of chemicals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

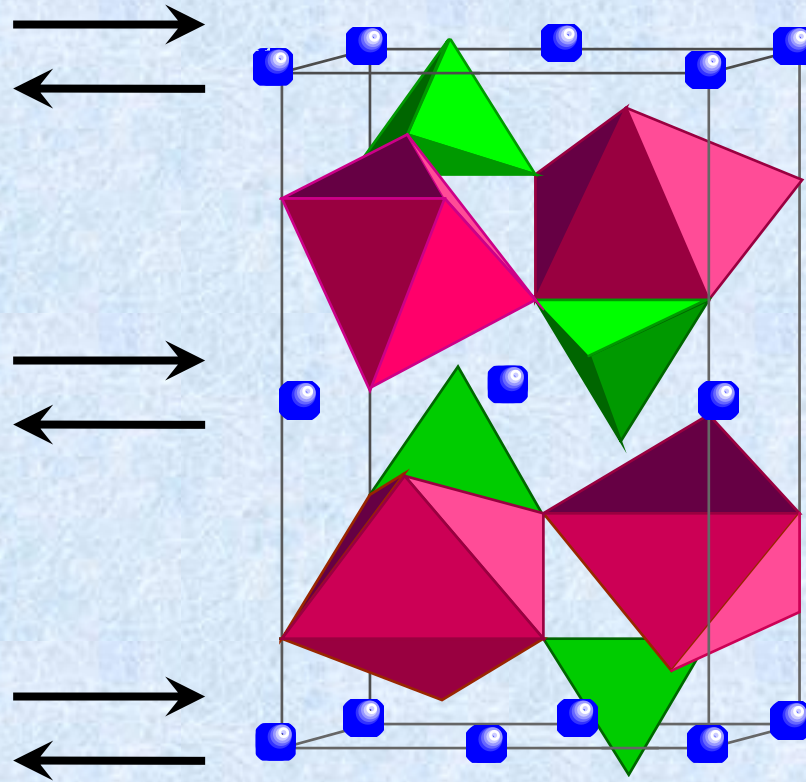
Electrochemical properties demonstrated by Padhi *et al.* (1997)



Intercalation – extraction of Li



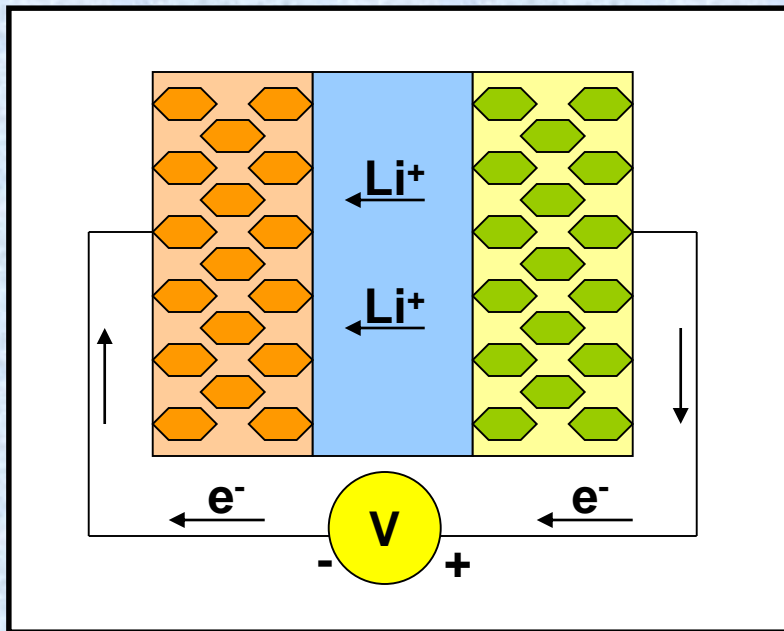
Heterosite, $\text{Fe}^{3+}(\text{PO}_4)$



