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

Pegmatite phosphates: from the field to the lab.

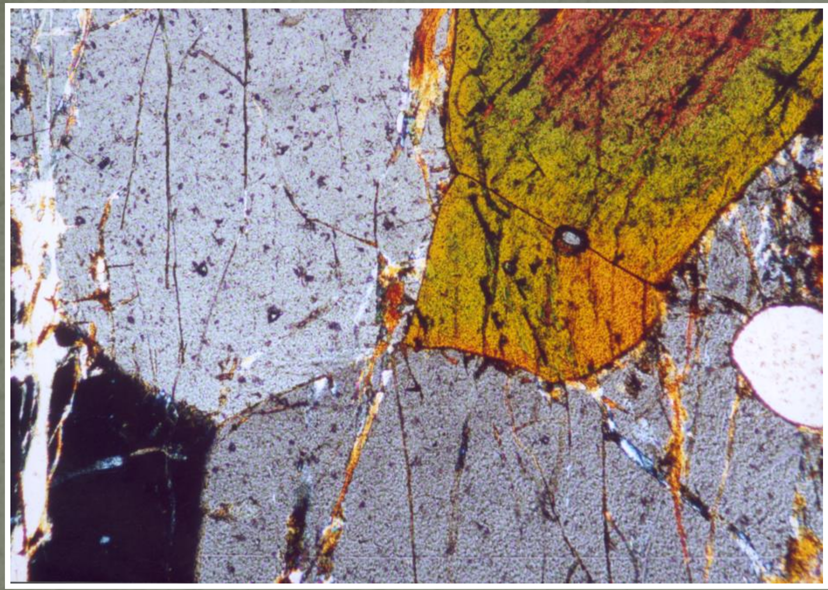
Prof. Frédéric Hatert

Pegmatite Workshop, 2017

Contents

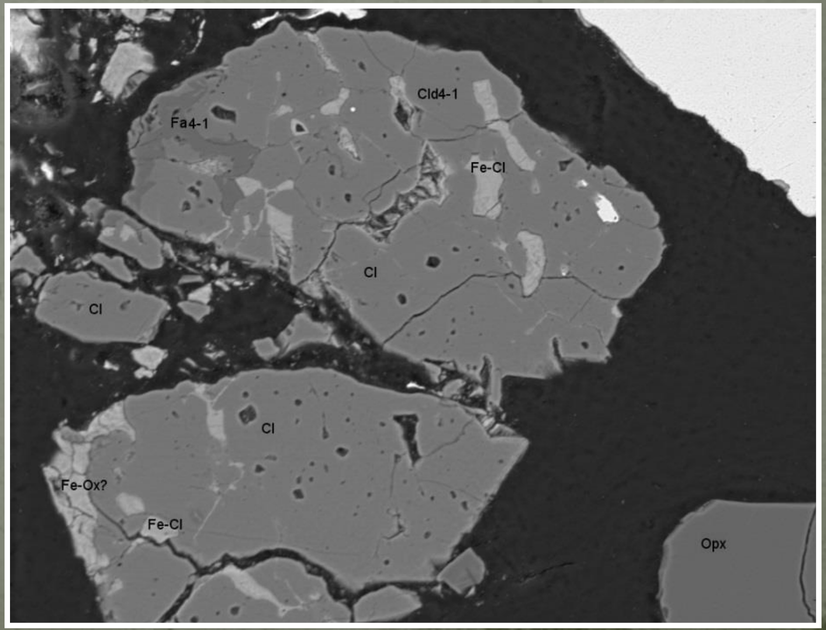
Occurrence

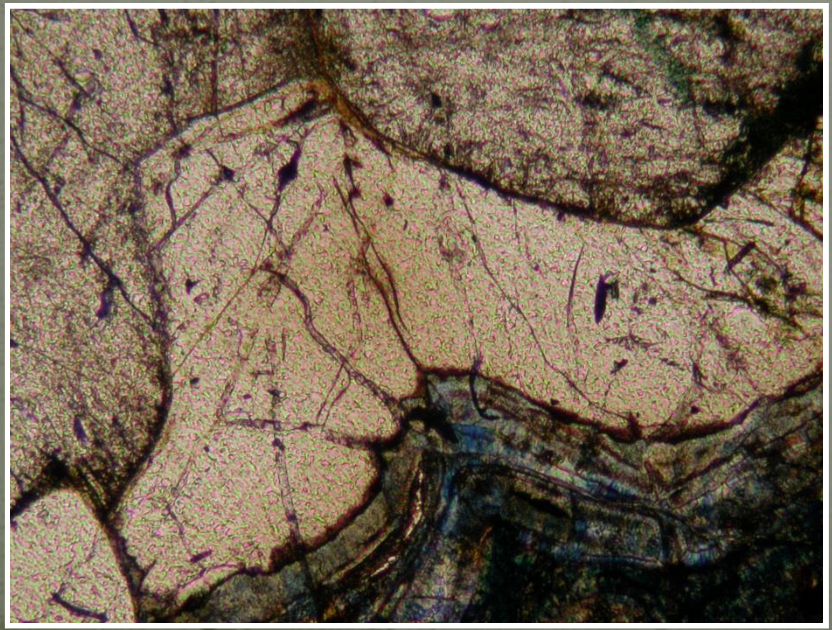
- -Granitic pegmatites
- -Metamorphic rocks
- -Meteorites



Fillowite + alluaudite, Kabira pegmatite, Uganda

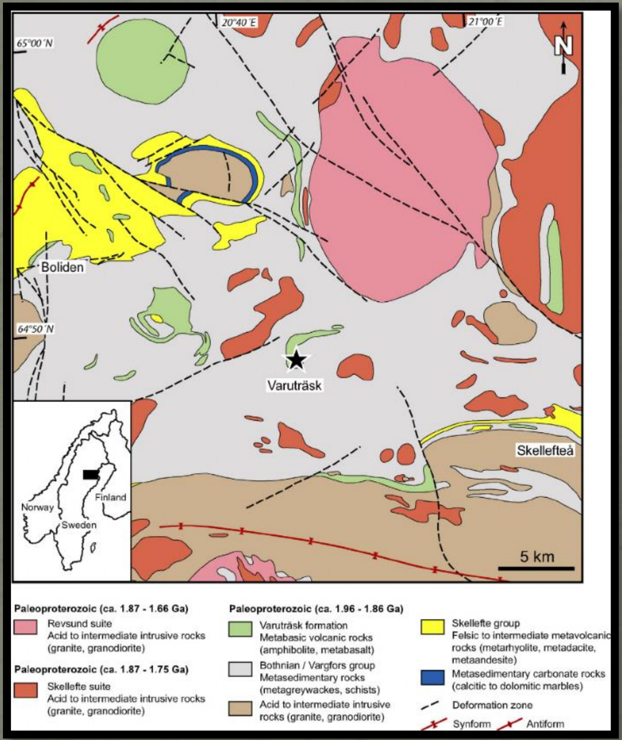
Chladniite, GRA 95209 meteorite





Johnsomervilleite, Loch Quoich, Scotland

The Varuträsk pegmatite



Percy Quensel (1881-1966)

Brian Mason (1917-2009)

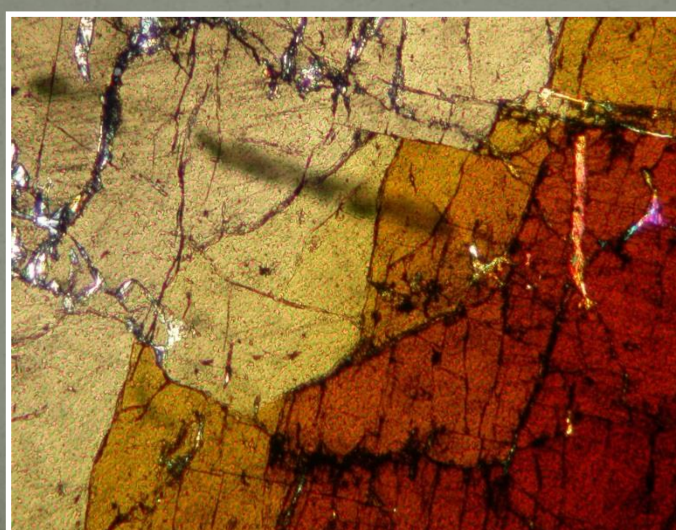
The triphylite group

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

(Lithiophilite) (Sicklerite) (Purpurite)

