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

Les phosphates de fer et de manganèse : comment les étudier, et à quoi peuvent-ils bien servir ?

Prof. Frédéric Hatert

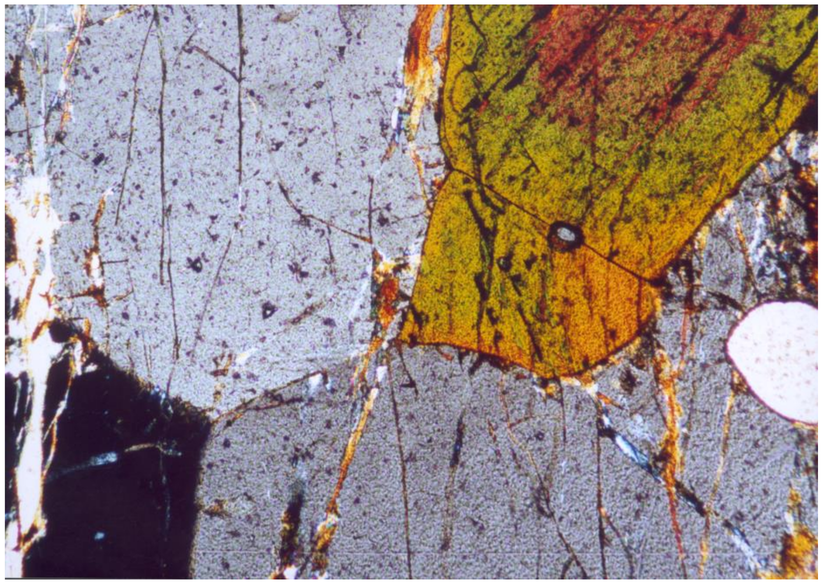
Chênée, le 7 décembre 2018

Plan de l’exposé

1. Introduction: triphylite et alluaudite
2. Observations de terrain: les pegmatites
3. Pétrographie: lames minces, analyses chimiques
4. Cristallochimie: structure cristalline
5. Synthèse: essais en laboratoire
6. Applications: batteries au lithium

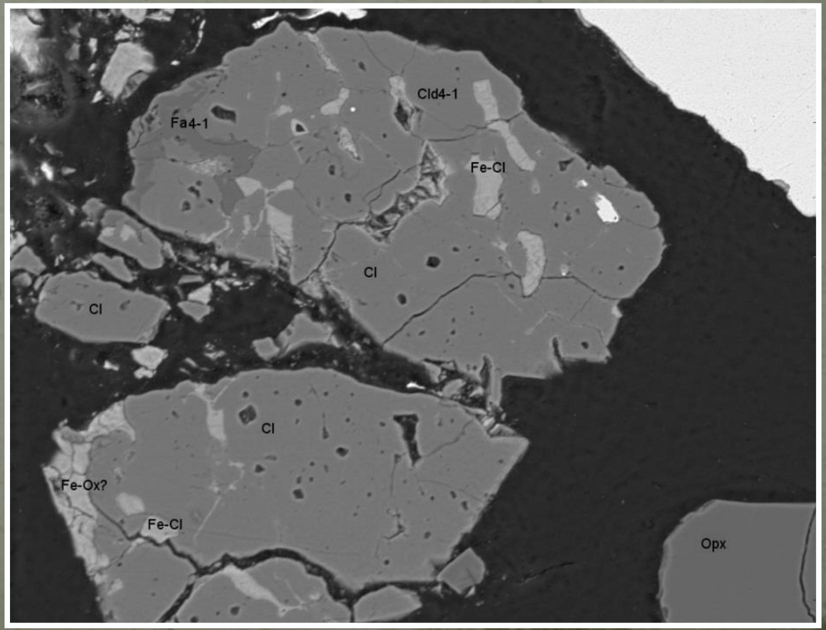
Gisements

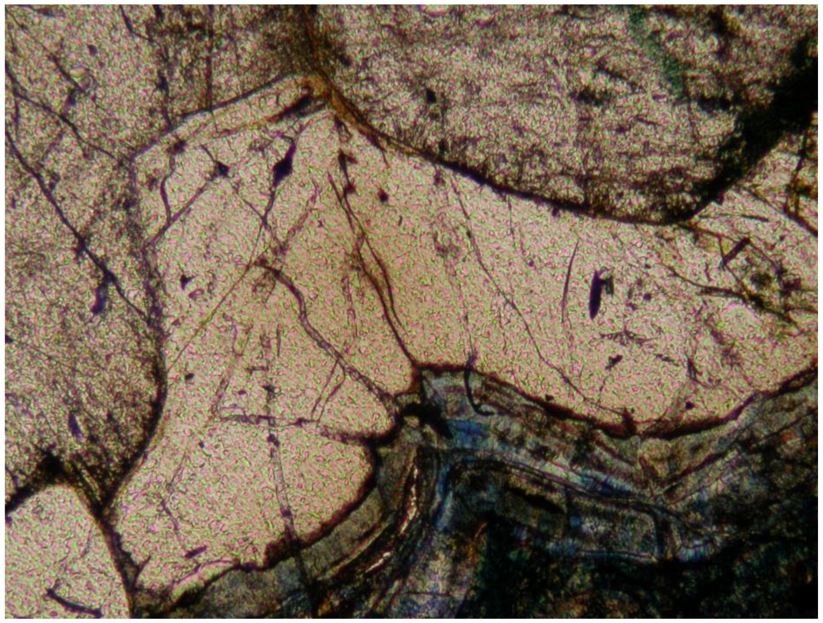
- Pegmatites granitiques
- Roches métamorphiques
- Météorites



Fillowite + alluaudite, pegmatite de Kabira, Ouganda

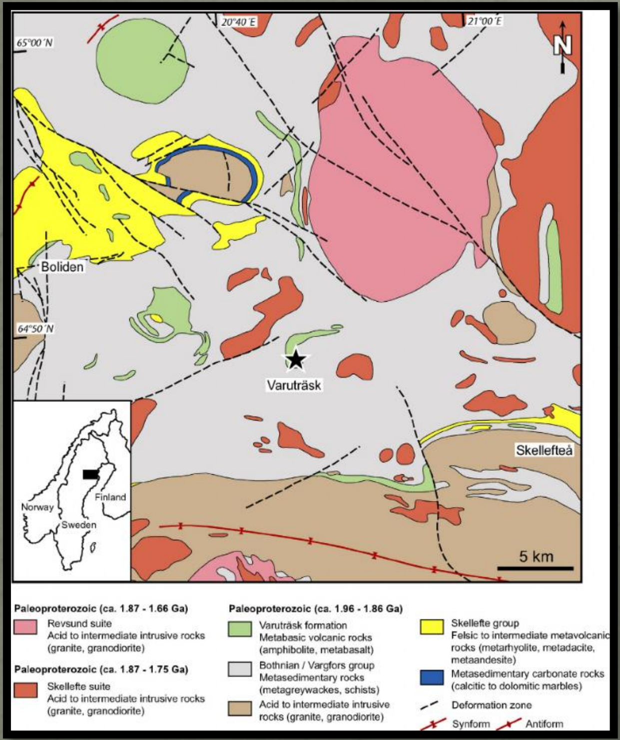
Chladniite, meteorite GRA 95209





Johnsomervilleite, Loch Quoich, Ecosse

La pegmatite de Varuträsk



Percy Quensel (1881-1966)

Brian Mason (1917-2009)

Triphylite et lithiophilite

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

(Lithiophilite) (Sicklérite) (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) (Ferrisicklérite) (Hétérosite)

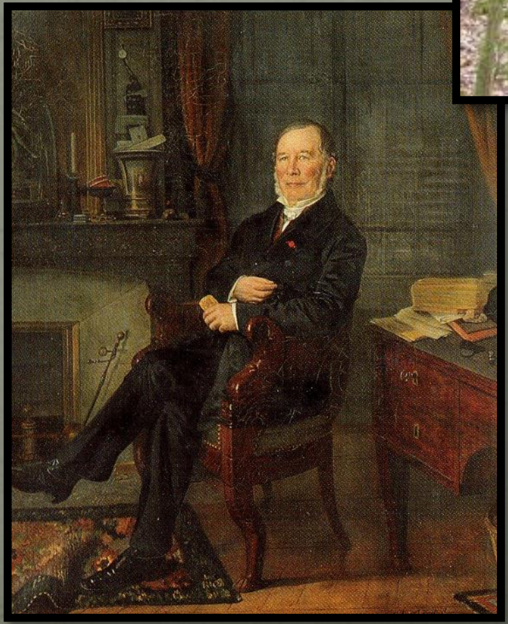
Séquence d'oxydation de « Quensel-Mason »

La varulite et l'alluaudite

Varulite, $Na_2Mn_2Fe^{3+}(PO_4)_3$
Varuträsk, Suède

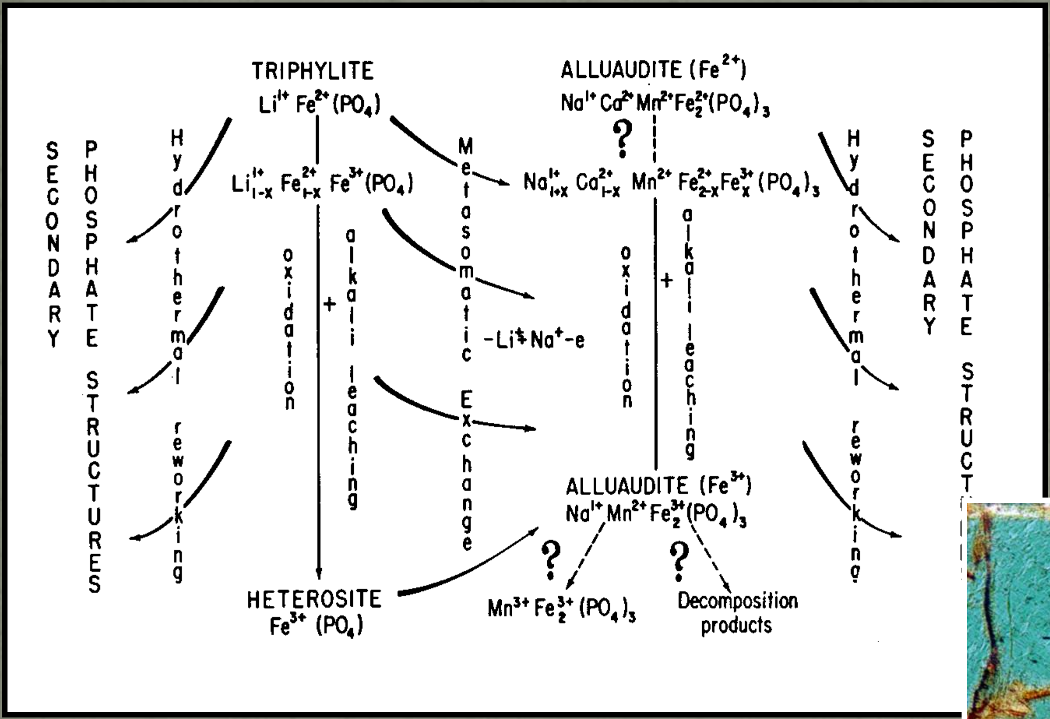
Pegmatite de Chanteloube
Alluaudite, $NaMnFe^{3+}_2(PO_4)_3$

Augustin-Alexis Damour (1808-1902)



François II Alluaud (1778-1866)
Maire de Limoges et minéralogiste

Stabilité des alluaudites?

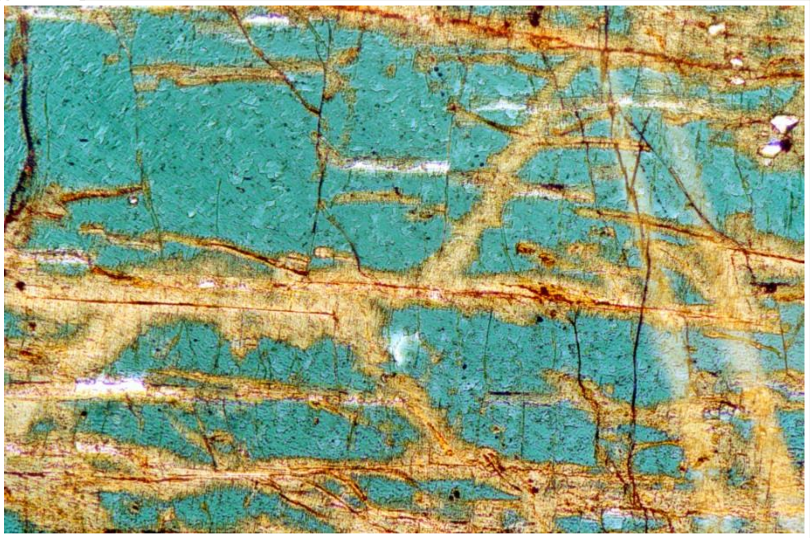


- Origine secondaire
- Origine primaire

Mécanisme d’oxidation

$Na_2MnFe^{2+}Fe^{3+}(PO_4)_3$ ⇨ $[]NaMnFe^{3+}{}_2(PO_4)_3$

$Na^+ + Fe^{2+}$ ⇨ $[] + Fe^{3+}$



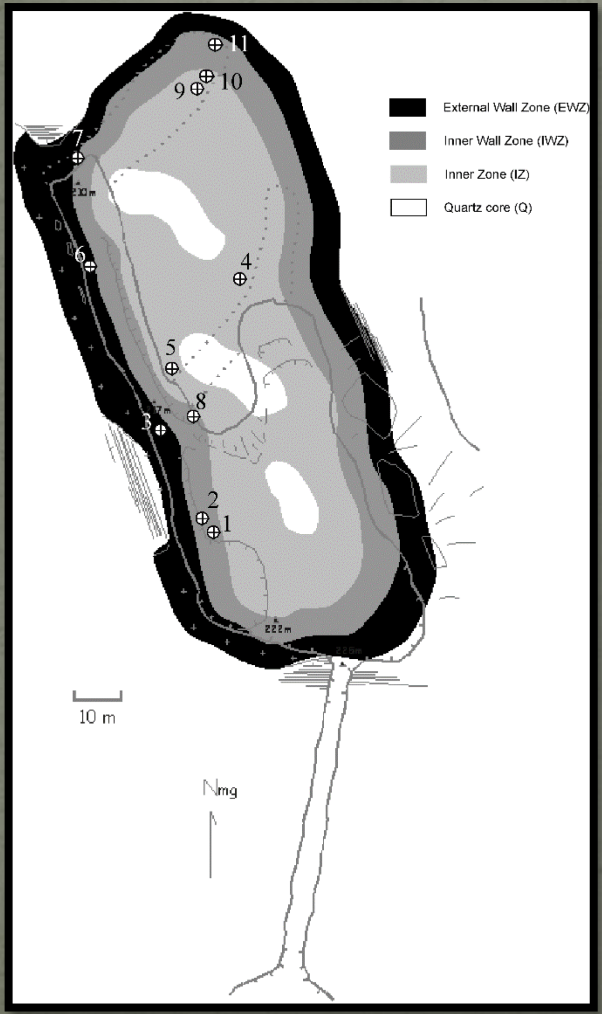
Alluaudite, pegmatite de Kibingo, Rwanda

Missions de terrain

Simon Philippo (MHNL)
Maxime Baijot (Ulg)
Jacques Cassedanne (Rio)

Encar Roda-Robles (Bilbao)
Miguel Galliski (Mendoza)

Zonation dans les pegmatites



MINERALOGY AND GEOCHEMISTRY OF PHOSPHATES AND SILICATES IN THE SAPUCAIA PEGMATITE, MINAS GERAIS, BRAZIL: GENETIC IMPLICATIONS

MAXIME BAIJOT AND FRÉDÉRIC HATERT[§]

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

SIMON PHILIPPO

Section Minéralogie, Musée national d'histoire naturelle, Rue Münster 25, L–2160 Luxembourg, Grand-Duché de Luxembourg

Les phosphates Fe-Mn des pegmatites

Pegmatite de Buranga, Rwanda

Pegmatite de Sapucaia, Brésil

De retour au laboratoire….