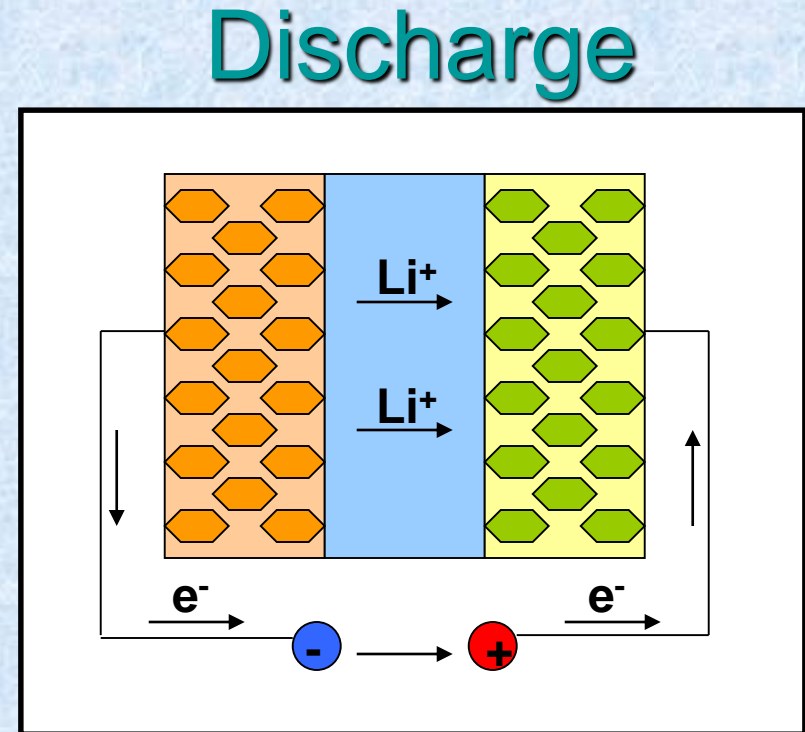
Triphylite, $\text{LiFe}^{2+}(\text{PO}_4)$

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

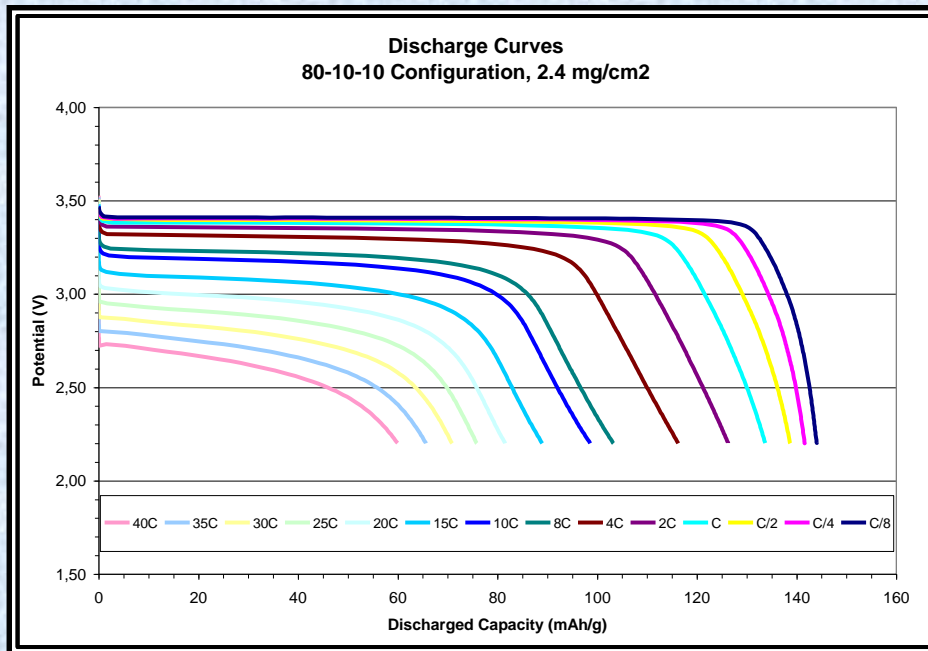
Performance

nature

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

LETTERS

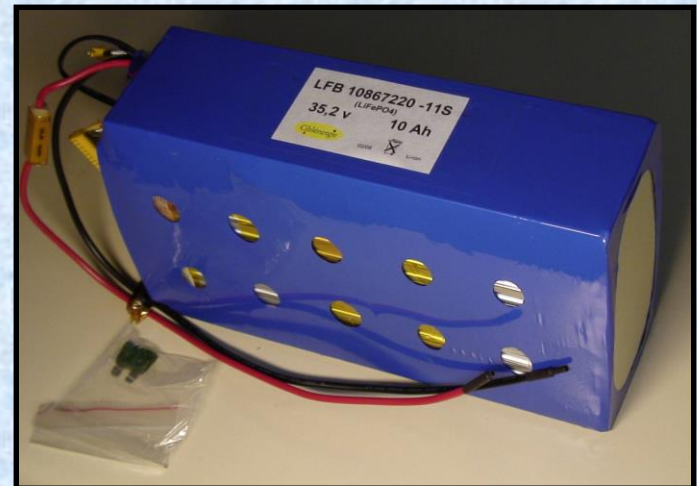
Battery materials for ultrafast charging and discharging