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

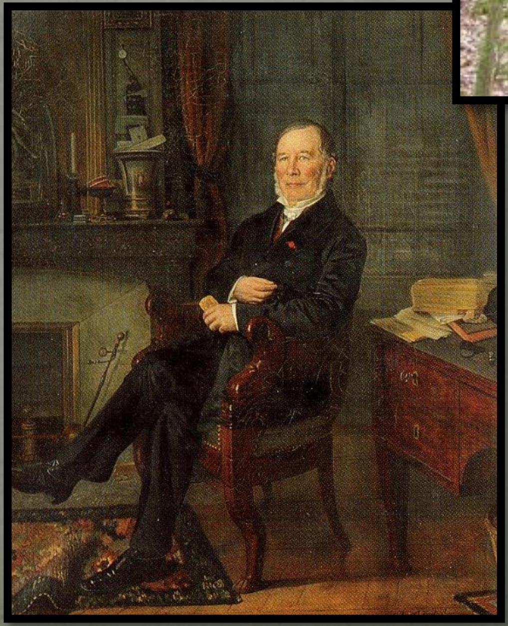
(Triphylite) (Ferrisicklerite) (Heterosite)



The alluaudite group

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

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

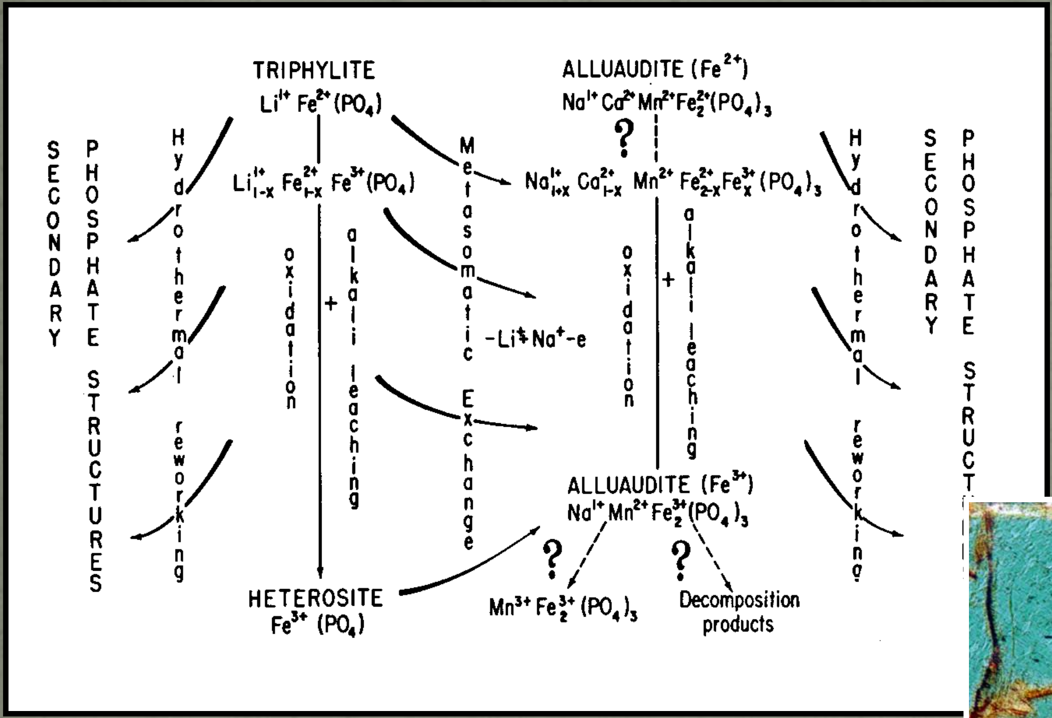


François II Alluaud (1778-1866)
Mayor of Limoges and mineralogist

Augustin-Alexis Damour
(1808-1902)