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Phosphates Fe-Mn

Pétrographie

Lames minces

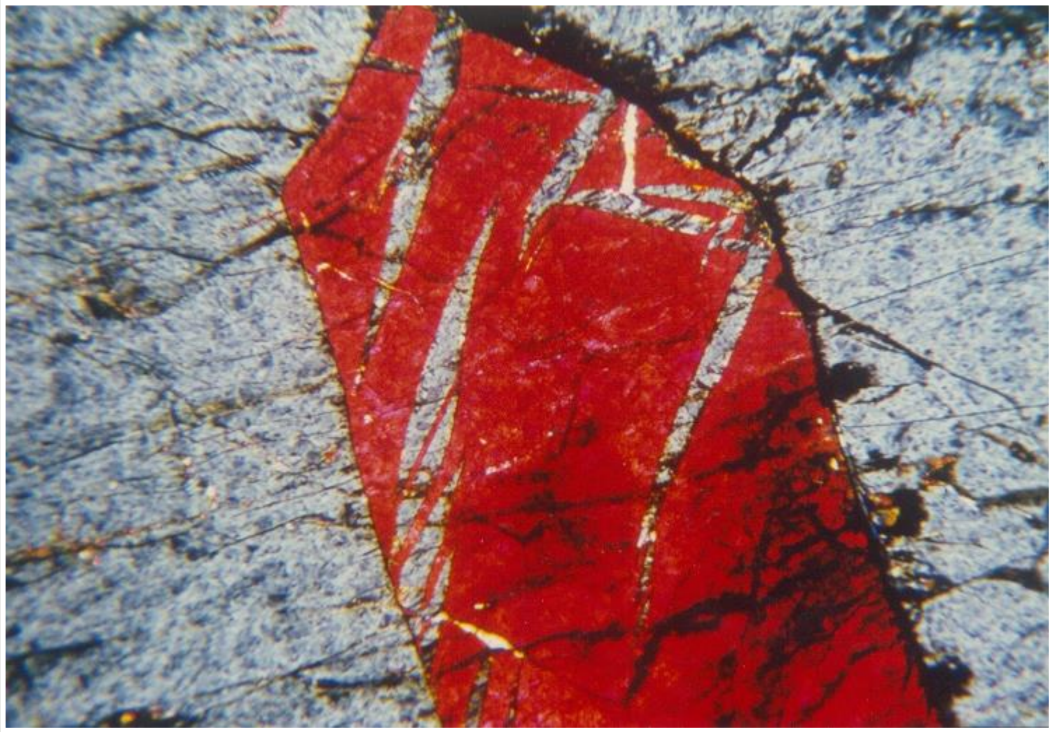
Phosphates d’aluminium

L’association triphylite + sarcopside

Intercroissances et inclusions dans les associations graftonite-sarcopside-triphylite

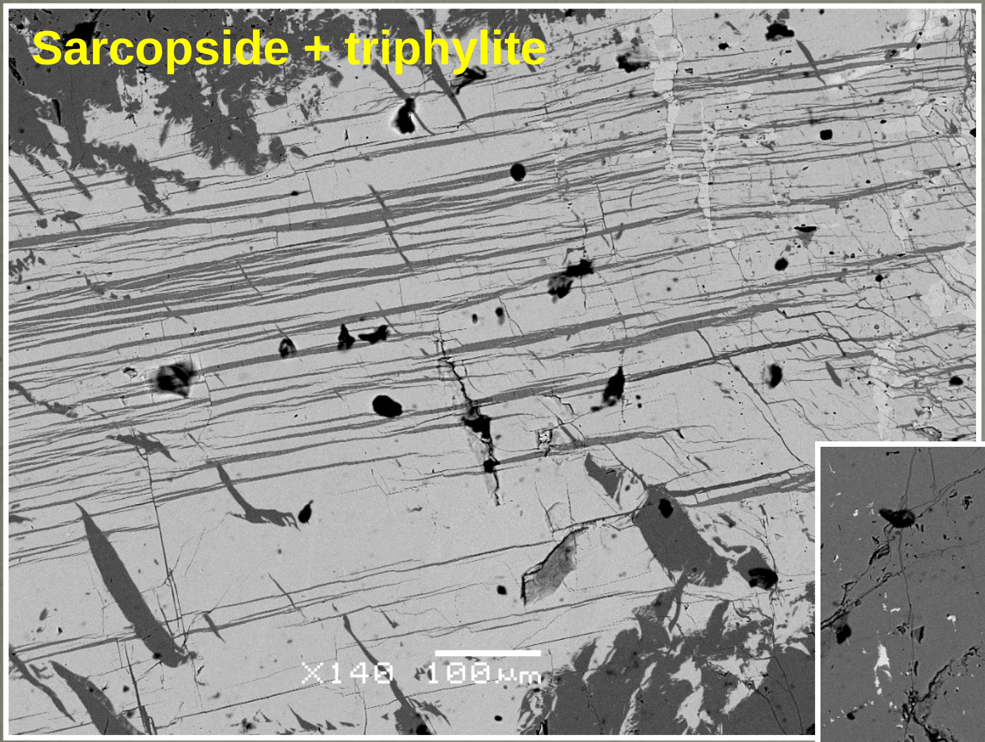
par André-Mathieu FRANSOLET,
Institut de Minéralogie, Université de Liège (1).

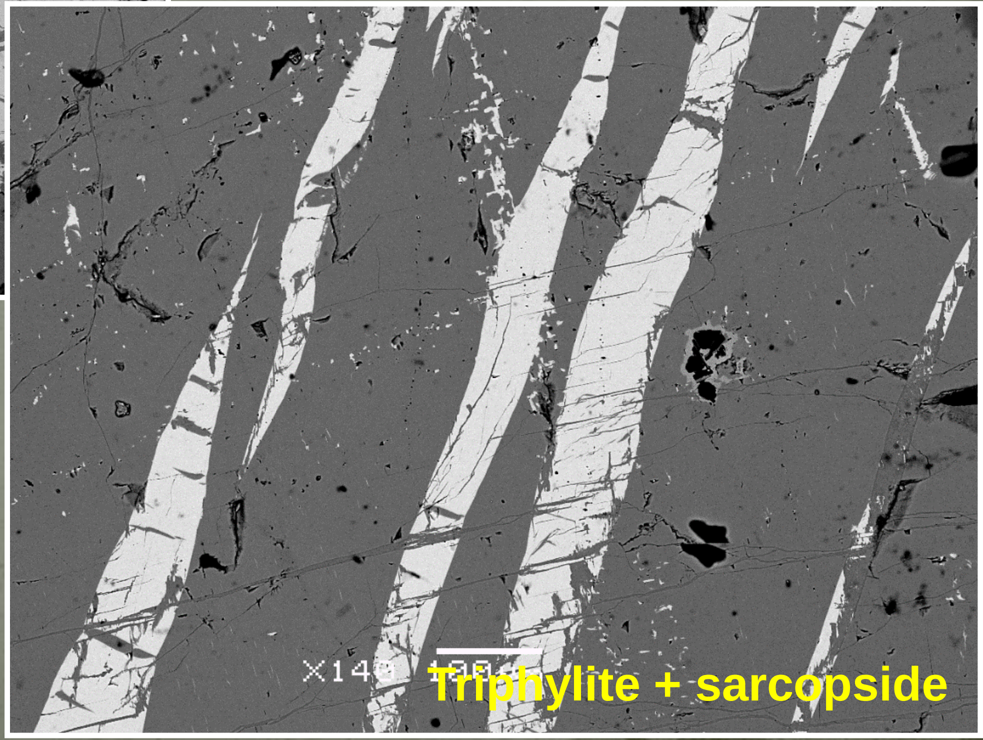
Fransolet, 1977



L’association triphylite + sarcopside

Pegmatite de Cañada, Espagne



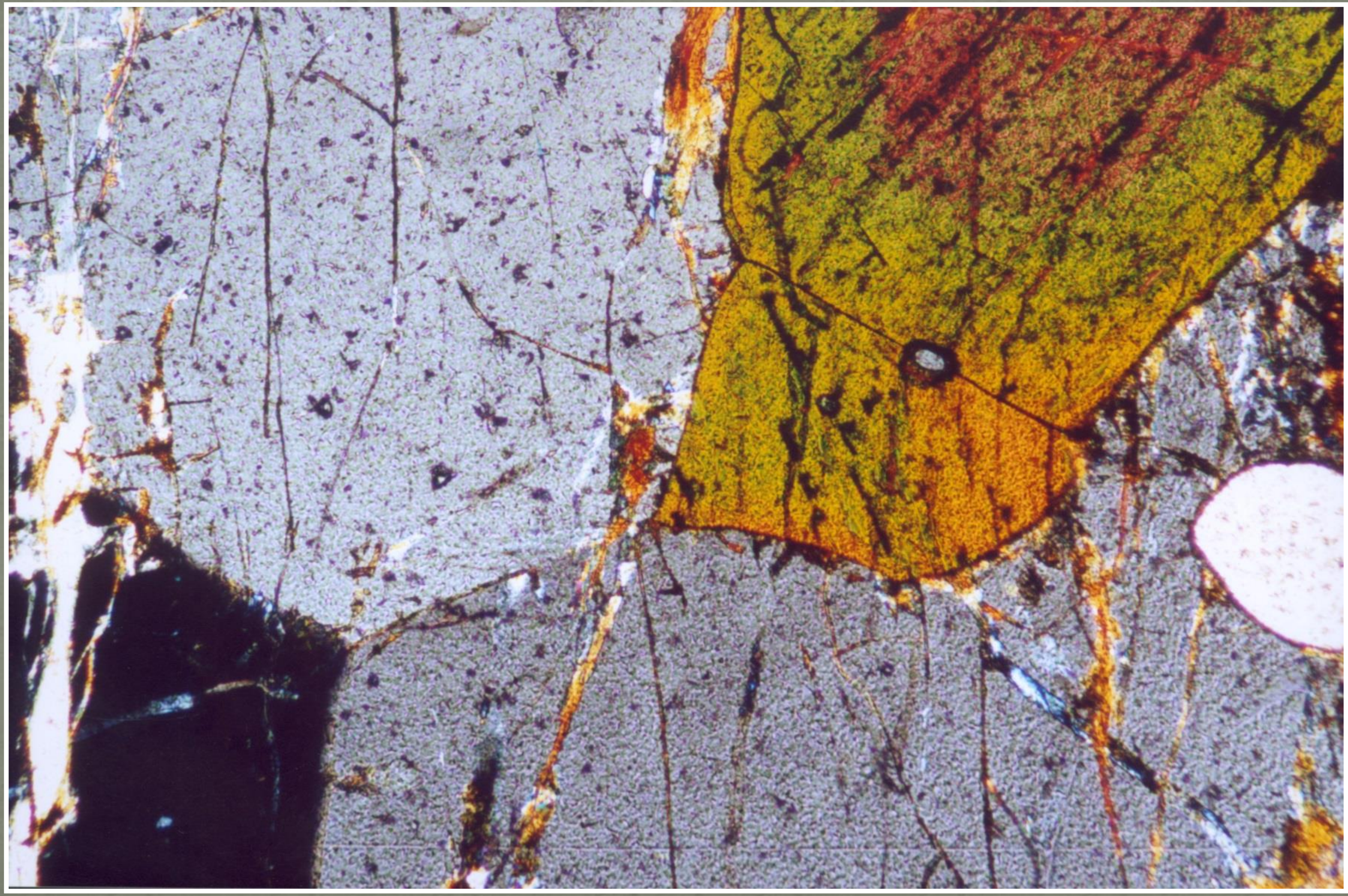


Textures lamellaires

↓

EXSOLUTIONS!!