Byoungwoo 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

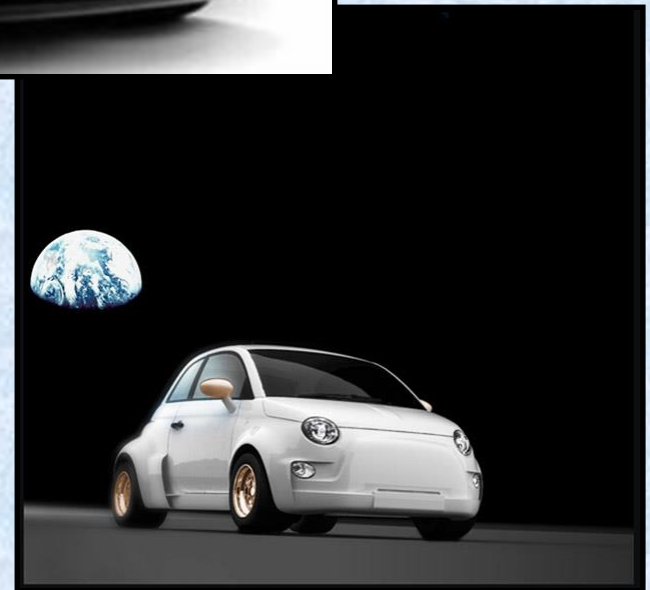
- Phostech Lithium was founded in 2001
- Based on the commercial potential of C-LiFePO₄ and other Phosphate-based cathode materials
- Obtained exclusive rights for the manufacture and sales of LiFePO₄ for Lithium-Ion battery applications with University of Texas and Hydro-Quebec
- Obtained through UDM 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