Université de Liège

Genesis of alluaudites

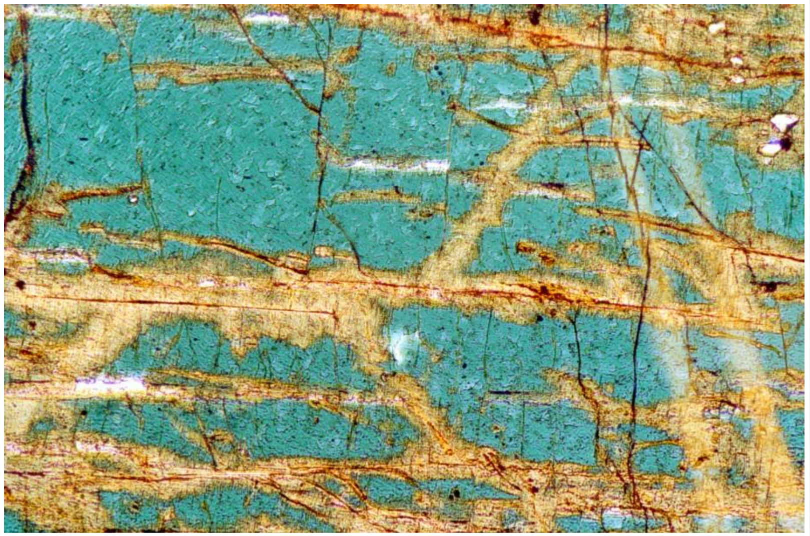


- **Secondary origin**
- **Primary origin**

Oxidation mechanism

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

$$Na^+ + Fe^{2+} \Rightarrow [] + Fe^{3+}$$



Alluaudite, Kibingo pegmatite, Rwanda

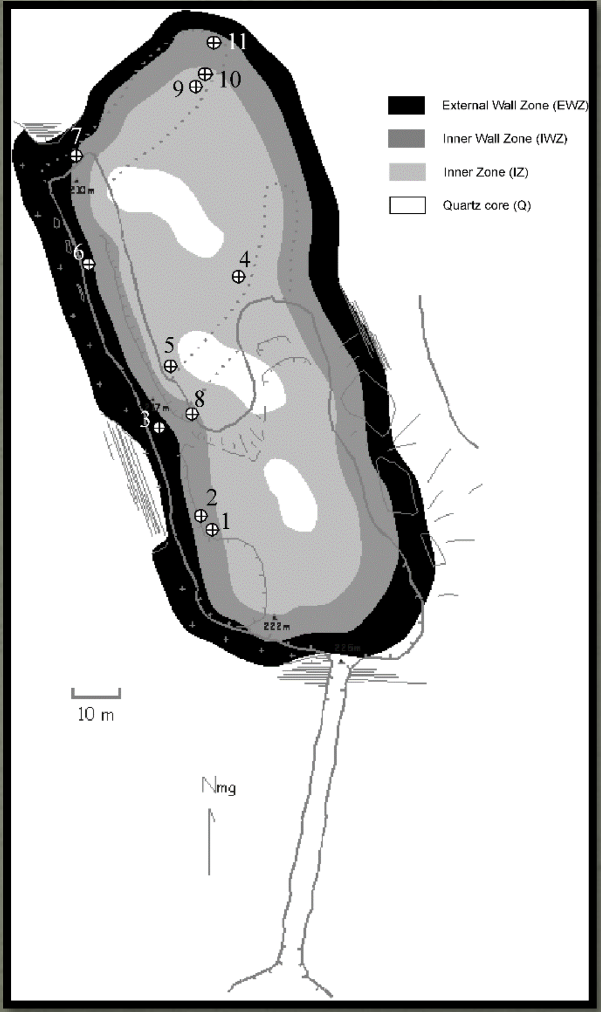
Université de Liège

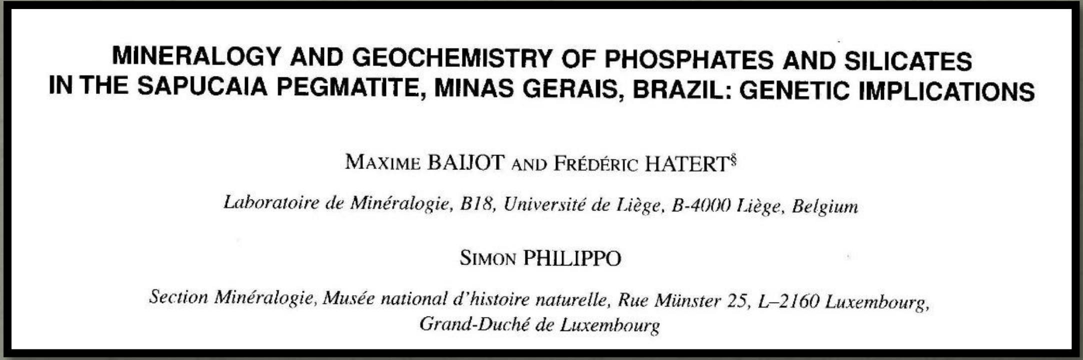
Let's go to the field!

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

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

Pegmatite zoning




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

Fe-Mn phosphates in pegmatites

Buranga pegmatite, Rwanda

Sapucaia pegmatite, Brazil

Back to the lab…

Fe-Mn phosphates

Petrography

Al phosphates

Thin sections

The triphylite + sarcopside assemblage

Université de Liège

Intercroissances et inclusions
dans les associations graftonite-sarcopside-triphylite

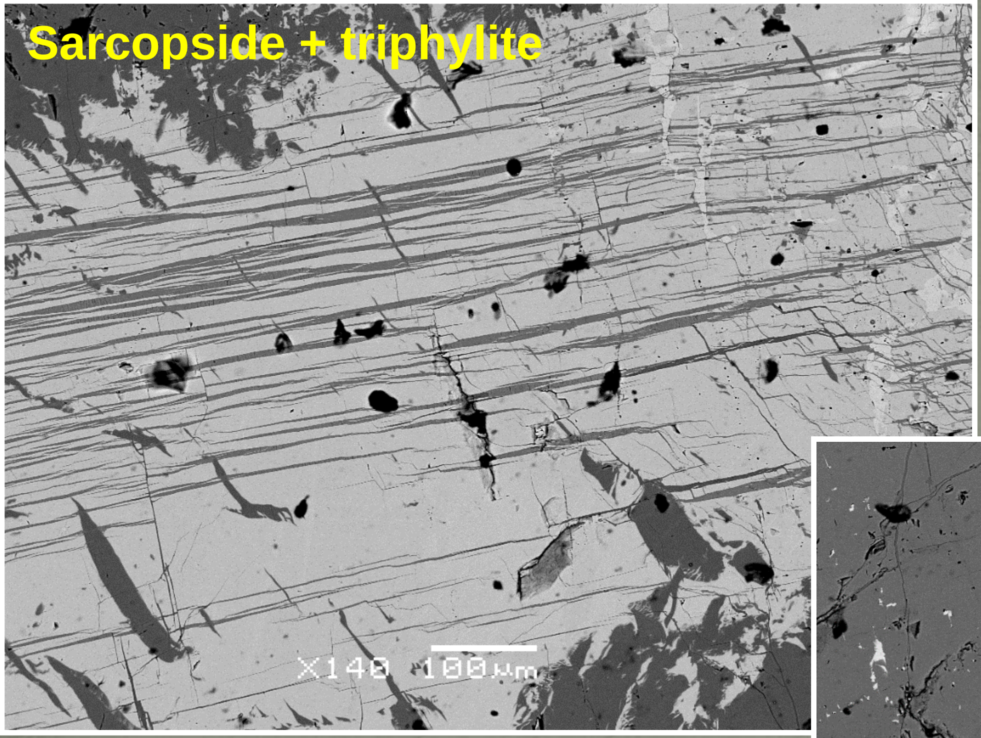
par André-Mathieu FRANSOLET,
Institut de Minéralogie, Université de Liège [1].