L'association alluaudite + fillowite



Alluaudite + fillowite, Kabira, Uganda

L'association triphylite + alluaudite

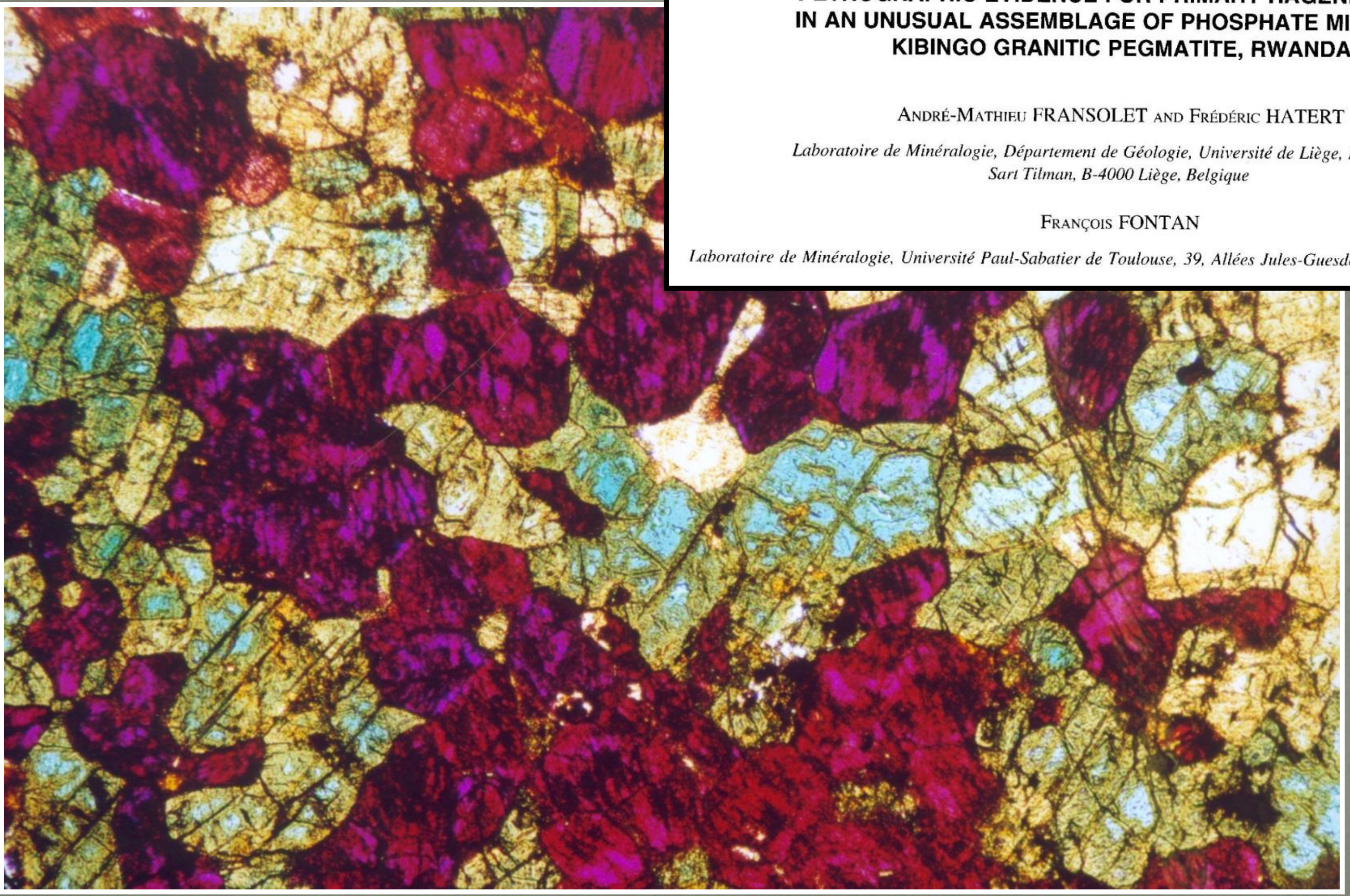
PETROGRAPHIC EVIDENCE FOR PRIMARY HAGENDORFITE IN AN UNUSUAL ASSEMBLAGE OF PHOSPHATE MINERALS, KIBINGO GRANITIC PEGMATITE, RWANDA

André-Mathieu FRANSOLET and Frédéric HATERT

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

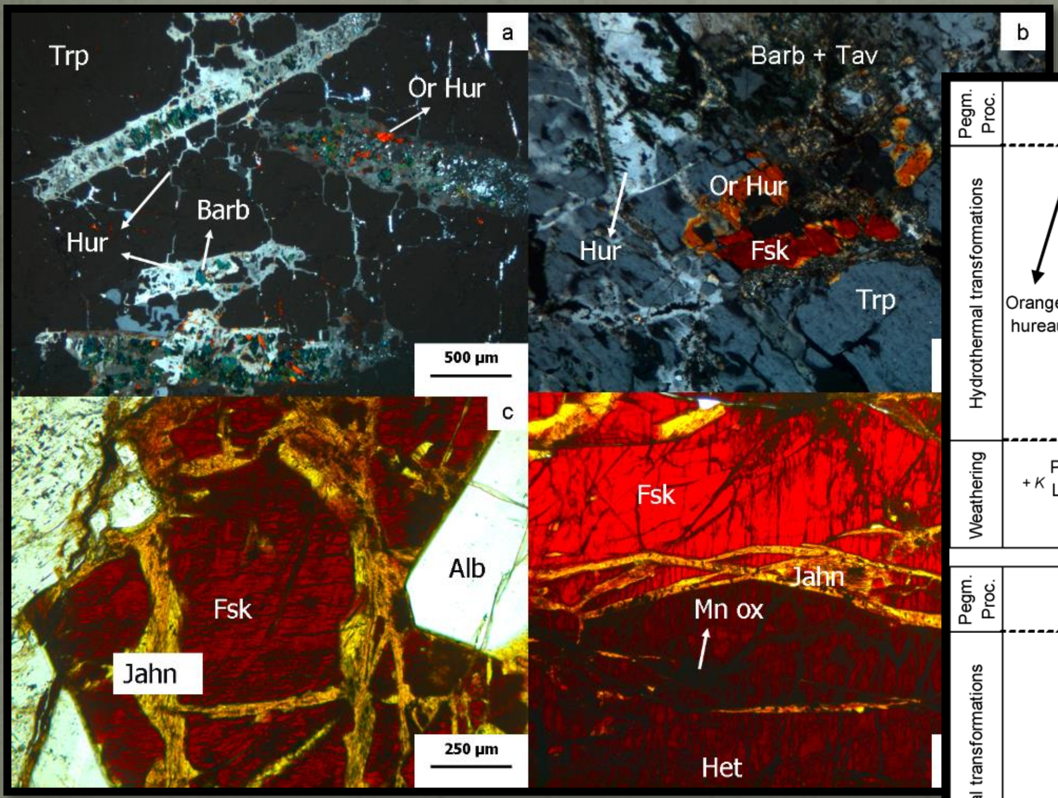
François FONTAN

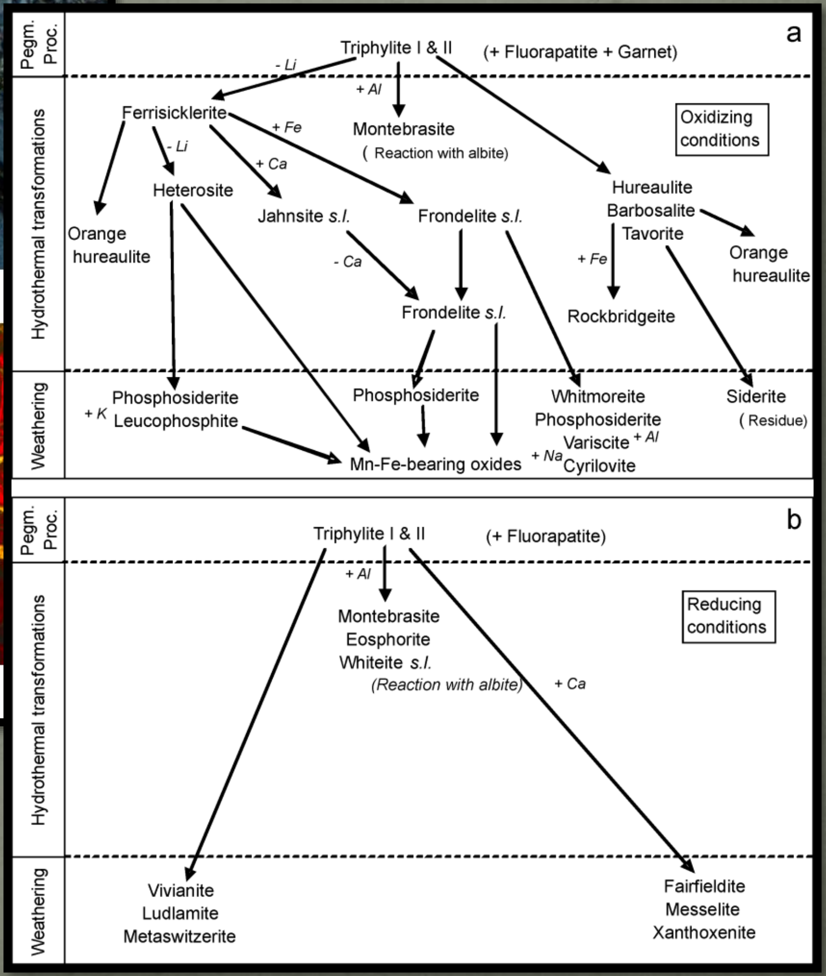
Laboratoire de Minéralogie, Université Paul-Sabatier de Toulouse, 39, Allées Jules-Guesde, F-31000 Toulouse, France



Hagendorfite, alluaudite et hétérosite, Kibingo, Rwanda

Complex assemblages from Sapucaia





Analyses chimiques à la microsonde

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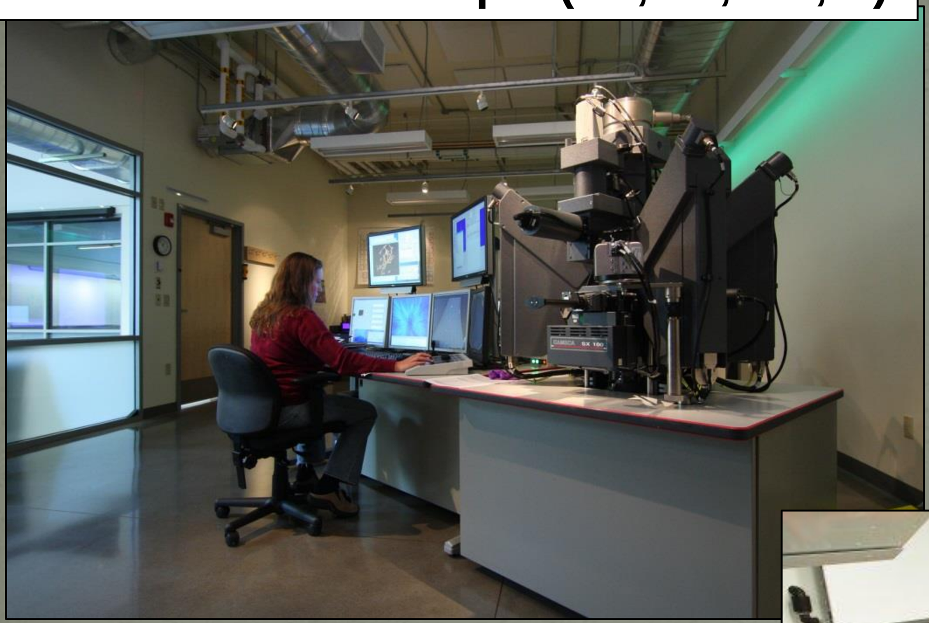
Microsonde électronique (Na, Fe, Mn, P)



Microsonde ionique (SIMS: Li)

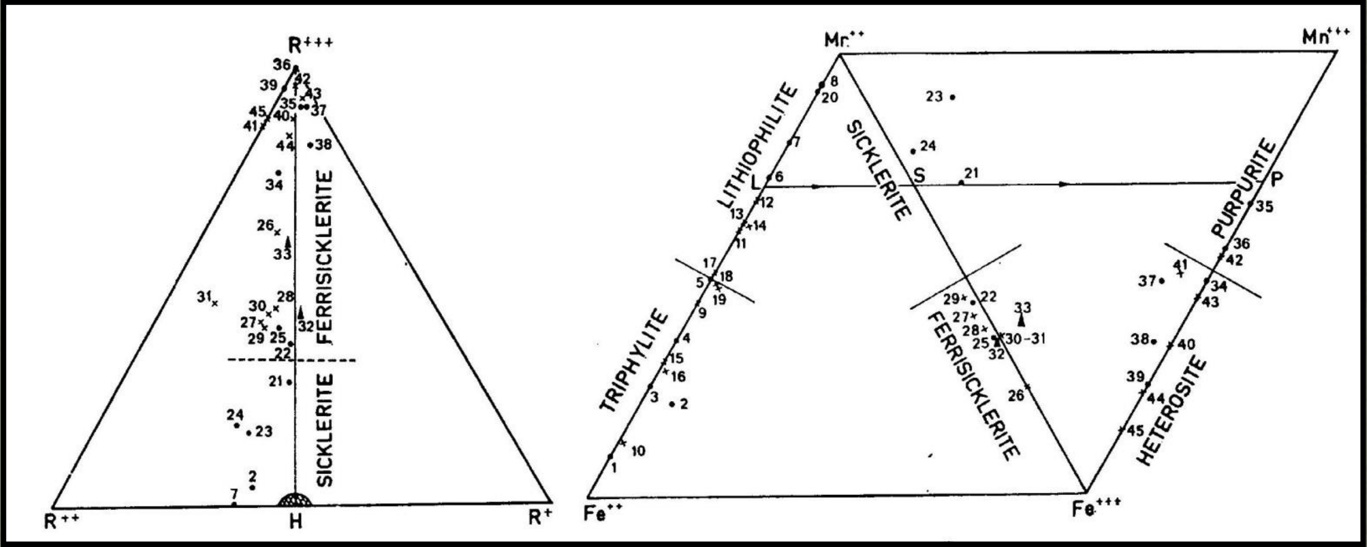
Oxidation de la série triphylite-lithiophilite

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

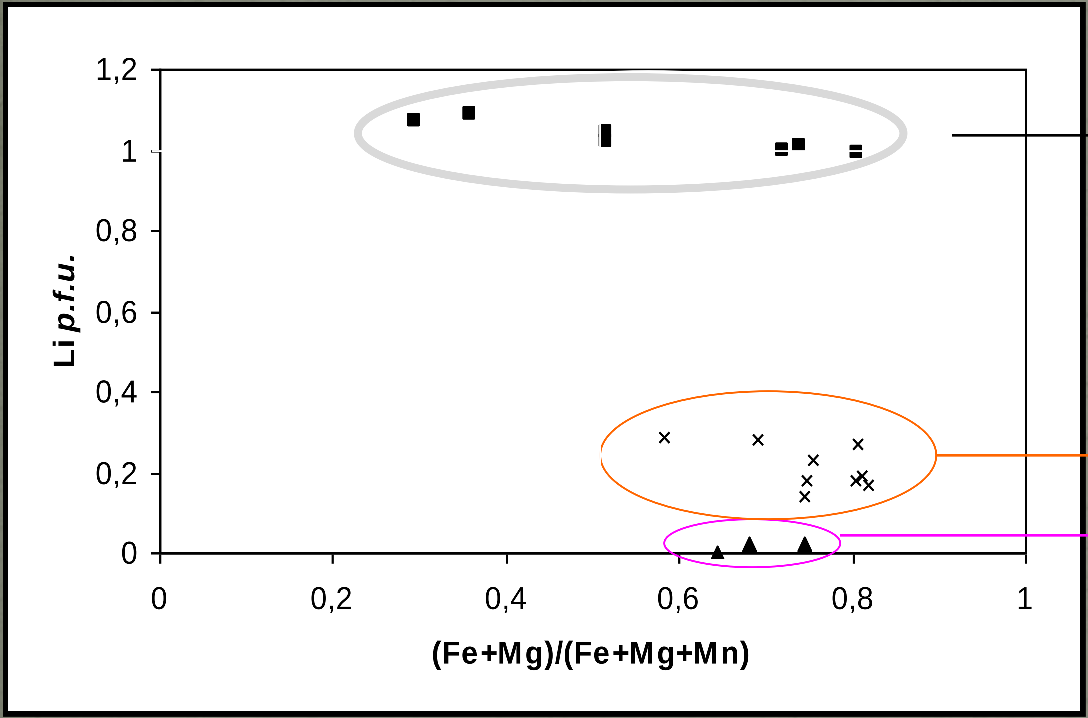


Le processus d'oxidation n'est pas continu!