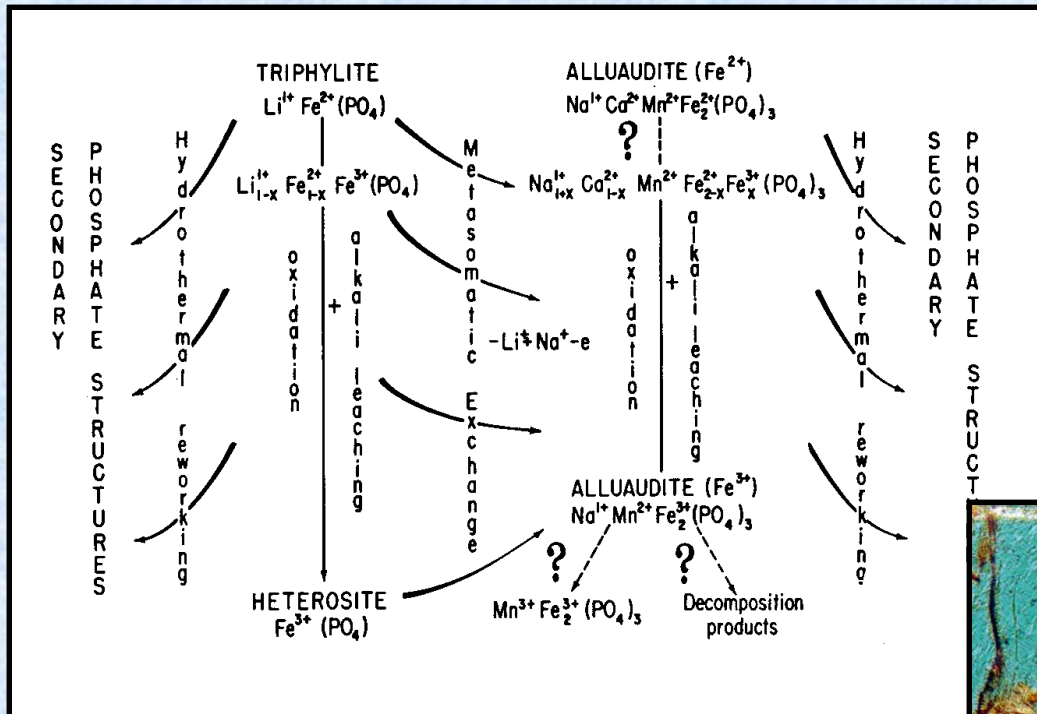
LiFePO₄-based batteries applications



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

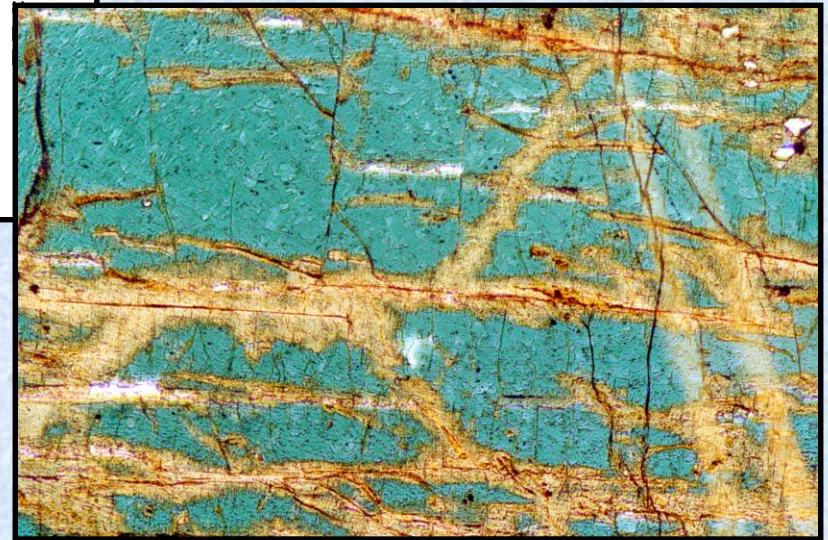
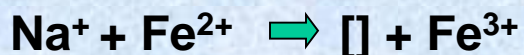
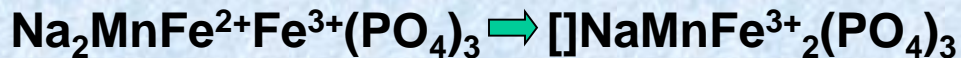