Fransolet, 1977

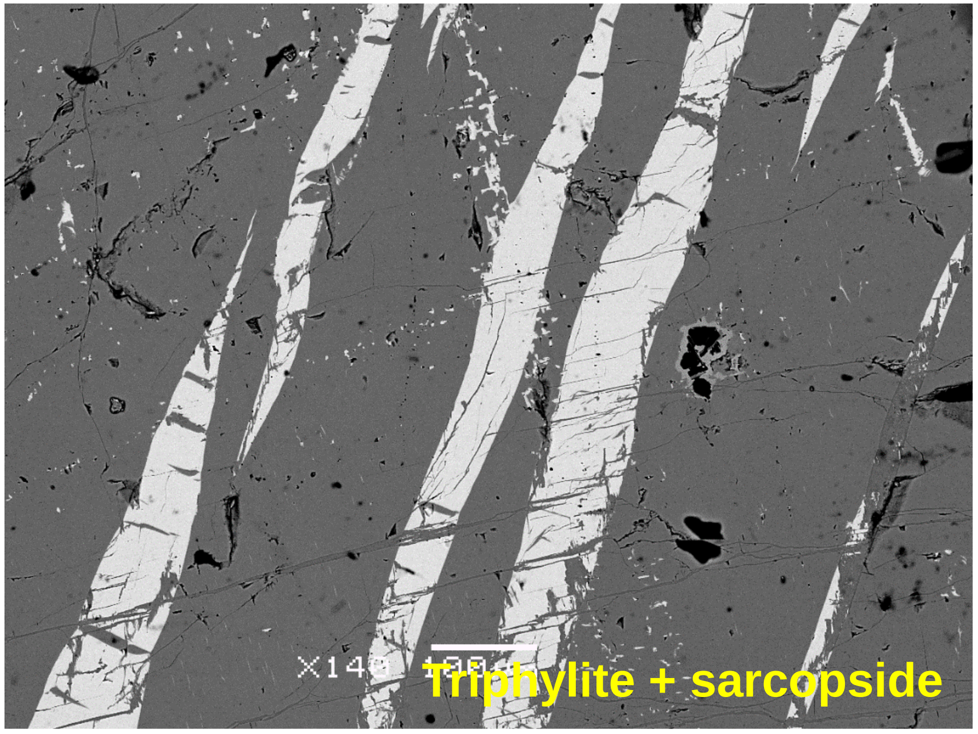
Sarcopside $(Fe,Mn)_3(PO_4)_2$

The triphylite + sarcopside assemblage

Université de Liège



Cañada pegmatite, Spain



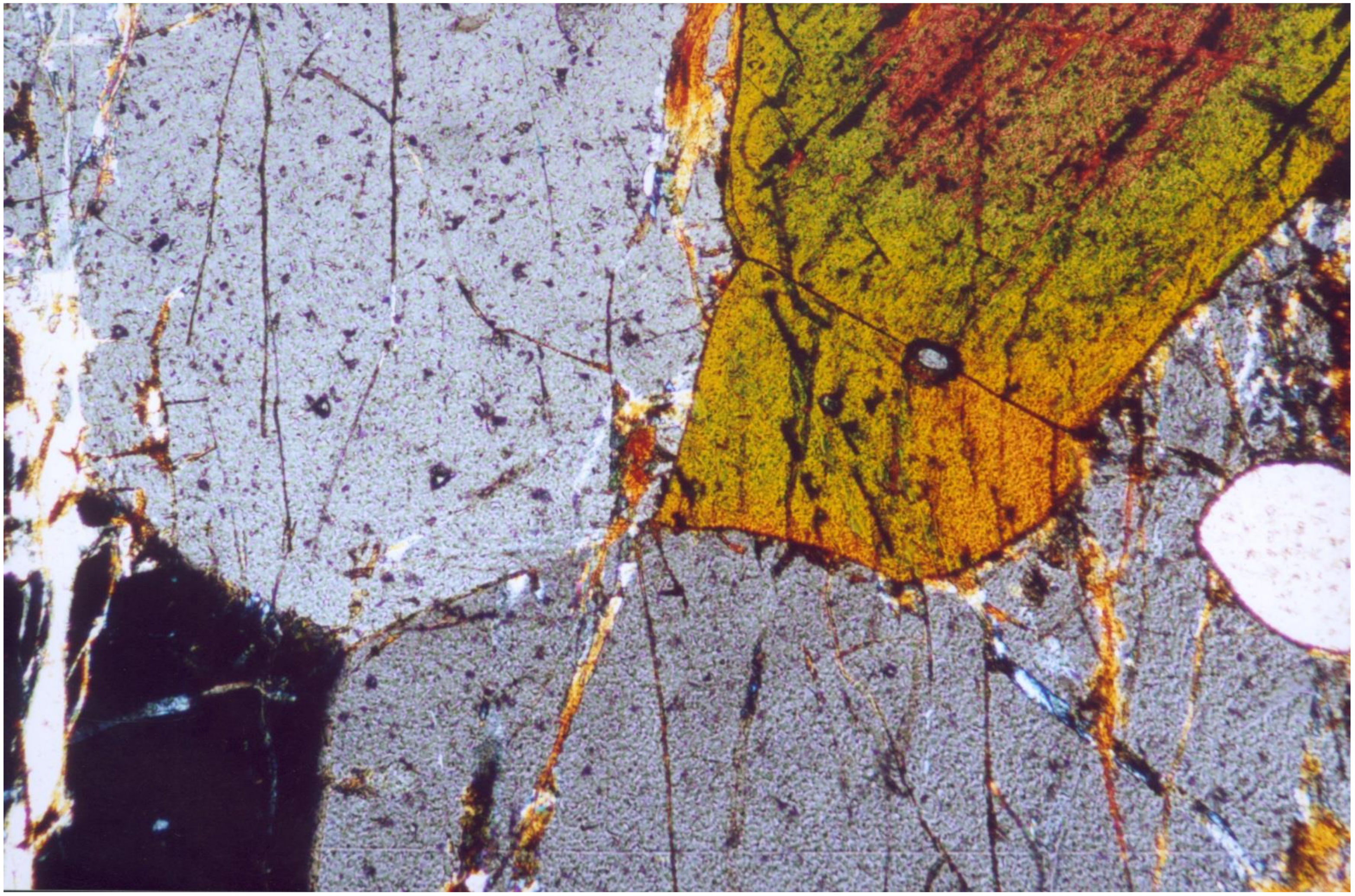
Lamellar textures

↓

EXSOLUTIONS!!

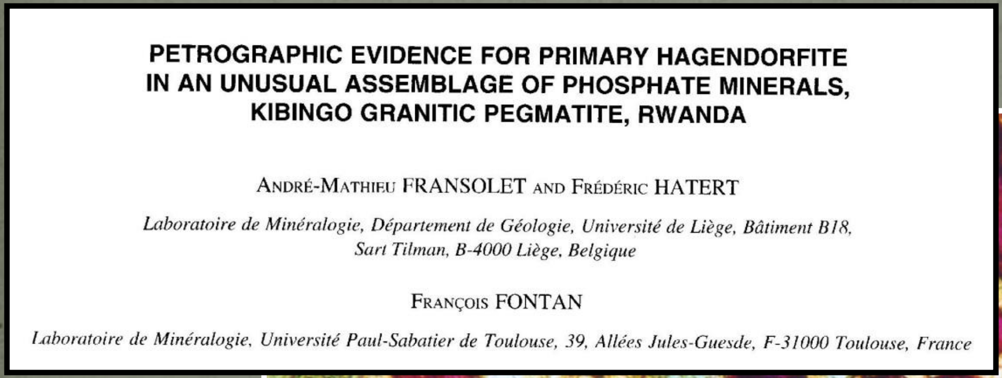
Pictures: E. Roda Robles

The alluaudite + fillowite assemblage



Alluaudite + fillowite, Kabira, Uganda

The triphylite + alluaudite assemblage



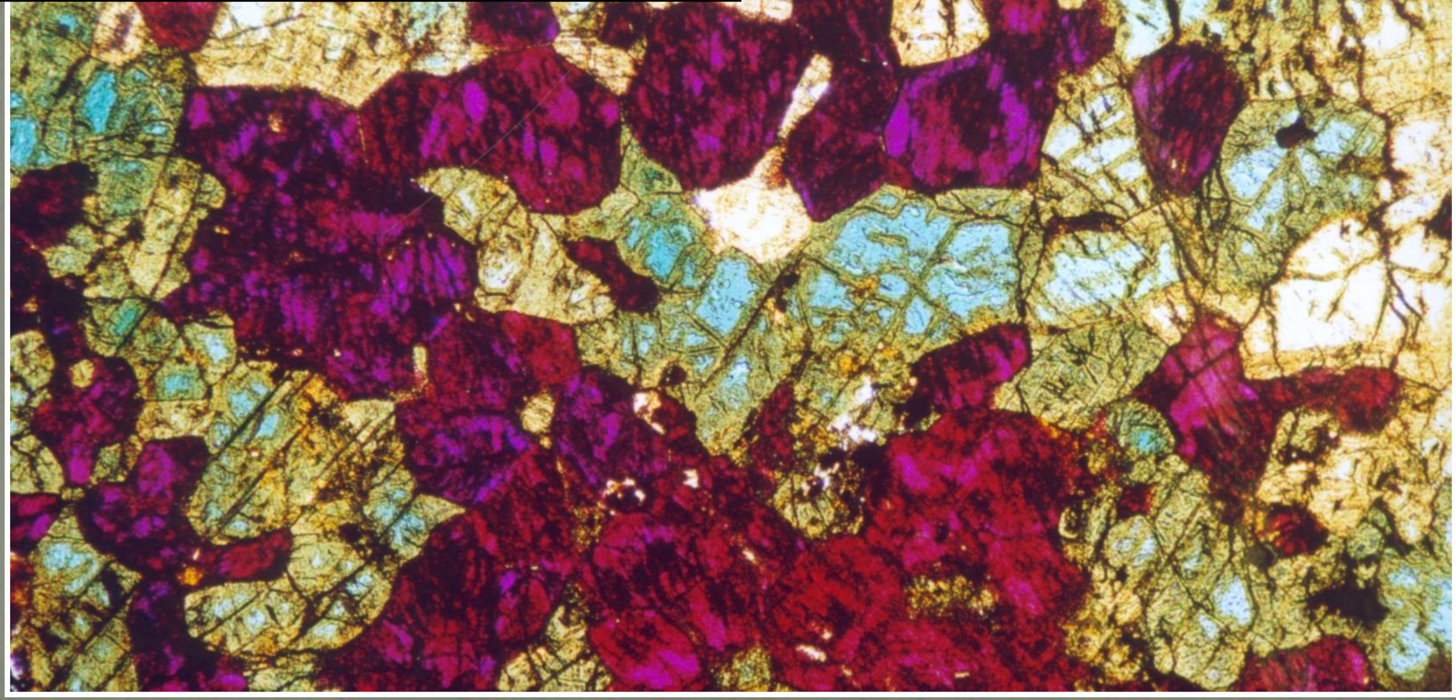
PETROGRAPHIC EVIDENCE FOR PRIMARY HAGENDORFITE IN AN UNUSUAL ASSEMBLAGE OF PHOSPHATE MINERALS, KIBINGO GRANITIC PEGMATITE, RWANDA