Analyses d'échantillons naturels

LIÈGE université

Analyses à la microsonde électronique, SIMS et déterminations structurales sur 19 échantillons



Triphylite-lithiophilite
0,99-1,07 Li *p.u.f.*

Ferrisicklérite
0,14-0,29 Li *p.u.f.*

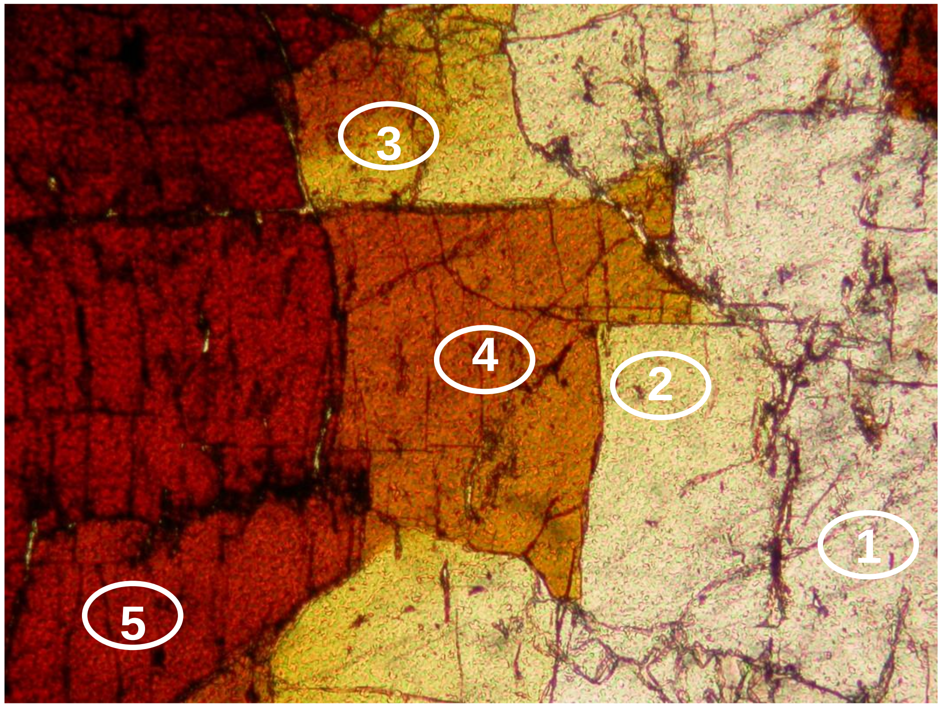
Hétérosite
0,00-0,02 Li *p.u.f.*

L'hétérosite peut contenir jusqu'à 0,21 % en poids de Li_2O, et la ferrisicklérite peut contenir seulement 1,31 % en poids de Li_2O

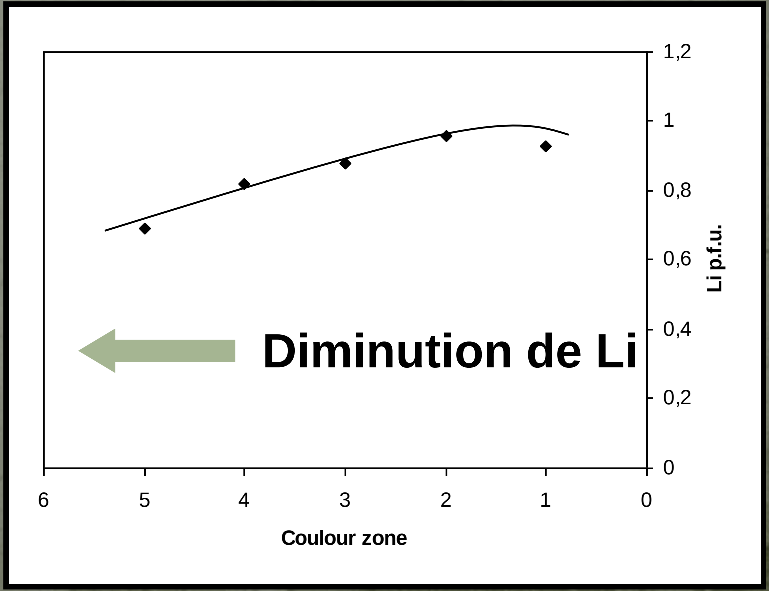
Contenus en Li proches!

La série lithiophilite-sicklérite

Echantillon de l' Altaï, Chine



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: $Li_{0,69}(Fe^{3+}_{0,16}Mn^{2+}_{0,62}Mn^{3+}_{0,19})(PO_4)$

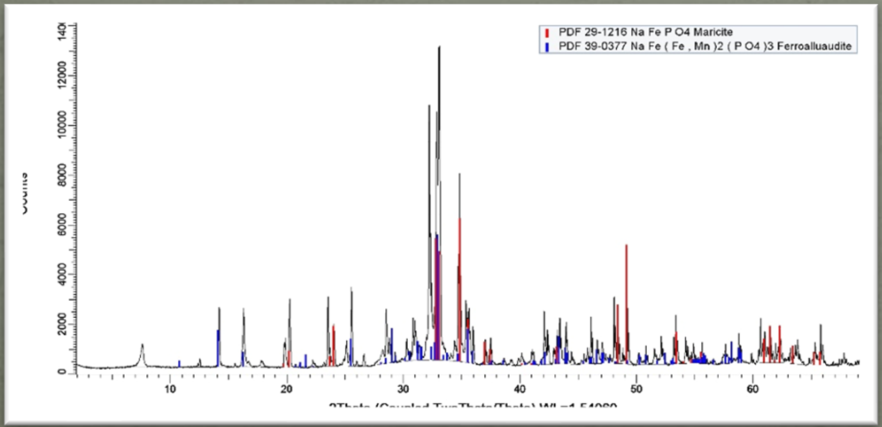


- La transition de la lithiophilite en sicklérite est progressive
- Le changement de couleur est lié à la présence de Mn^{3+}

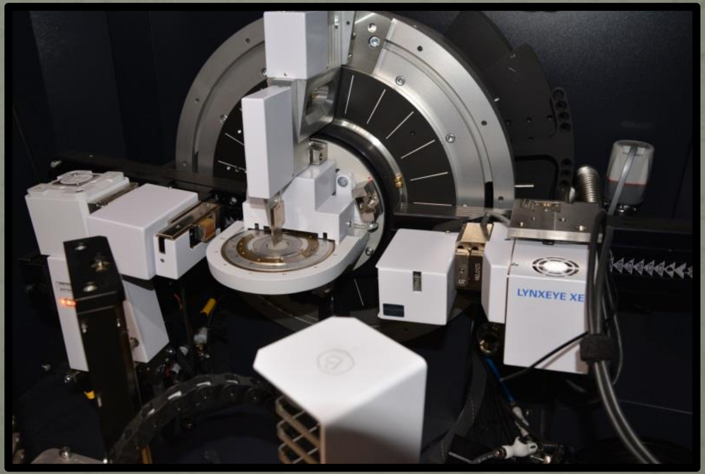
Diffraction des rayons X sur poudres

Préparation de l’échantillon

Passeur automatique



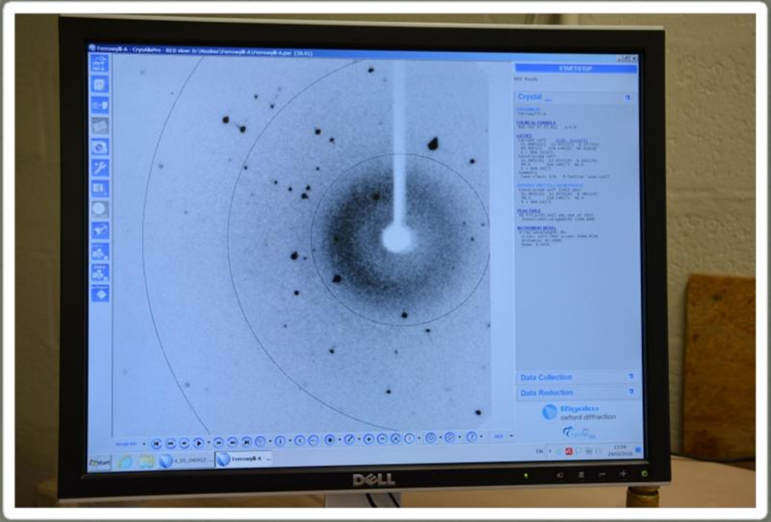
Diffractogramme de poudres



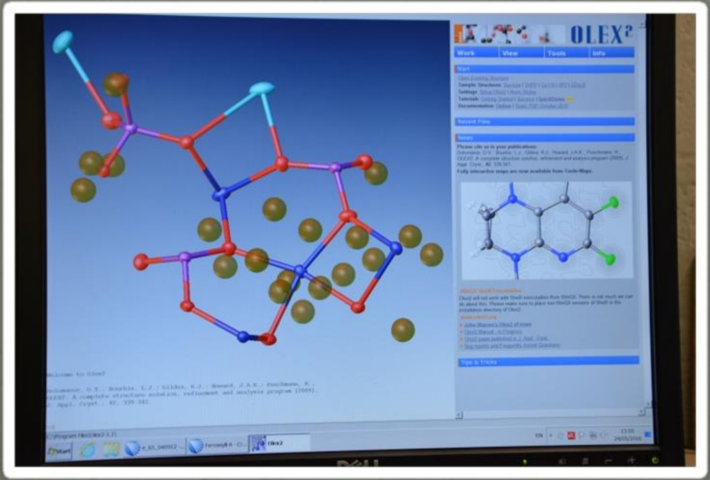
Diffractomètre de poudres

Diffraction sur monocristaux

Diffractomètre à 4 cercles

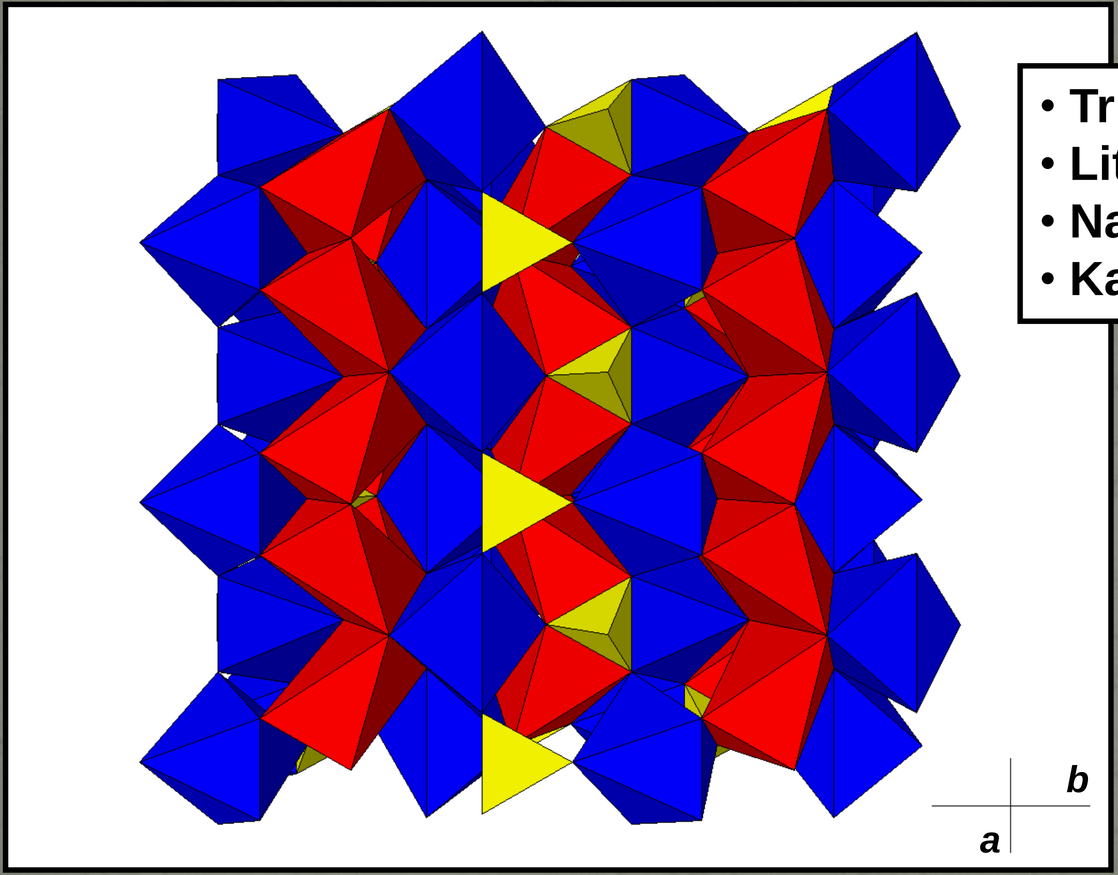


Taches de diffraction



Détermination de la structure

La structure olivine



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

Octaèdres rouges: M1 (Li, Na)
Octaèdres bleus: M2 (Fe, Mn)

Groupe spatial
Pmnb

a = 6,092 Å
b = 10,429 Å
c = 4,738 Å

La karenwebberite, une nouvelle espèce…

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

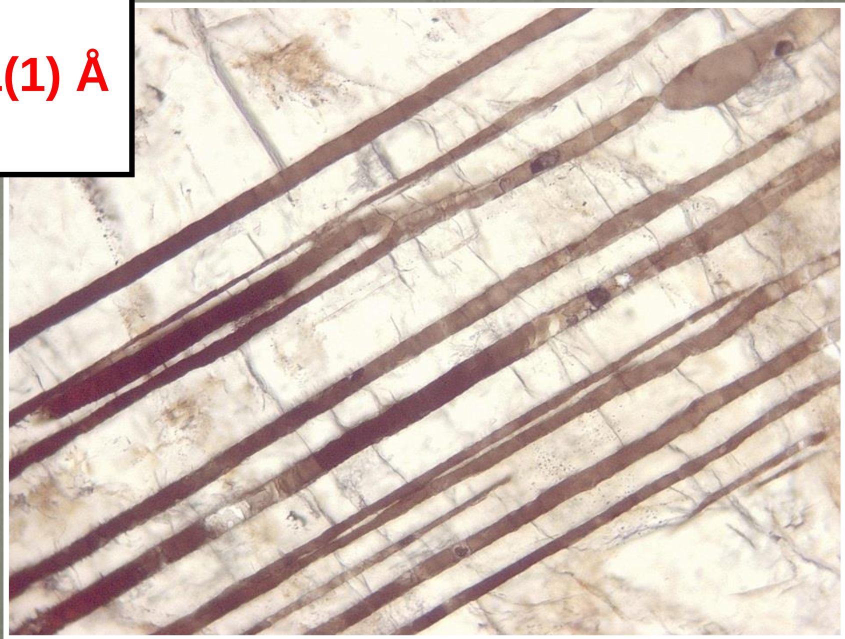
Karenwebberite, $Na(Fe^{2+},Mn^{2+})PO_4$, a new member of the triphylite group from the Malpensata pegmatite, Lecco Province, Italy

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

La zavalíaite aussi!