The alluaudite group of minerals



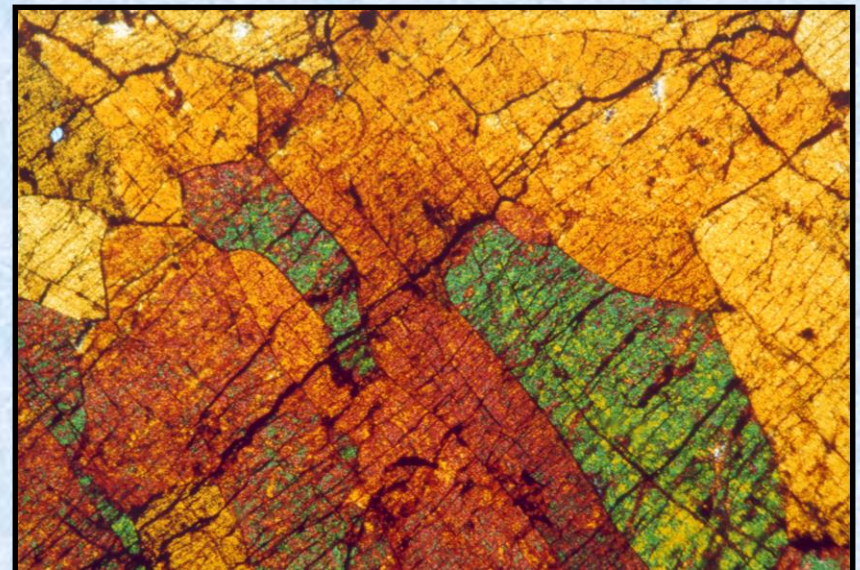
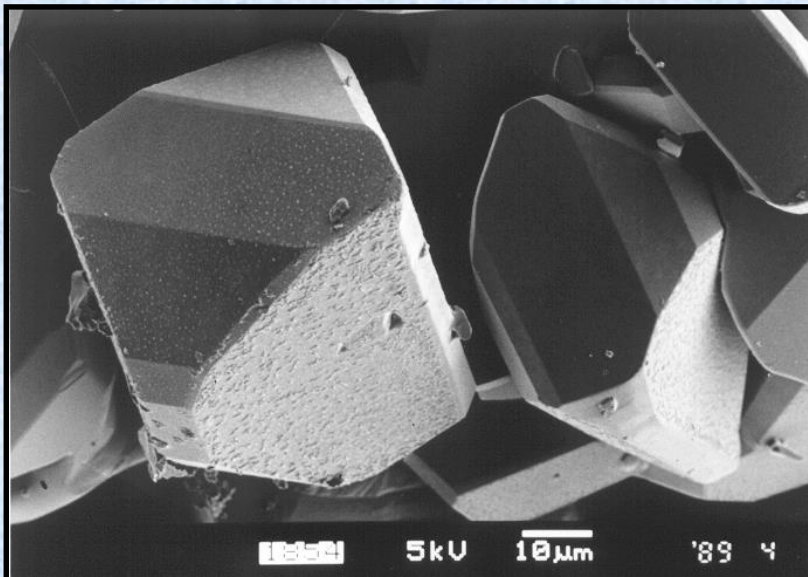
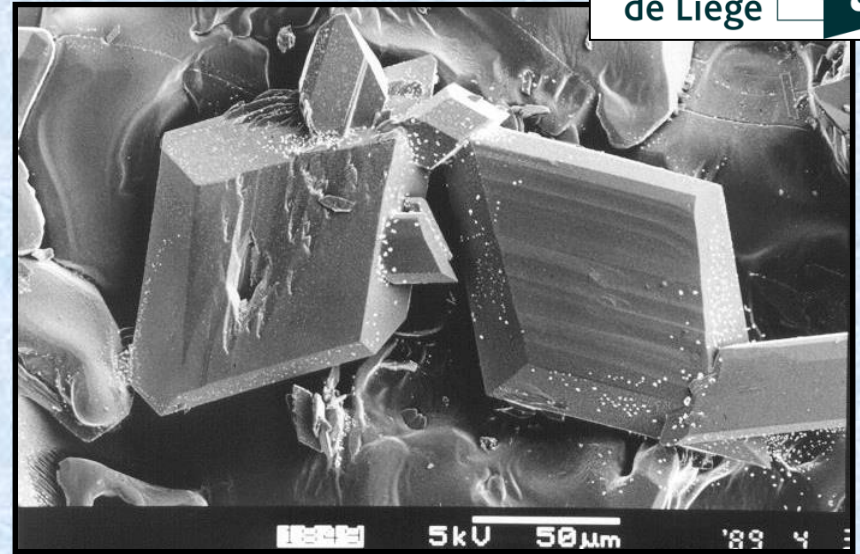
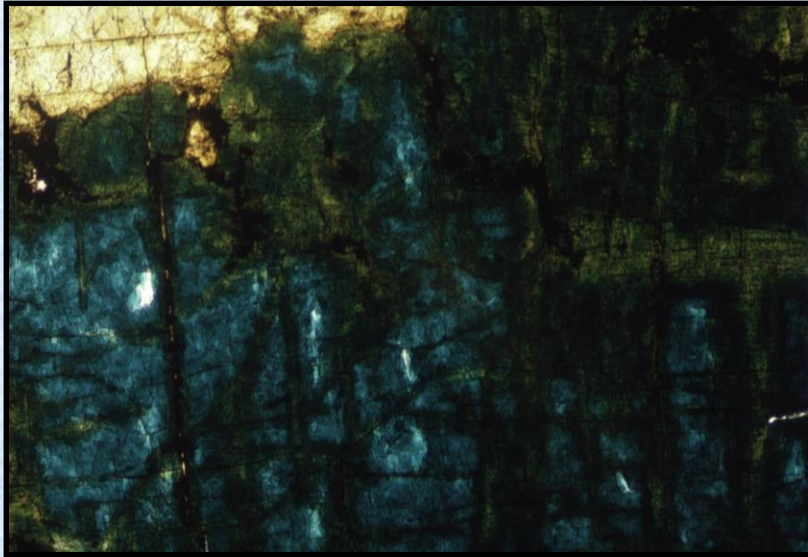
- Secondary origin
- Primary origin