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

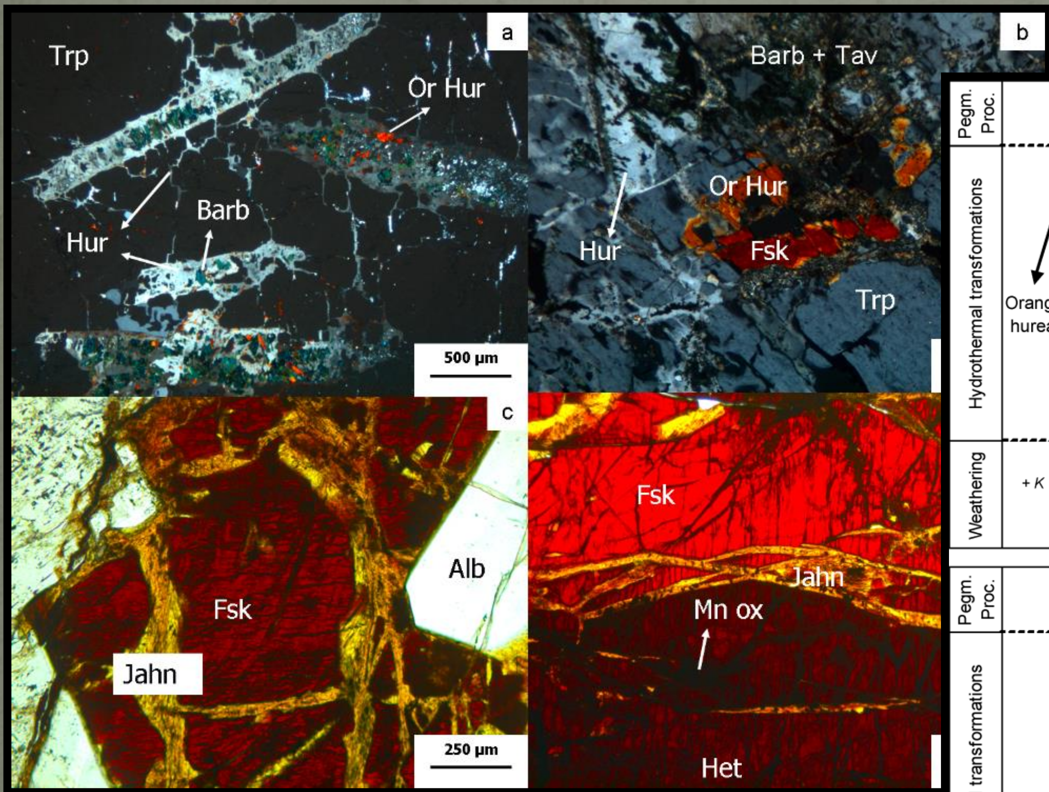
Laboratoire de Minéralogie, Université Paul-Sabatier de Toulouse, 39, Allées Jules-Guesde, F-31000 Toulouse, France

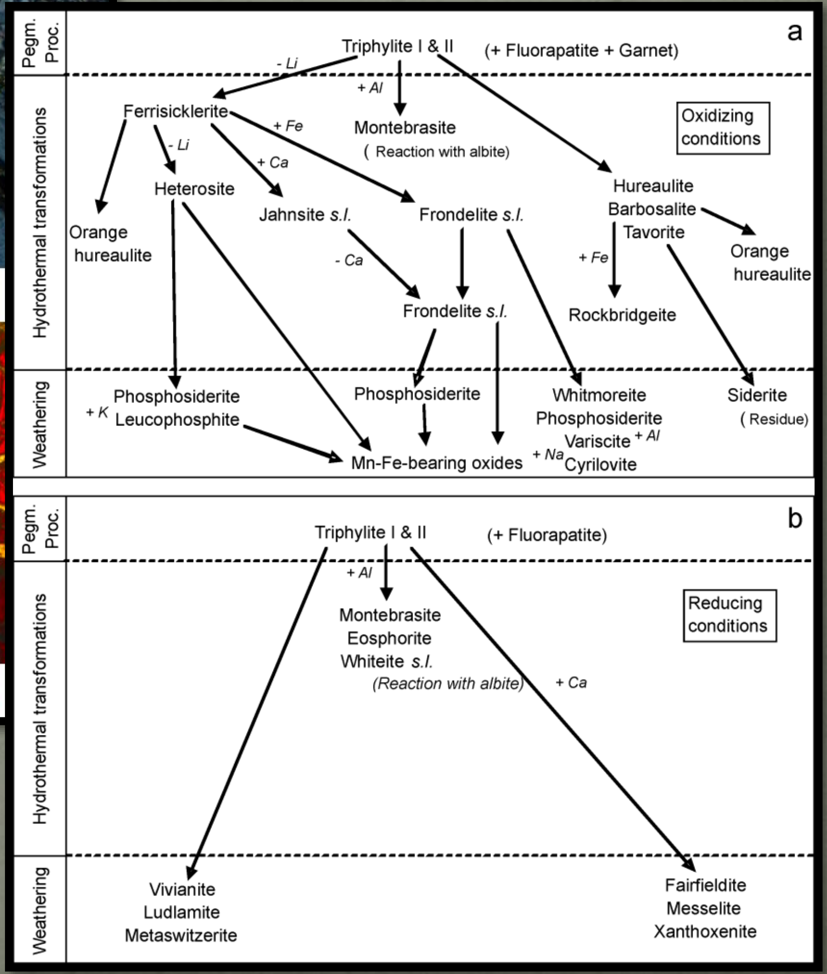


Hagendorfite, alluaudite, and heterosite, Kibingo pegmatite, Rwanda

Complex assemblages from Sapucaia

Université de Liège



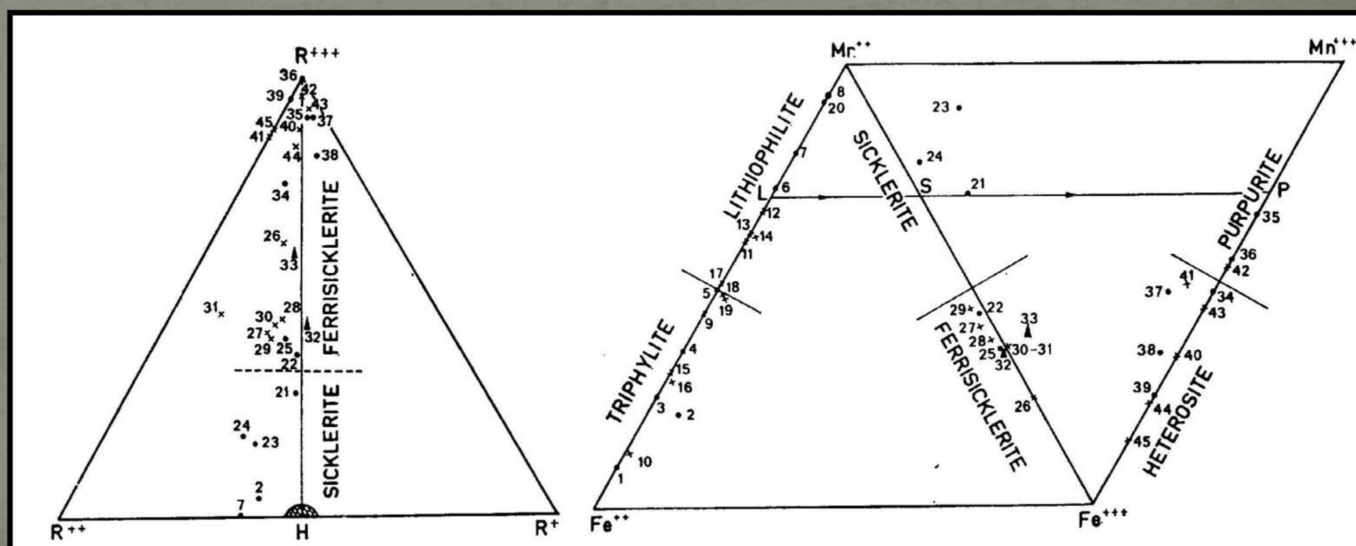


Electron-microprobe analyses

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

par François FONTAN *, Paul HUVELIN **, Marcel ORLIAC * et François PERMINGEAT *.