ZAVALÍAITE, $(Mn^{2+},Fe^{2+},Mg)_3(PO_4)_2$, A NEW MEMBER OF THE SARCOPSIDE GROUP FROM THE LA EMPLEADA PEGMATITE, SAN LUIS PROVINCE, ARGENTINA

FRÉDÉRIC HATERT§

Laboratoire de Minéralogie, Département de Géologie, Université de Liège, Bâtiment B18, Sart Tilman, B–4000 Liège, Belgium

ENCARNACIÓN RODA-ROBLES

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

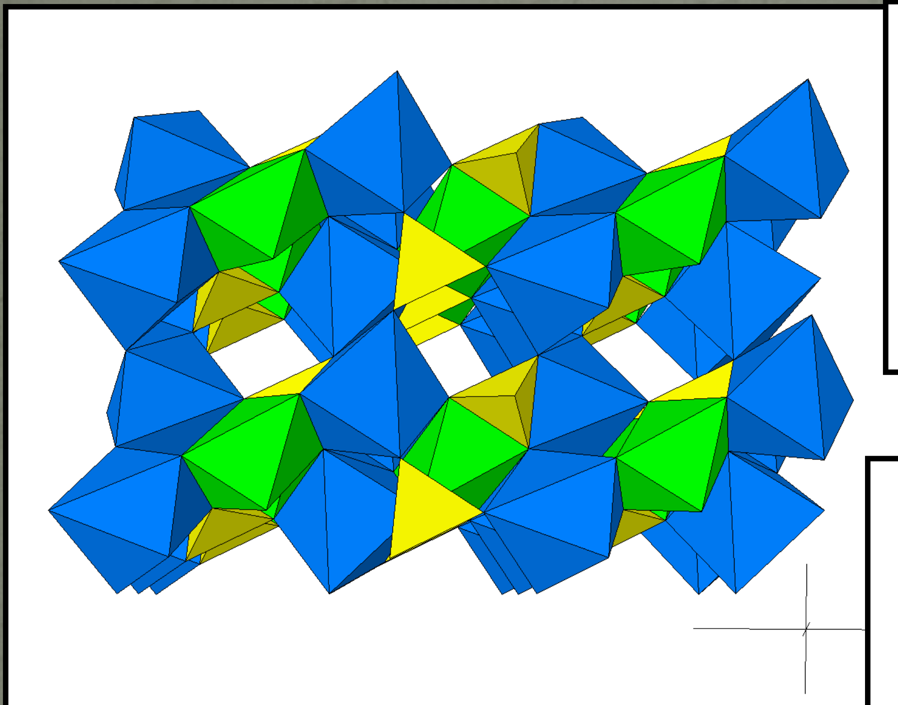
a = 6,088(1) Å
b = 4,814(1) Å
c = 10,484(2) Å
β = 89,42(3)°
G.S. $P2_1/c$

Argentine

$Mn_3(PO_4)_2$

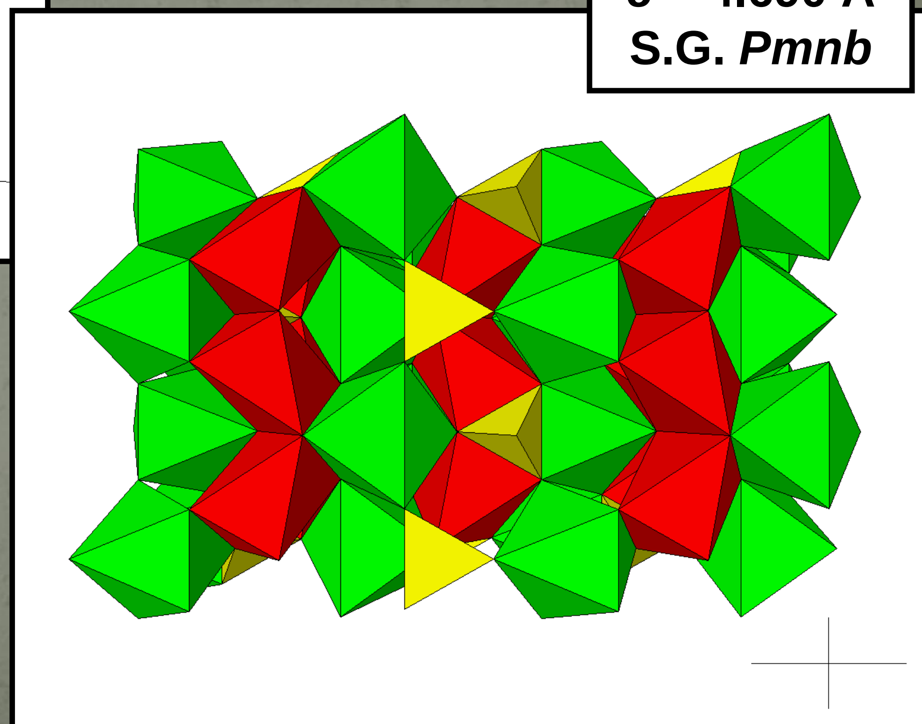
Florencia Márquez Zavalía

La structure sarcopside



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

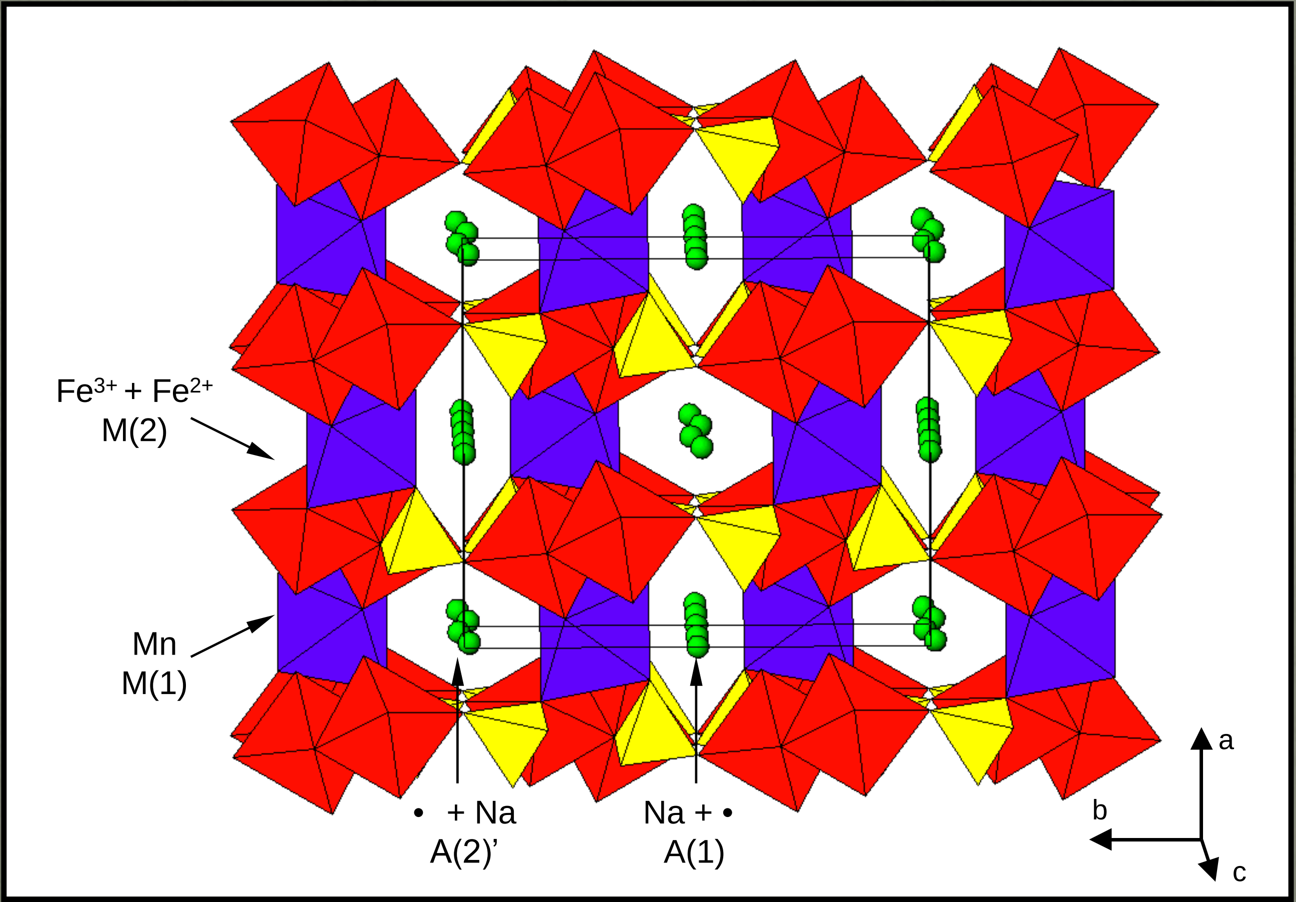
Triphylite
a = 5.987 Å
b = 10.286 Å
c = 4.690 Å
S.G. *Pmnb*



- Structures similaires
- 50 % des positions M(1) sont lacunaires dans le sarcopside

La structure alluaudite

A(2)’: Disphénoèdre déformé
A(1): Cube déformé
M(1): Octaèdre très déformé
M(2): Octaèdre déformé



*C*2/*c*, *Z* = 4

$[A(2)A(2)'A(2)''_2][A(1)A(1)'A(1)''2]M(1)M(2)_2(PO_4)_3$

Cristallochimie des alluaudites

- **Moore & Ito (1979)**

$A(2)' \Rightarrow Na^{+}$, [], K^{+}
$A(1) \Rightarrow Na^{+}$, Mn^{2+}, Ca^{2+}, •
$M(1) \Rightarrow Mn^{2+}$, Fe^{2+}, Ca^{2+}, Mg^{2+}
$M(2) \Rightarrow Fe^{3+}$, Fe^{2+}, Mn^{2+}, Mg^{2+}, Li^{+}

- **Hatert *et al.***

Crystal chemistry of the divalent cation in alluaudite-type phosphates: A structural and infrared spectral study of the $Na_{1.5}(Mn_{1-x}M^{2+}_{x})_{1.5}Fe_{1.5}(PO_4)_3$ solid solutions ($x = 0$ to 1, $M^{2+} = Cd^{2+}$, Zn^{2+})

Frédéric Hatert *

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

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

Crystal chemistry of the hydrothermally synthesized $Na_2(Mn_{1-x}Fe^{2+}_{x})_2Fe^{3+}(PO_4)_3$ 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 Grandjean[3]

Cation	Ionic radius (Å) [VI]	[VIII]	Site 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

Synthèses hydrothermales

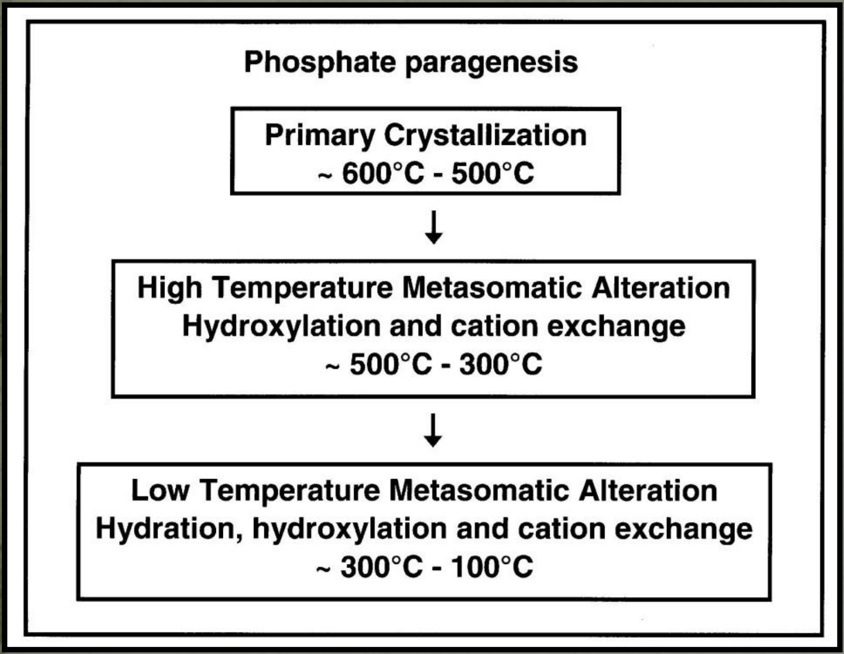
Laboratoire hydrothermal

Tubes en or

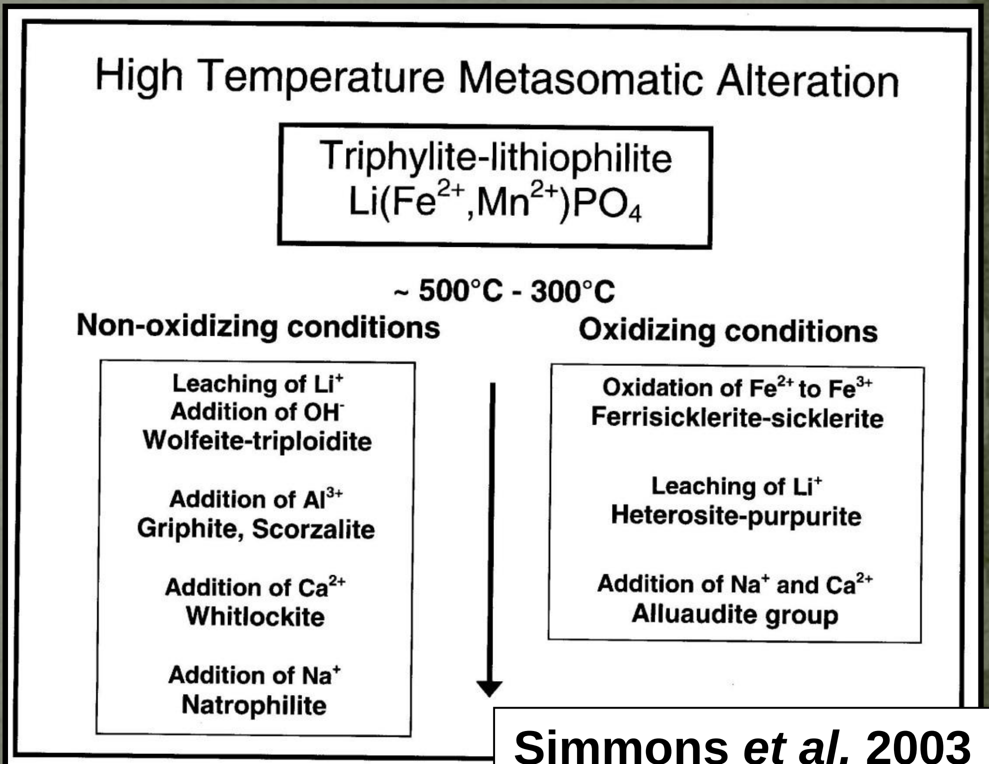
Capsules en or ouvertes

Bombe hydrothermale

Stabilité de la ferrisicklérite



- **Température de cristallisation de la ferrisicklérite?**
- **Degré d'oxydation nécessaire?**