Oxidation mechanism



Alluaudite, Kibingo pegmatite, Rwanda

The alluaudite group of minerals



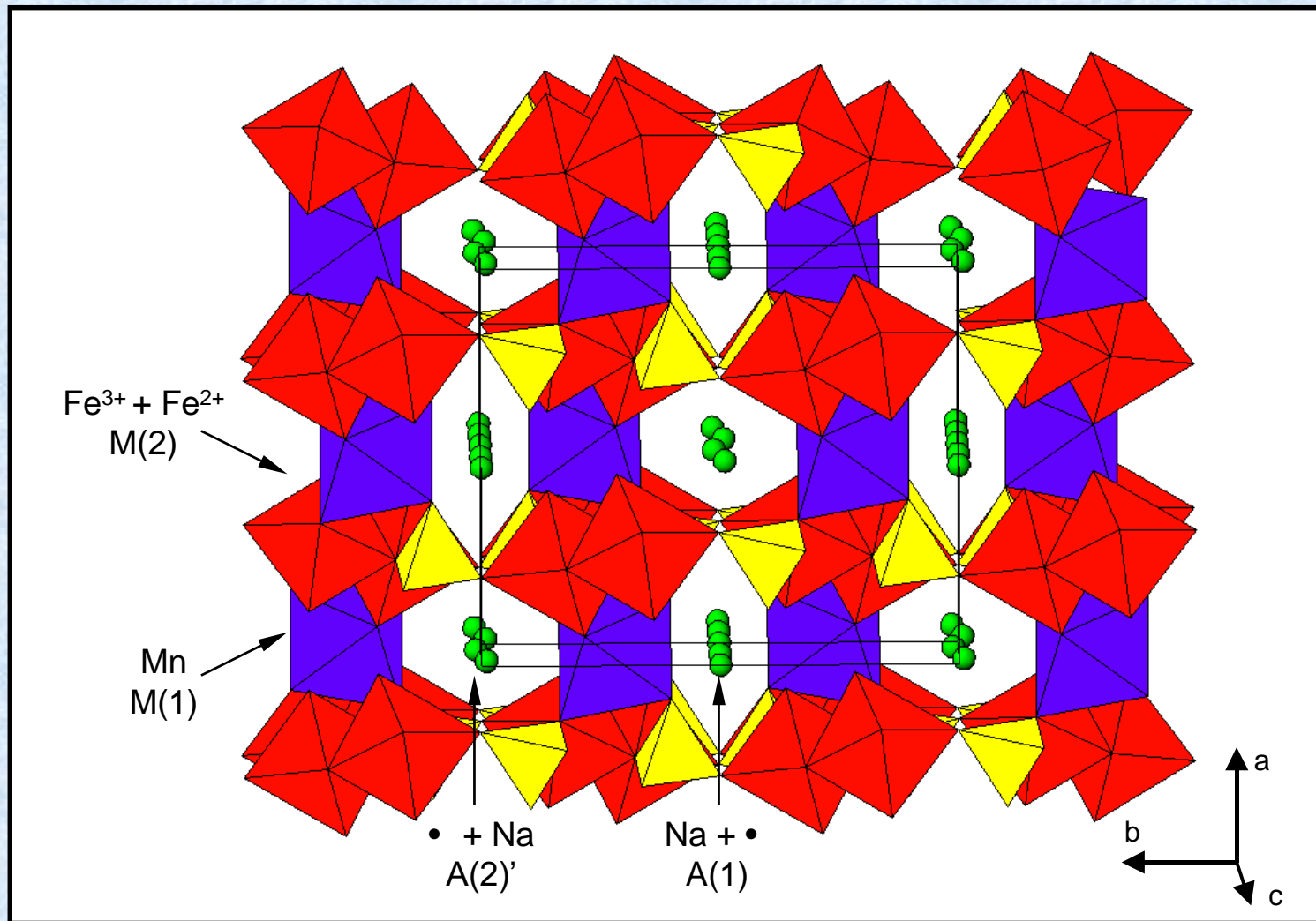
The alluaudite structure

$A(2)'$: gabled disphenoid

$A(1)$: distorted cube

$M(1)$: very distorted octahedron

$M(2)$: distorted octahedron



Synthesis experiments

HYDROTHERMAL SYNTHESSES

- Tuttle-type cold-seal bombs
- $T = 400-800\text{ °C}$
- $P = 1\text{ kbar}$
- Oxygen fugacity: Ni/NiO (NNO) buffer