1976

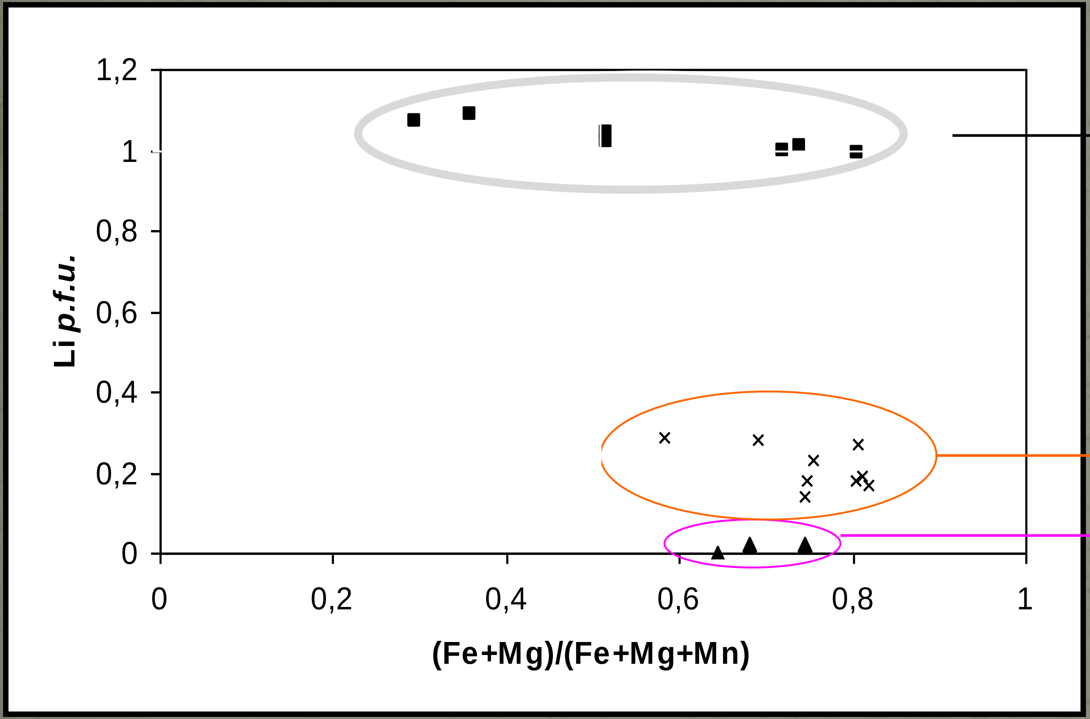


This oxidation is not a continuus process!

SIMS analyses of Li contents

Université de Liège

EMPA, SIMS and crystal-structure analysis of 19 samples



Triphylite-lithiophilite
0.99-1.07 Li *p.f.u.*

Ferrisicklerite
0.14-0.29 Li *p.f.u.*

Heterosite
0.00-0.02 Li *p.f.u.*

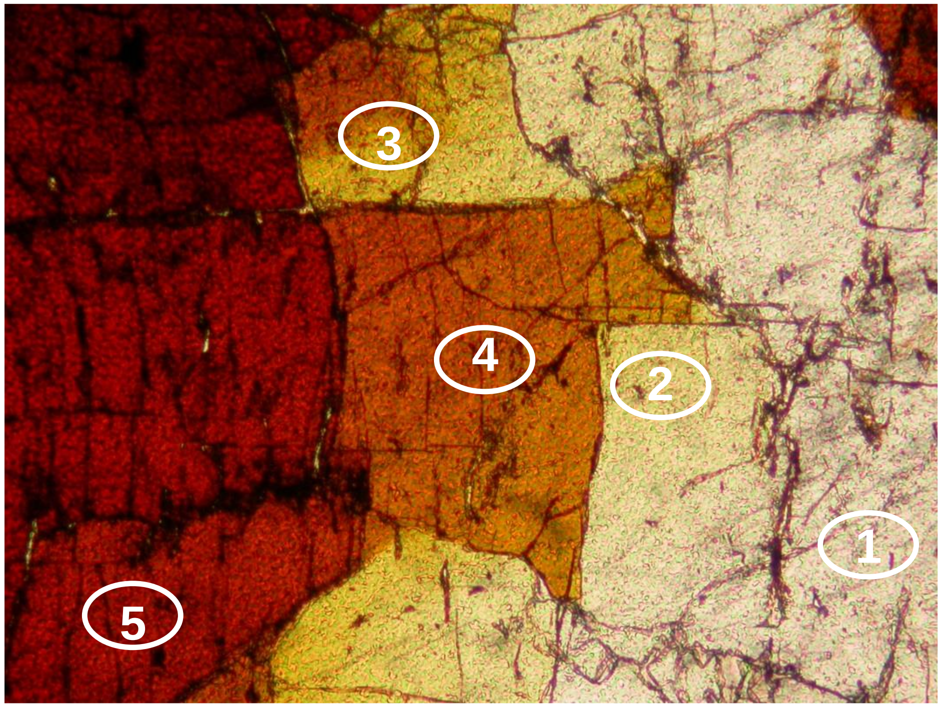
Heterosite may contain up to 0.21 wt. % Li_2O, and ferrisicklerite may show a low Li-content of 1.31 wt. % Li_2O

Close Li-contents!

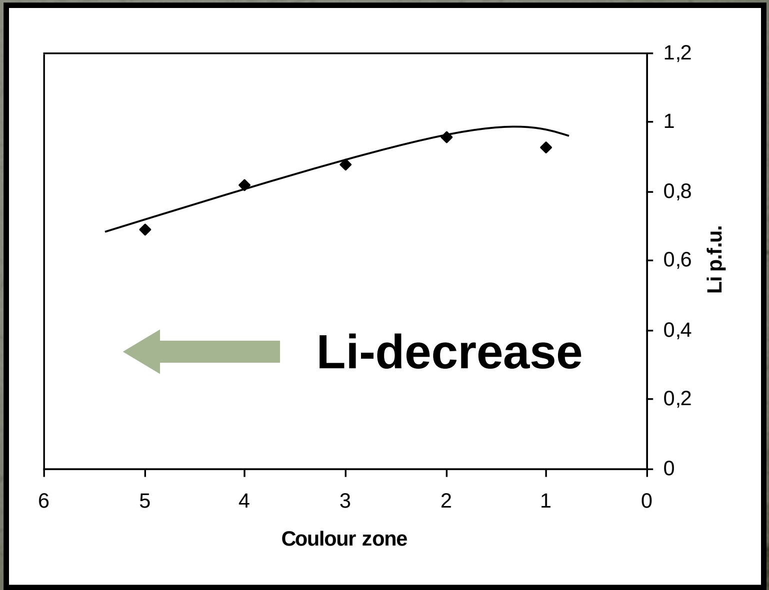
Oxidation of sicklerite

Université de Liège

Sample from the Altaï Mountains, China



1: $Li_{0.93}(Fe^{2+}_{0.03}Fe^{3+}_{0.13}Mn^{2+}_{0.80})(PO_4)$
2: $Li_{0.96}(Fe^{2+}_{0.08}Fe^{3+}_{0.08}Mn^{2+}_{0.81})(PO_4)$
3: $Li_{0.88}(Fe^{3+}_{0.16}Mn^{2+}_{0.80}Mn^{3+}_{0.01})(PO_4)$
4: $Li_{0.82}(Fe^{3+}_{0.16}Mn^{2+}_{0.75}Mn^{3+}_{0.06})(PO_4)$
5: $Li_{0.69}(Fe^{3+}_{0.16}Mn^{2+}_{0.62}Mn^{3+}_{0.19})(PO_4)$