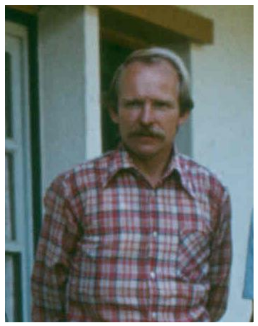


Simmons *et al.* 2003

Expériences préliminaires

- **200-600°C, 1-3 kbar**
- **Basse fO_2: triphylite**
- **Haute fO_2: $LiFe^{3+}PO_4(OH)$**

Stabilité de la ferrisicklérite

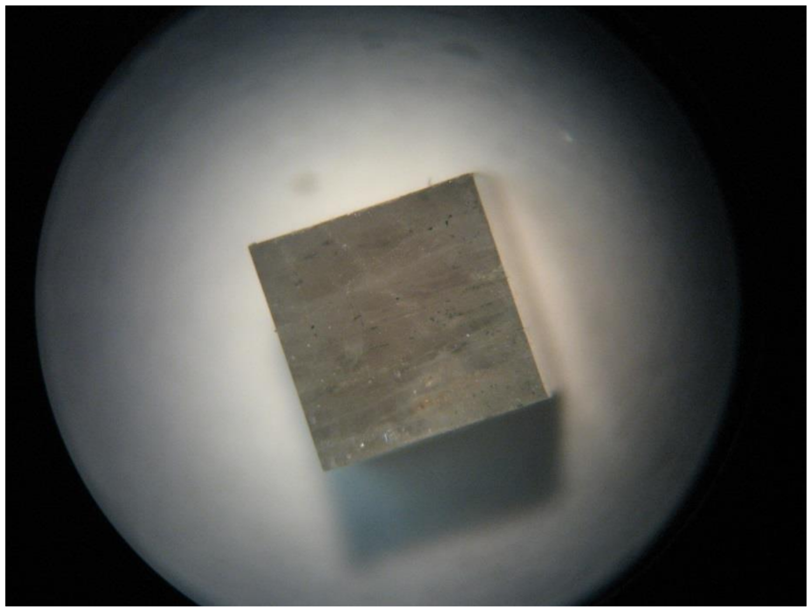


Echantillon 9706.41, Palermo, USA
Collection Paul Keller, Stuttgart

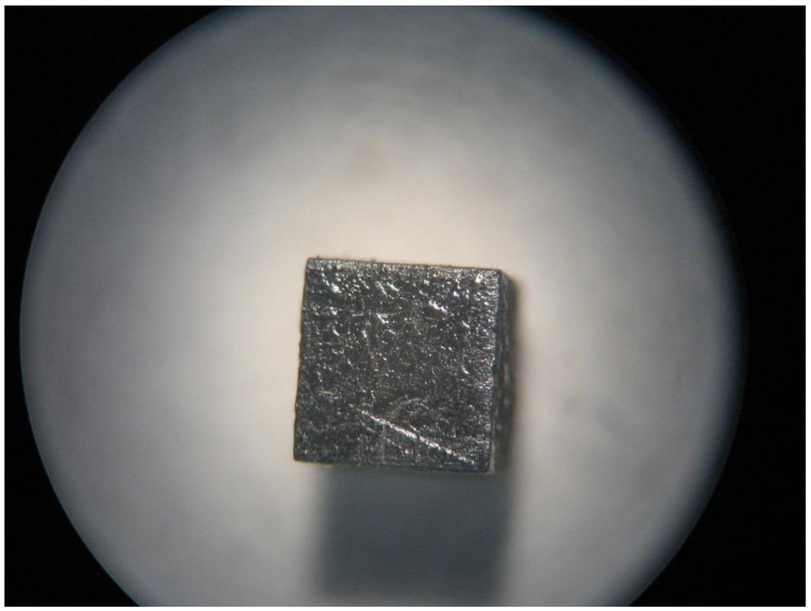
X $LiFePO_4$ = 0,74(1)   100% Fe^{2+}
X $LiMnPO_4$ = 0,21(1)
X $LiMgPO_4$ = 0,05(1)

0,1n HCl, 21mg $KMnO_4$, 120°C, 28 jours

Avant expérience

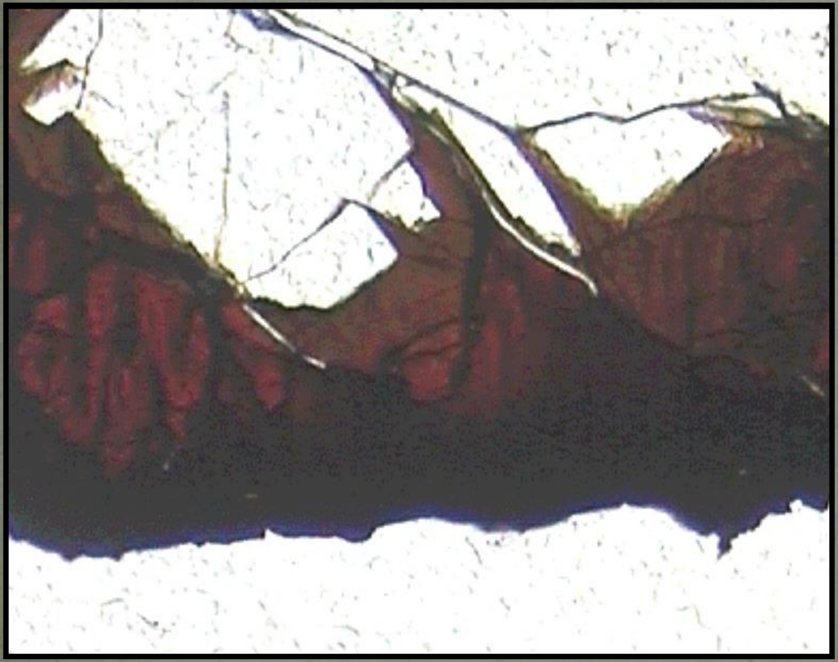


Après expérience



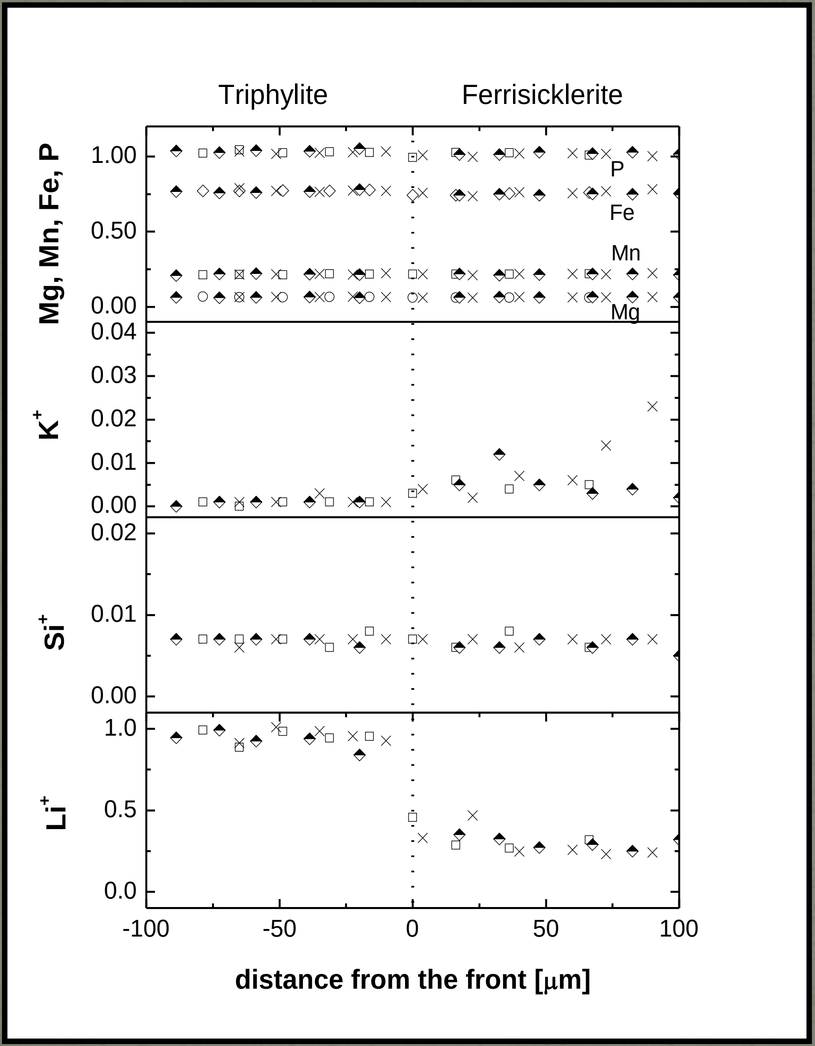
Stabilité de la ferrisicklérite

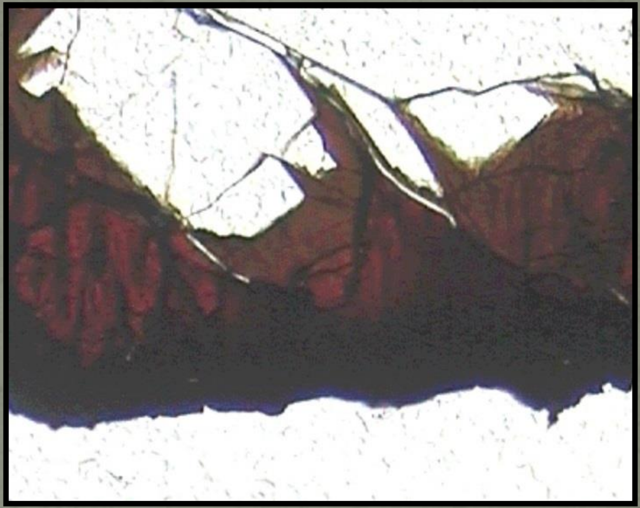
- **Première synthèse hydrothermale de ferrisicklérite**
- **Très basse température**
- **Très haute fO_2**

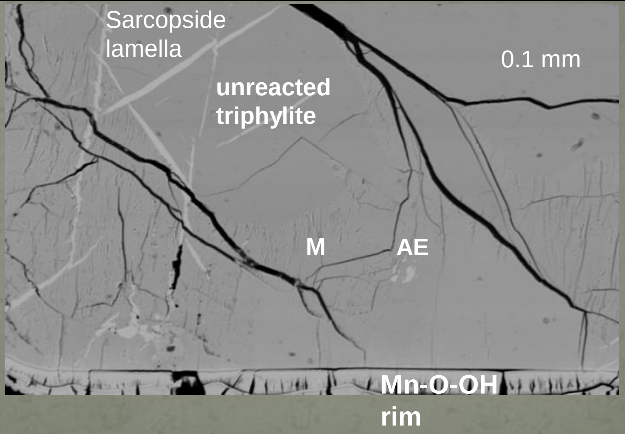


La ferrisicklérite est un minéral d'altération de basse température ?

Diminution du contenu en lithium

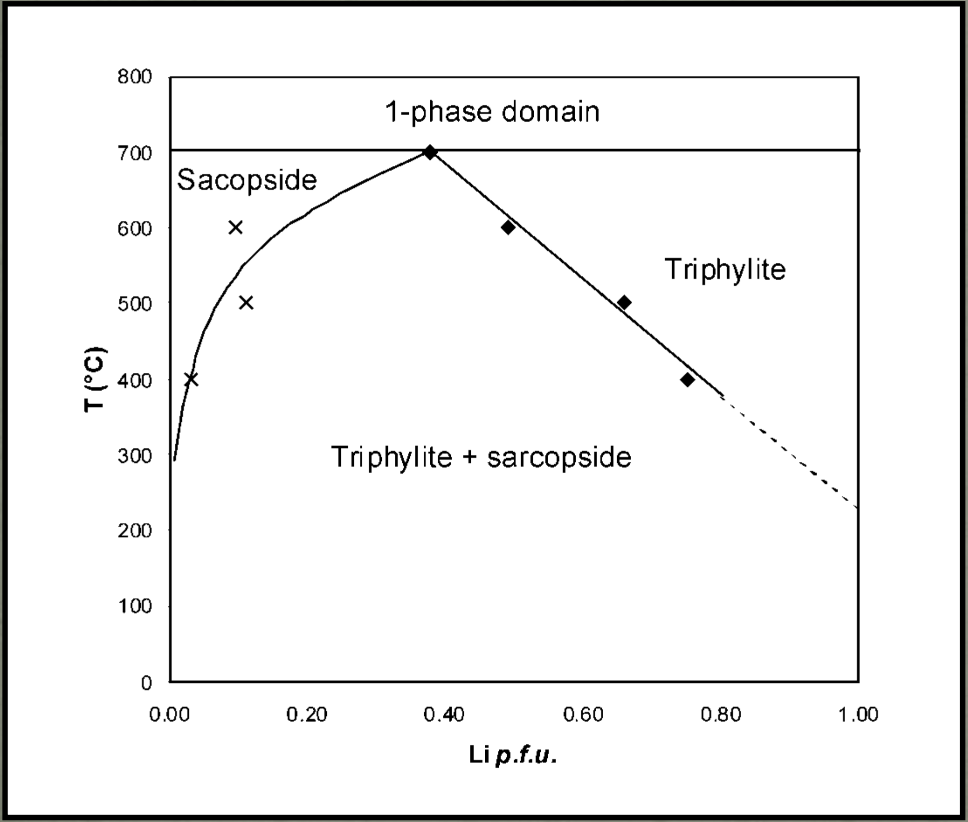






Contact net entre la triphylite et la ferrisicklérite!