SOLID STATE SYNTHESSES

- Pt crucible
- $650-950\text{ °C}$
- $P = 1\text{ atm.}$



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

X : Complete occupancy of the site

p : Partial occupancy of the site

Solid-state synthesis
and hydrothermal
experiments



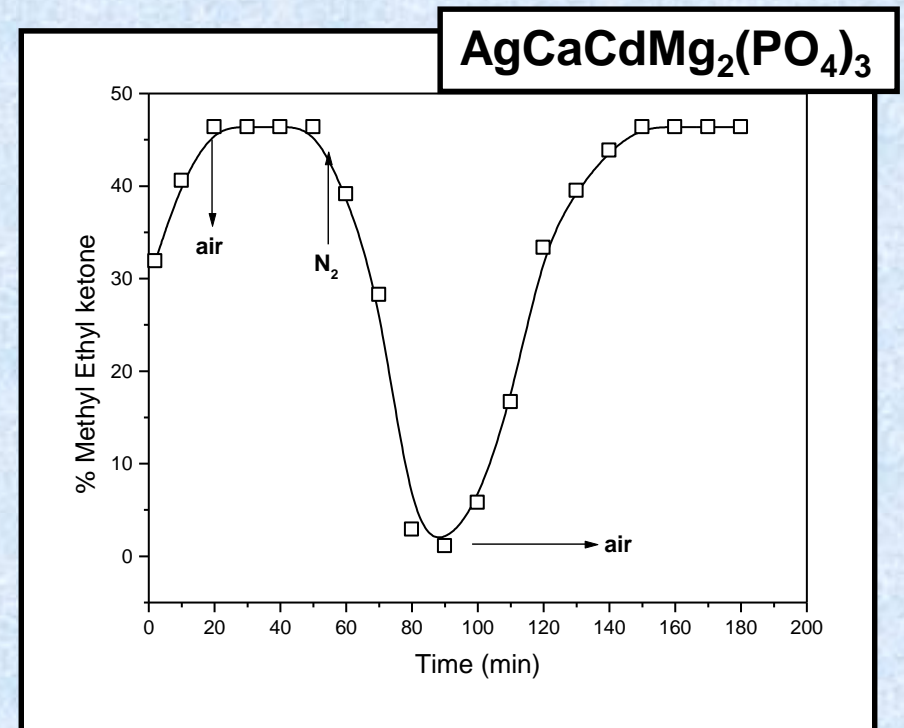
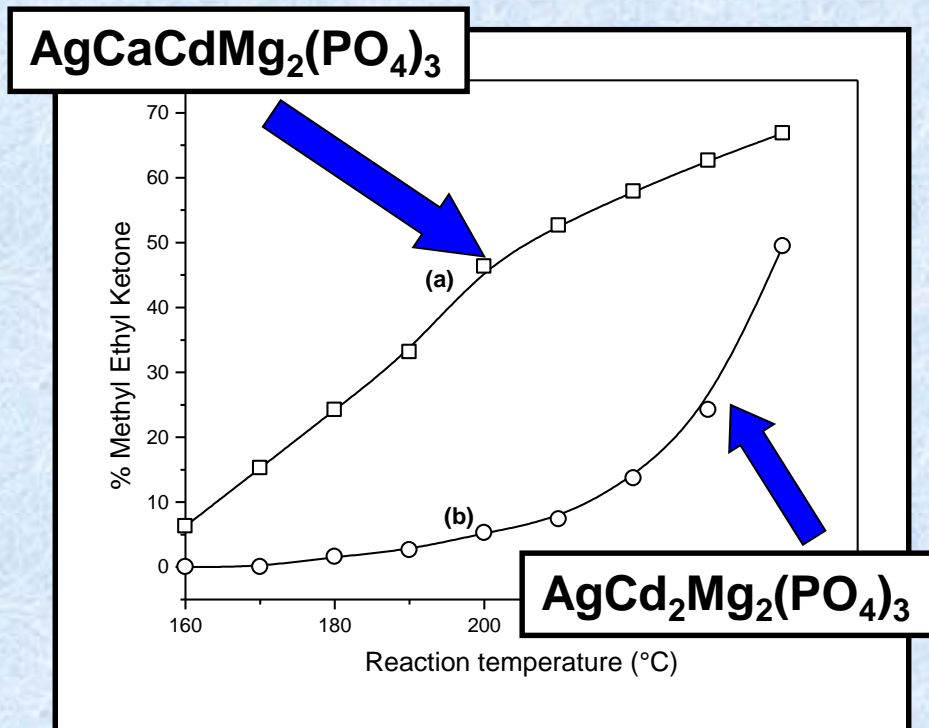
X-ray structure
refinements



Cationic
distribution

Applications: catalytic properties

Probe reaction: Butan-2-ol \Rightarrow Methyl ethyl ketone + butenes + CO₂



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

The role of lithium in alluaudites



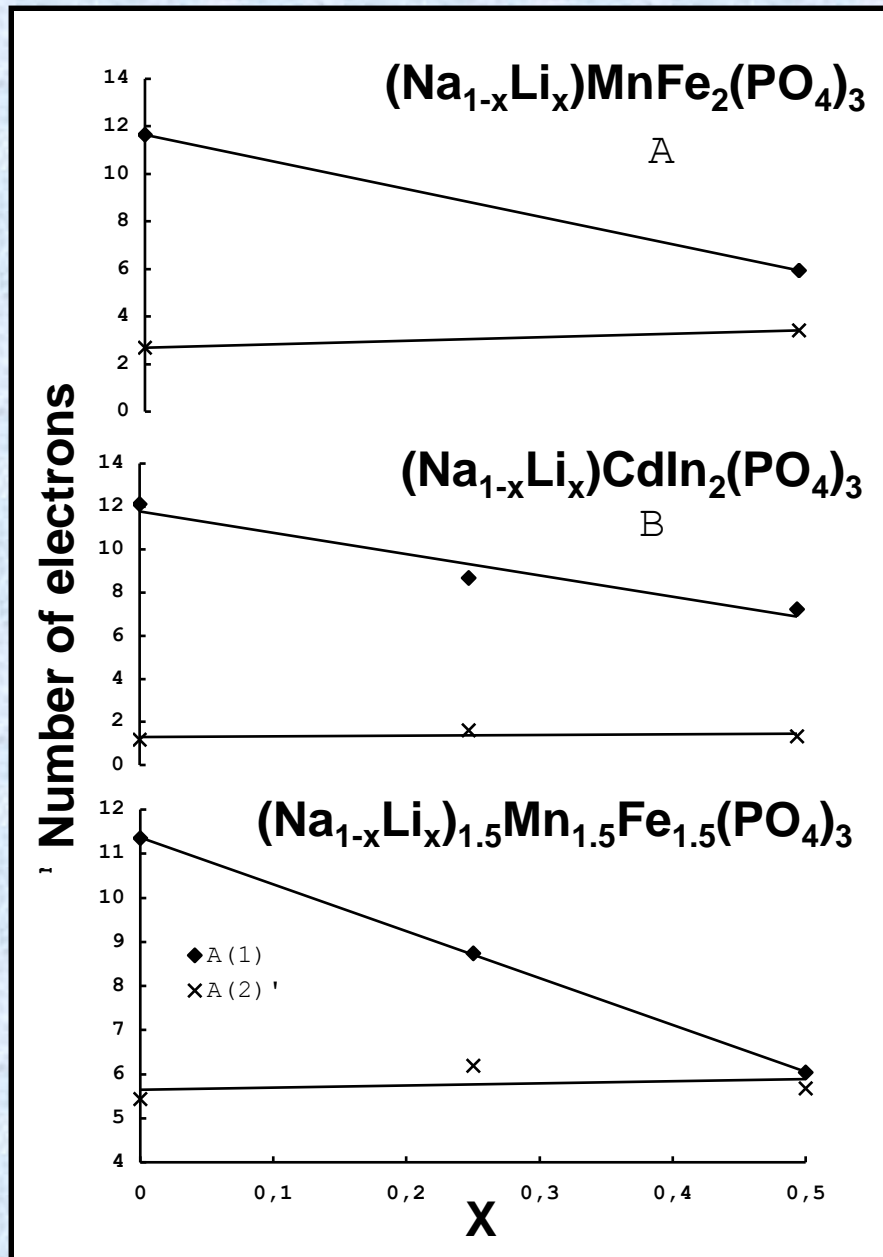
Single-crystal structure refinements
Variations of the unit-cell parameters
Mössbauer spectroscopy