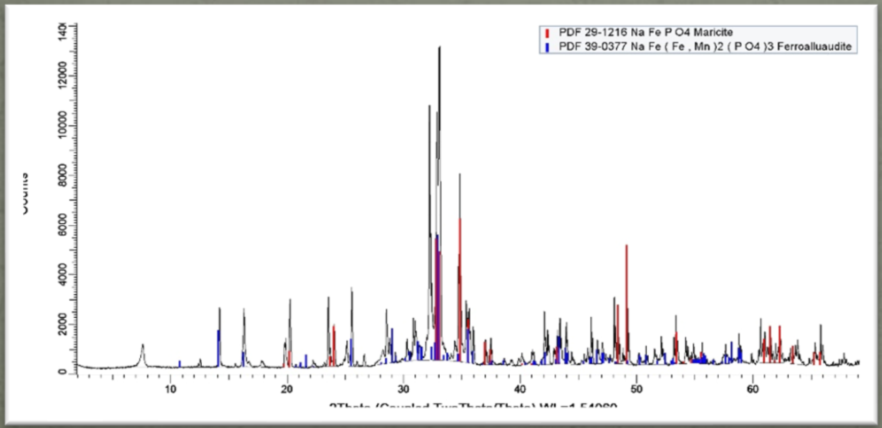
- **The transition from lithiophilite to sicklerite is progressive**
- **The change in colour is due to the presence of Mn^{3+}**

Université de Liège

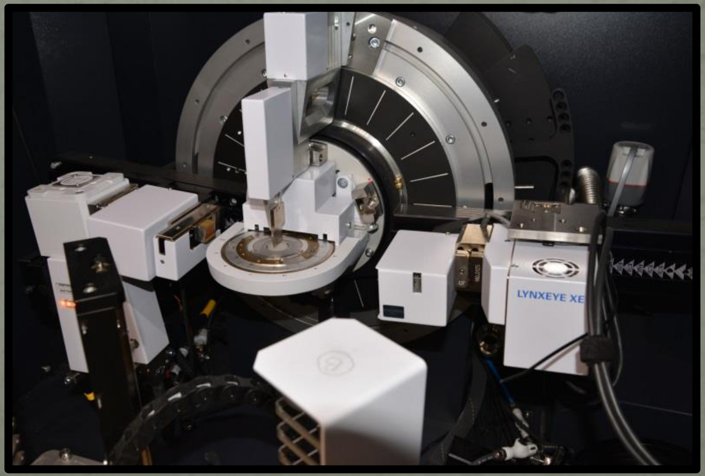
X-ray powder diffraction

Sample preparation

Sample holder



Powder pattern

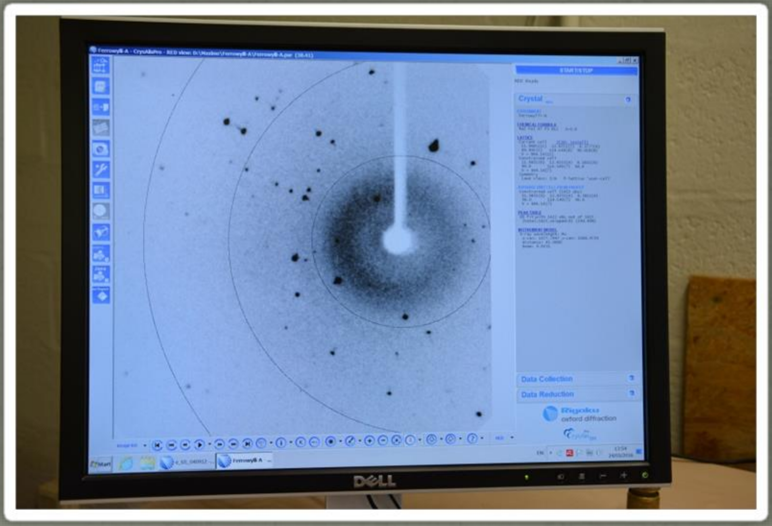


Powder diffractometer

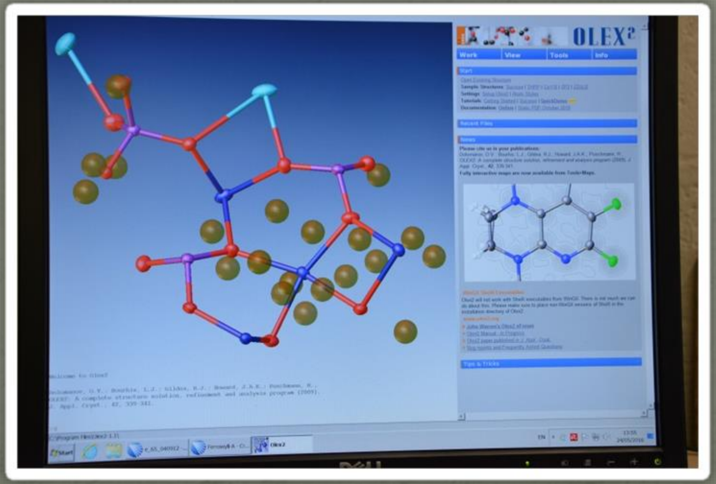
Université de Liège

Single-crystal X-ray diffraction

4-circle diffractometer



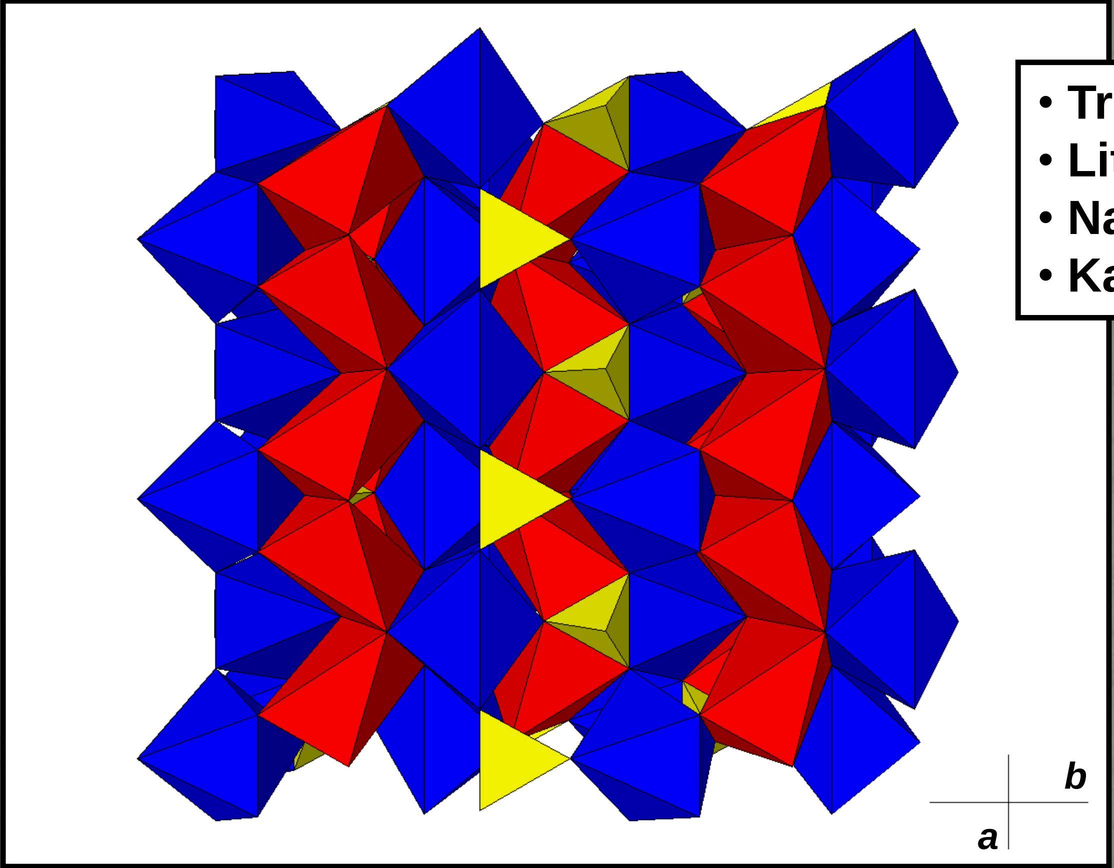
Diffraction spots



Structure determination

Université de Liège

The triphylite structure



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

S.G. *Pmnb*

***a* = 6.092 Å**
***b* = 10.429 Å**
***c* = 4.738 Å**

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

Karenwebberite, a new mineral...