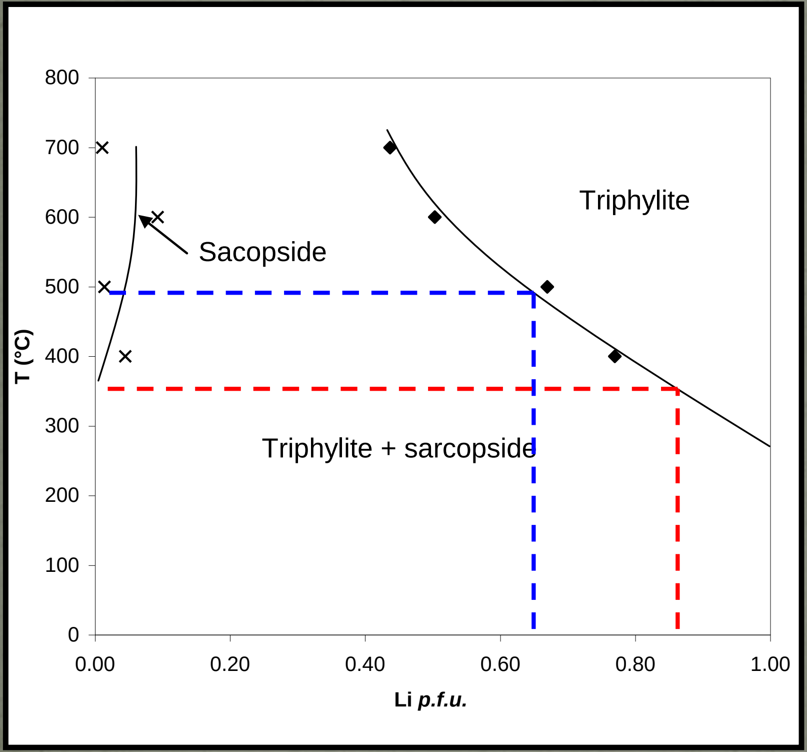
Stabilité de l'association triphylite + sarcopside

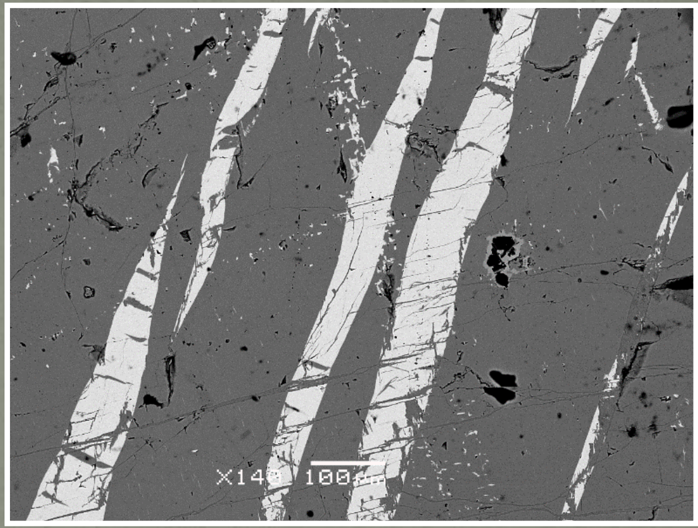


$LiFe^{2+}_{2,5}(PO_4)_2$

- Diminution du contenu en Li de la triphylite, de 0,72 *a.p.u.f.* à 400°C, à 0,48 *a.p.u.f.* à 600°C
- Augmentation du contenu en Li du sarcopside, de 0,01 *a.p.u.f.* à 400°C, à 0,05 *a.p.u.f.* à 600°C
- 1 seule phase au-dessus de 700°C

Estimation des températures de cristallisation





Cañada

35 % sarcopside et 65 % triphylite

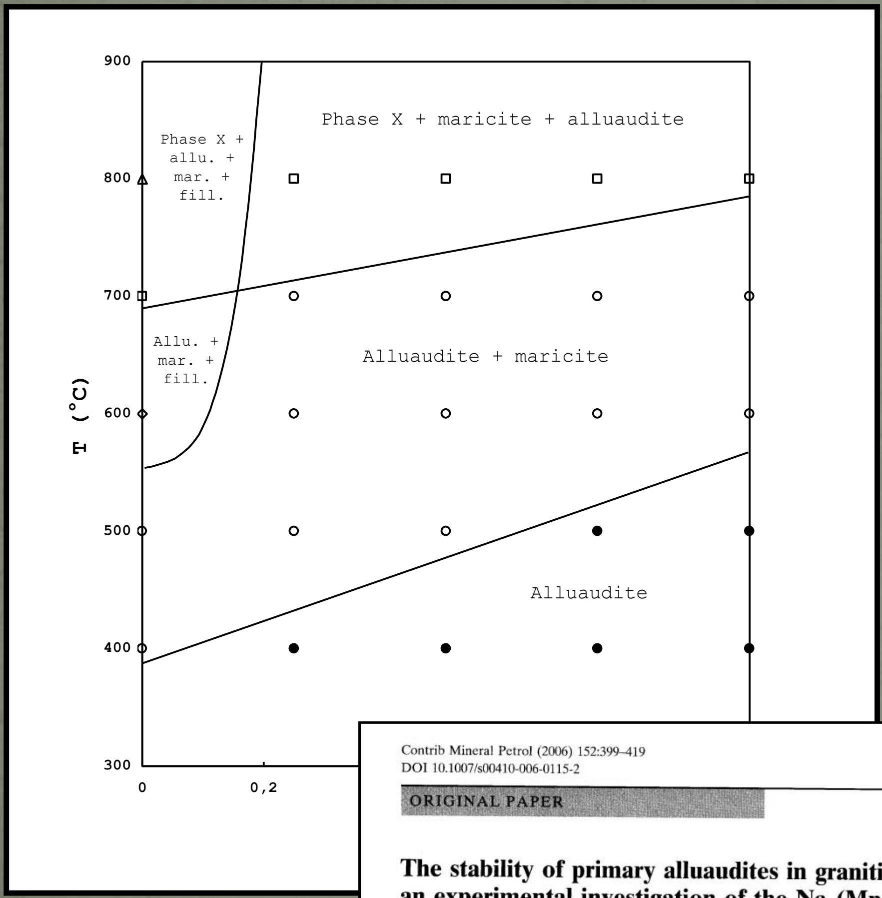
T ~ 500°C

Tsoabismund

15 % sarcopside et 85 % triphylite

T ~ 350°C

La solution solide $Na_2(Mn_{1-x}Fe^{2+}_x)_2Fe^{3+}(PO_4)_3$



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 $Na_2(Mn_{2-2x}Fe_{1+2x})(PO_4)_3$ system

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

- **Basse T** ⇒ **alluaudite**
- **Haute T** ⇒ **"Phase X"**
- **Mn** ⇒ **fillowite [$NaMn_4(PO_4)_3$]**

Pas de maricite [$NaFePO_4$] dans les pegmatites

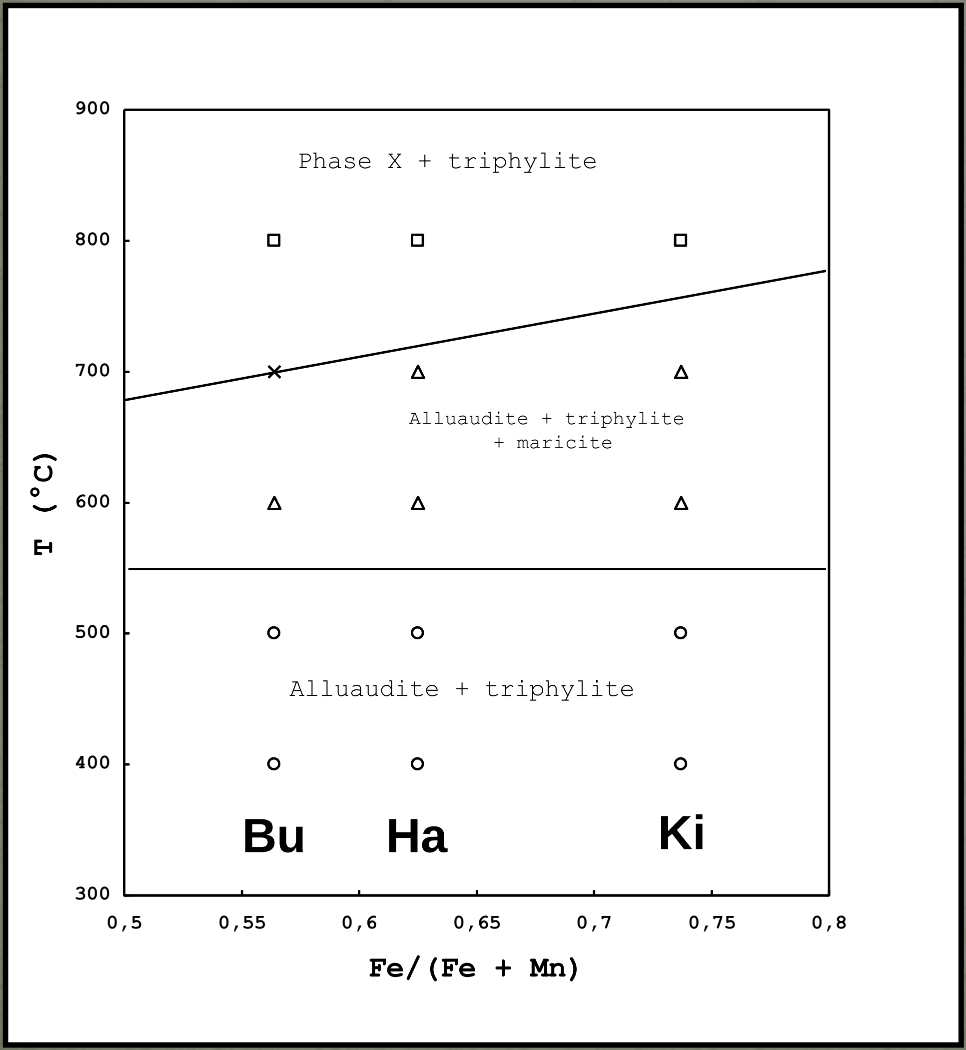
⇓

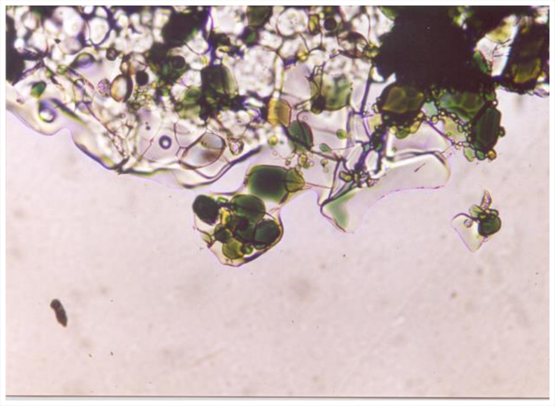
Varulite
$Na_2Mn_2Fe^{3+}(PO_4)_3$
350-400°C

Hagendorfite
$Na_2MnFe^{2+}Fe^{3+}(PO_4)_3$
450-500°C

Ferrohagendorfite
$Na_2Fe^{2+}_2Fe^{3+}(PO_4)_3$
550-600°C

Stabilité de l'association triphylite + alluaudite





Pas de maricite dans les pegmatites

↓

L'association alluaudite + triphylite est stable en-dessous de 500-600°C

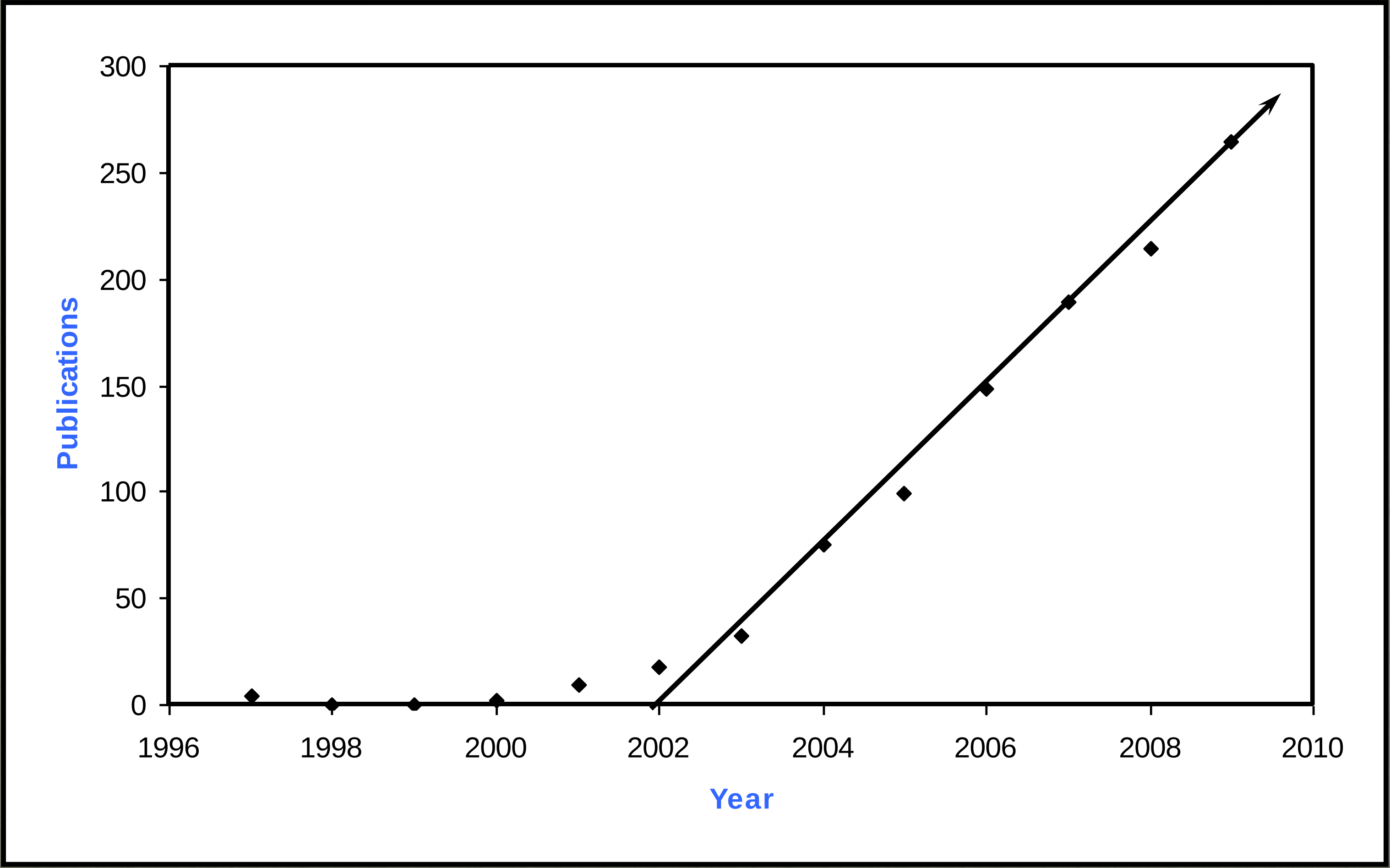
Bu = Buranga, Rwanda
Ha = Hagendorf-Süd, Allemagne
Ki = Kibingo, Rwanda