X-ray Rietveld refinements



X-ray Rietveld refinements

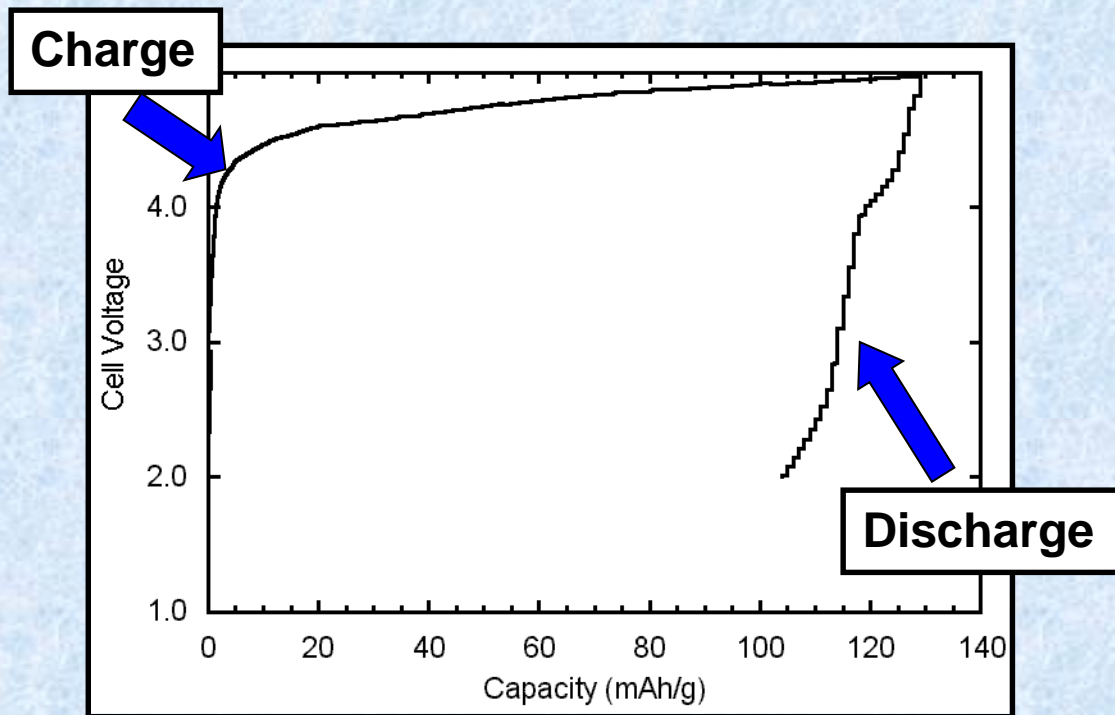


Number of electrons on A(1) and A(2)'



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
- Investigation of synthetic alluaudites and of natural olivine-type phosphates allowed one to better understand the crystal chemistry of these phosphates.
- 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.