Applications: Batteries au lithium

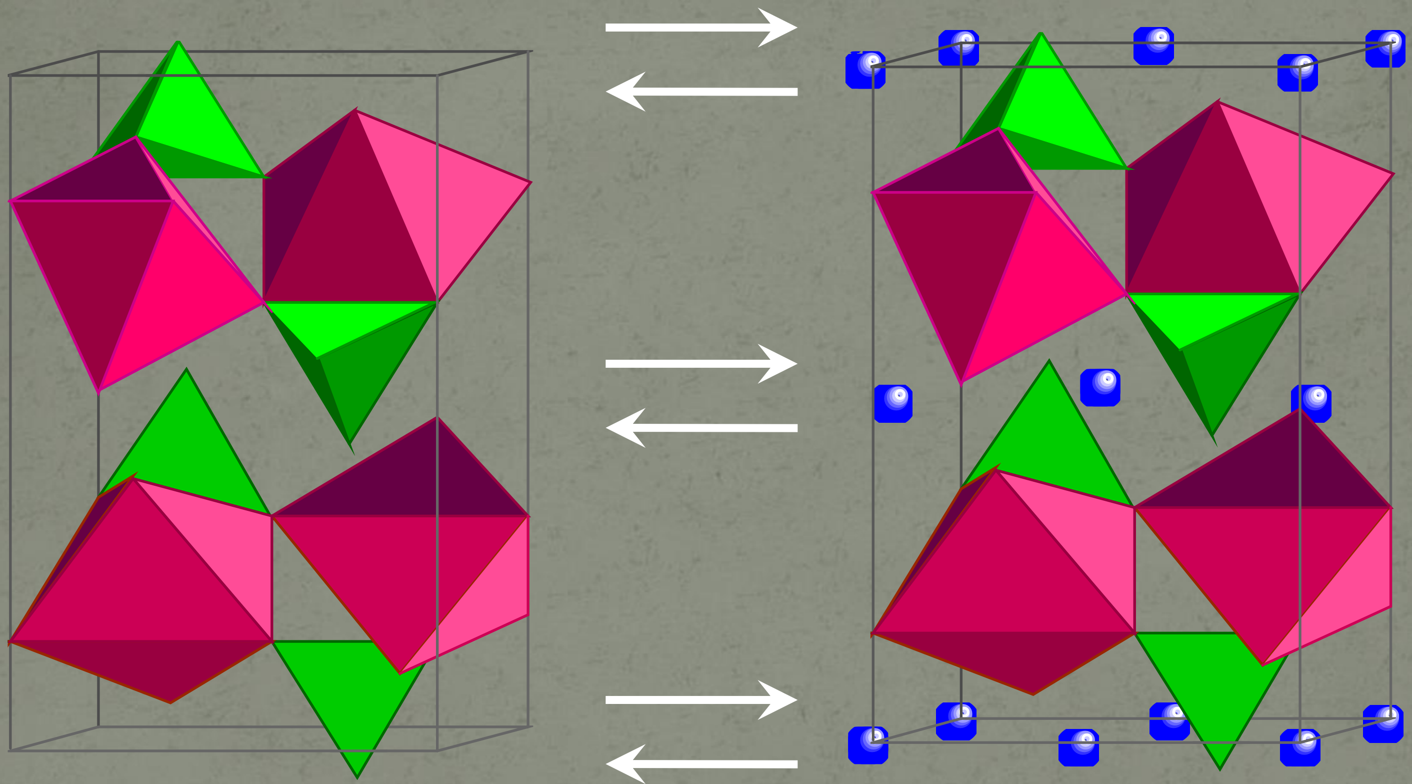
	Layered struct.		Spinel	Triphylite
	$LiCoO_2$	$LiNiCoO_2$	$LiMn_2O_4$	$LiFePO_4$
Capacity (mAh/g)	140-150	170-180	110-120	160-170
Potentiel (V)	3,9	3,8	4,0	3,4
Resistance to cycling	Poor	Poor	+/-	Good
Exchange speed	Good	Good	Good	Good
Electrode density	Good	+/-	+/-	Poor
Security	+/-	?	Good	Good
Cost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

$LiFe^{2+}(PO_4)$ comme matériau de cathode

Propriétés électrochimiques démontrées par Padhi *et al*. (1997)



Intercalation – extraction de Li

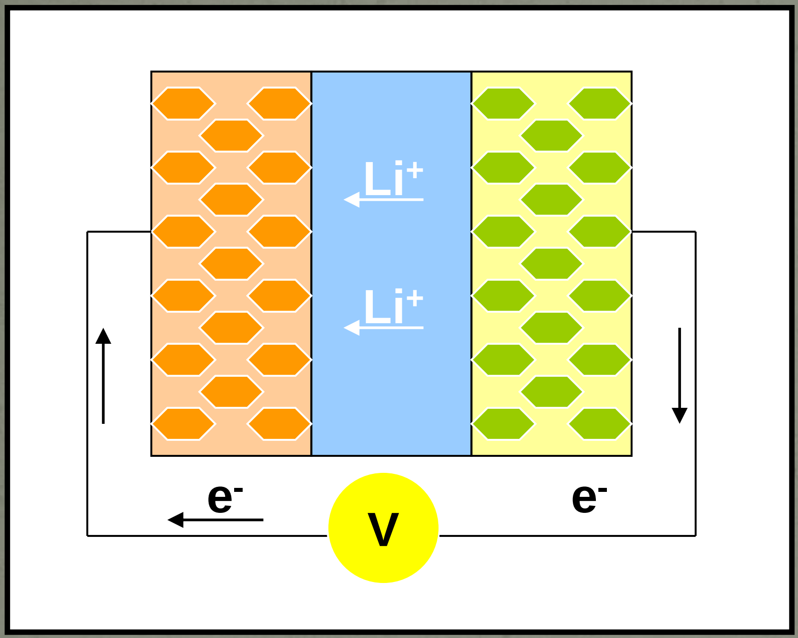


Hétérosite, $Fe^{3+}(PO_4)$ **Triphylite, $LiFe^{2+}(PO_4)$**

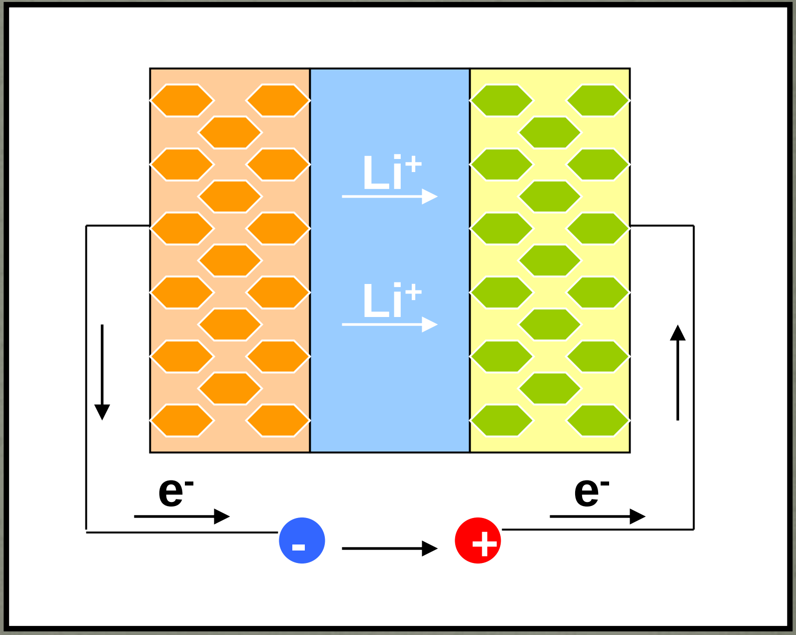
Mécanisme d'oxydation naturelle observé par Quensel (1937) et Mason (1941)

Principe des batteries au lithium

Discharge



Charge



$LiFe^{2+}(PO_4)$ Metallic Li Electrolyte

Performance

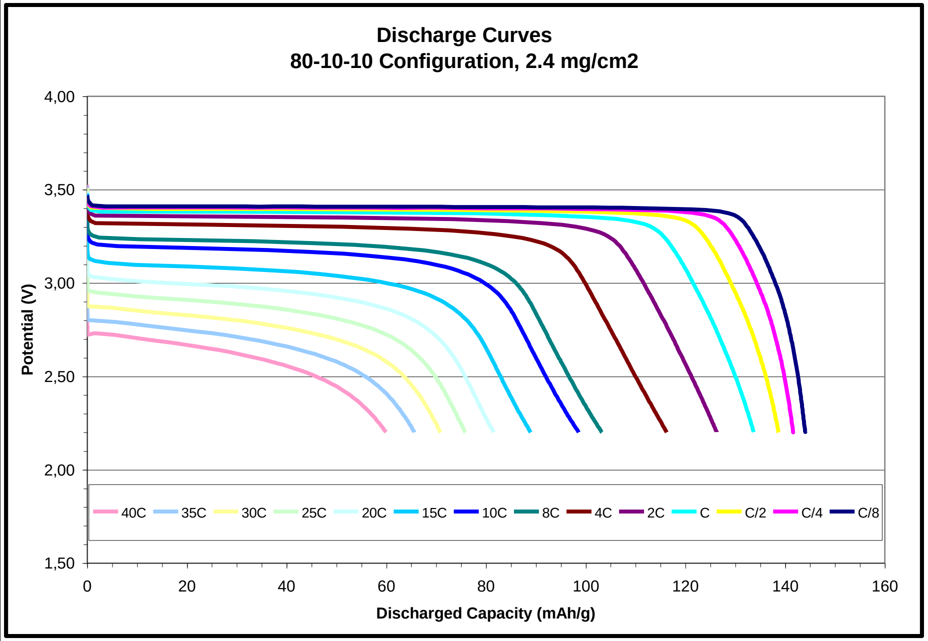
LIÈGE université

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

LETTERS

Battery materials for ultrafast charging and discharging

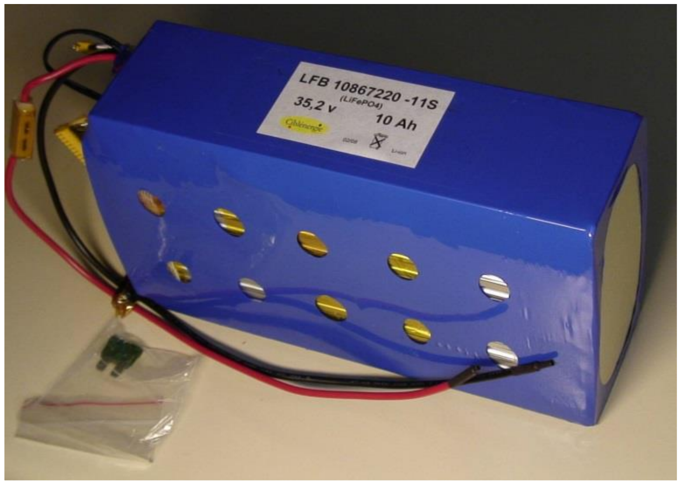
Byoungwoo Kang[1] & Gerbrand Ceder[1]



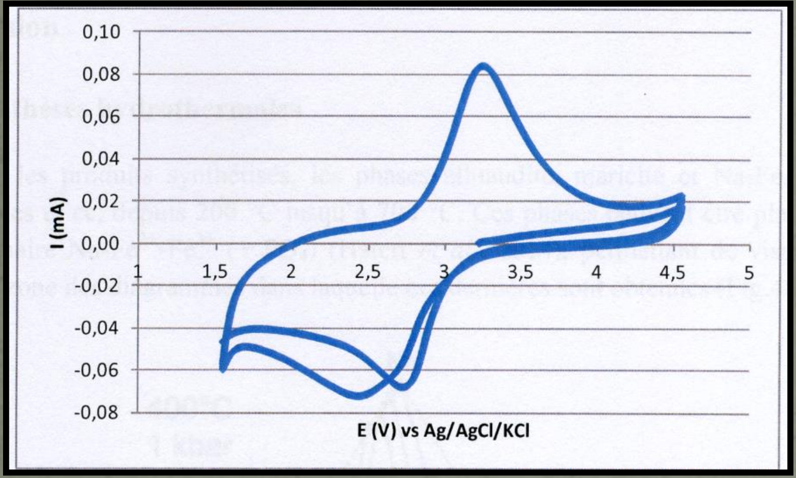
The storage of electrical energy at high charge and discharge rate is an important technology in today's society, and can enable hybrid and plug-in hybrid electric vehicles and provide back-up for wind and solar energy. It is typically believed that in electrochemical systems very high power rates can only be achieved with super-capacitors, which trade high power for low energy density as they only store energy by surface adsorption reactions of charged species on an electrode material[1–3]. 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 $LiFePO_4$ (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.

Production de batteries à base de $LiFePO_4$

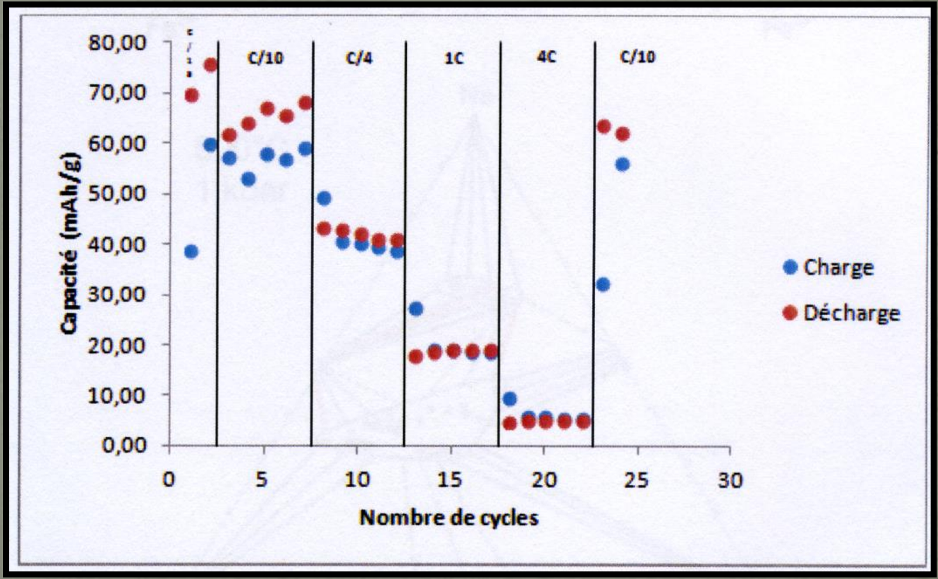
- Voitures
- Vélos électriques
- Ordinateurs portables
- Stockage d'énergie



Etude électrochimique d'alluaudites



$Na_{2.25}Fe^{3+}_{2.25}(PO_4)_3$



Résultats très prometteurs!

Conclusion

La Minéralogie des phosphates n'a pas encore dit son dernier mot…..

Namibie, 2015