Université de Liège

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

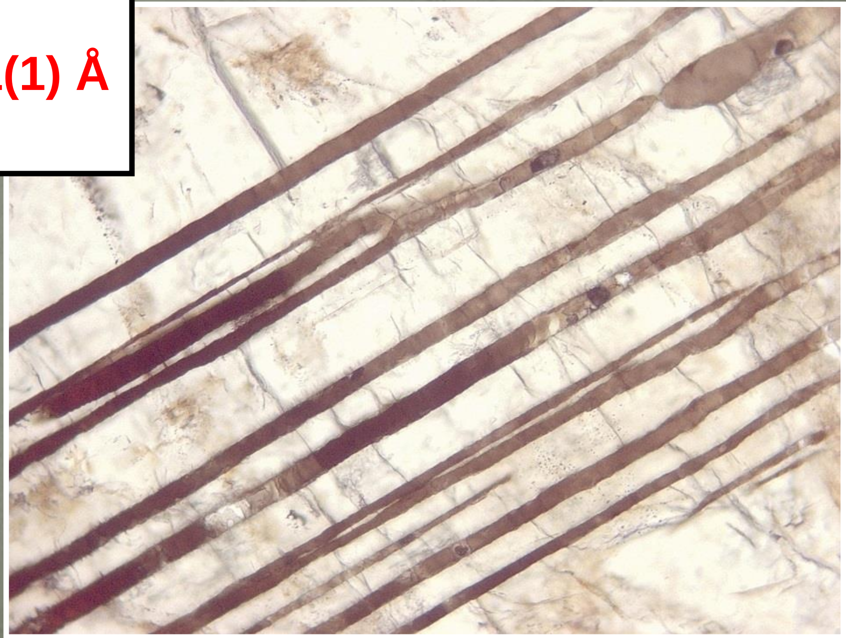
Pietro Vignola,[1] Frédéric Hatert,[2,*] André-Mathieu Fransolet,[2] Olaf Medenbach,[3] Valeria Diella,[1] and Sergio Andò[4]

$NaFe^{2+}PO_4$

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

Pbnm

Karen Louise Webber



Malpensata pegmatite, Italy

Université de Liège

Zavalíaite, a new mineral...

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

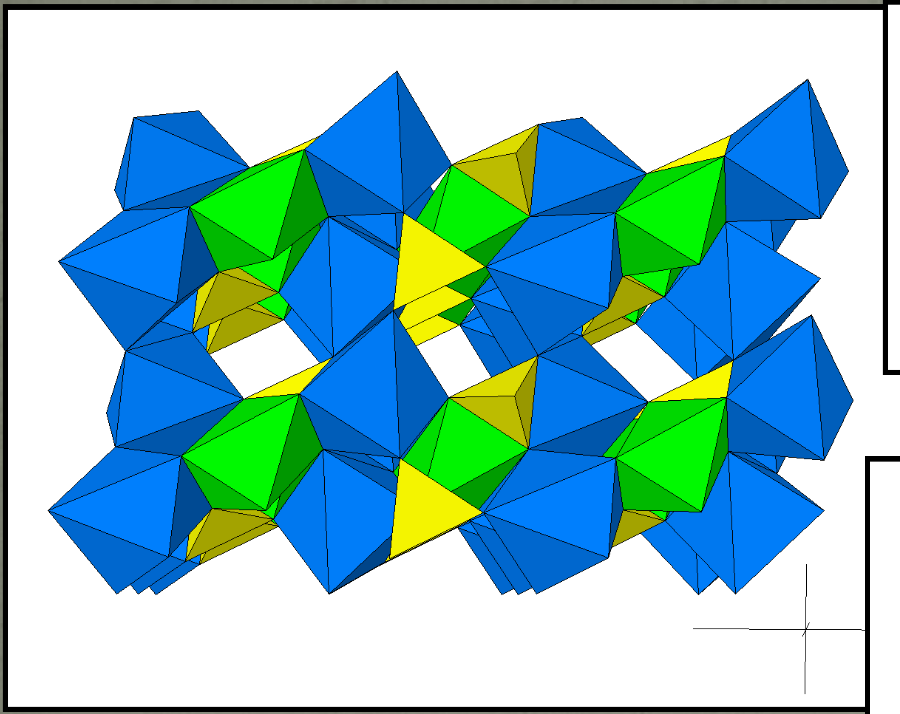
Departimento de Mineralogía y Petrología, Universidad del País Vasco/EHU, Apdo. 644, E–48080 Bilbao, Spain

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

$Mn_3(PO_4)_2$

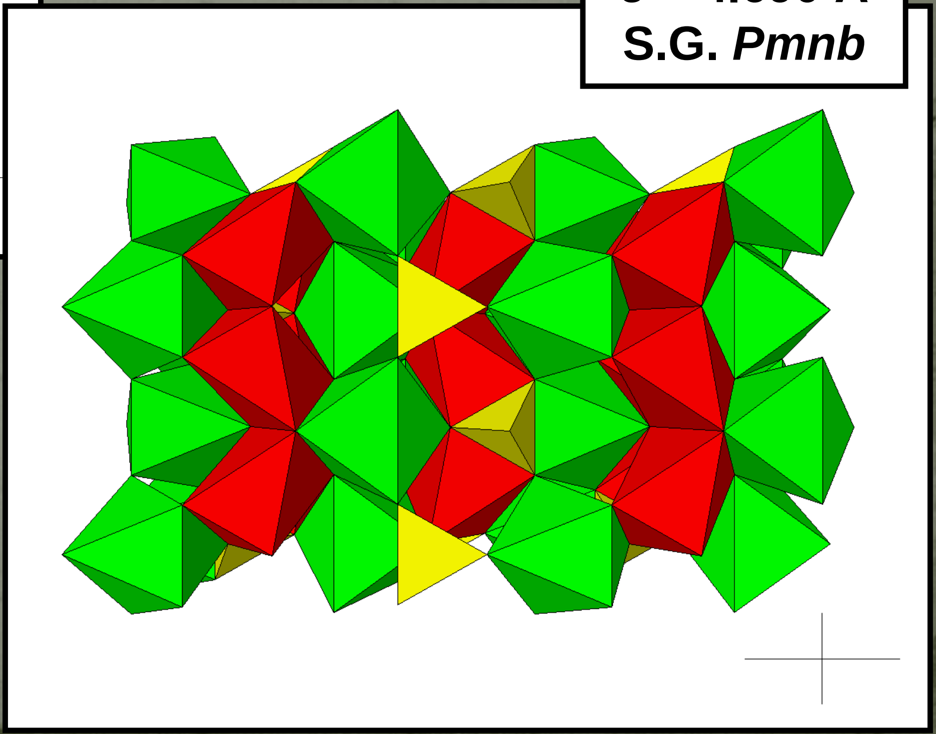
Florencia Márquez Zavalía

The sarcopside structure



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

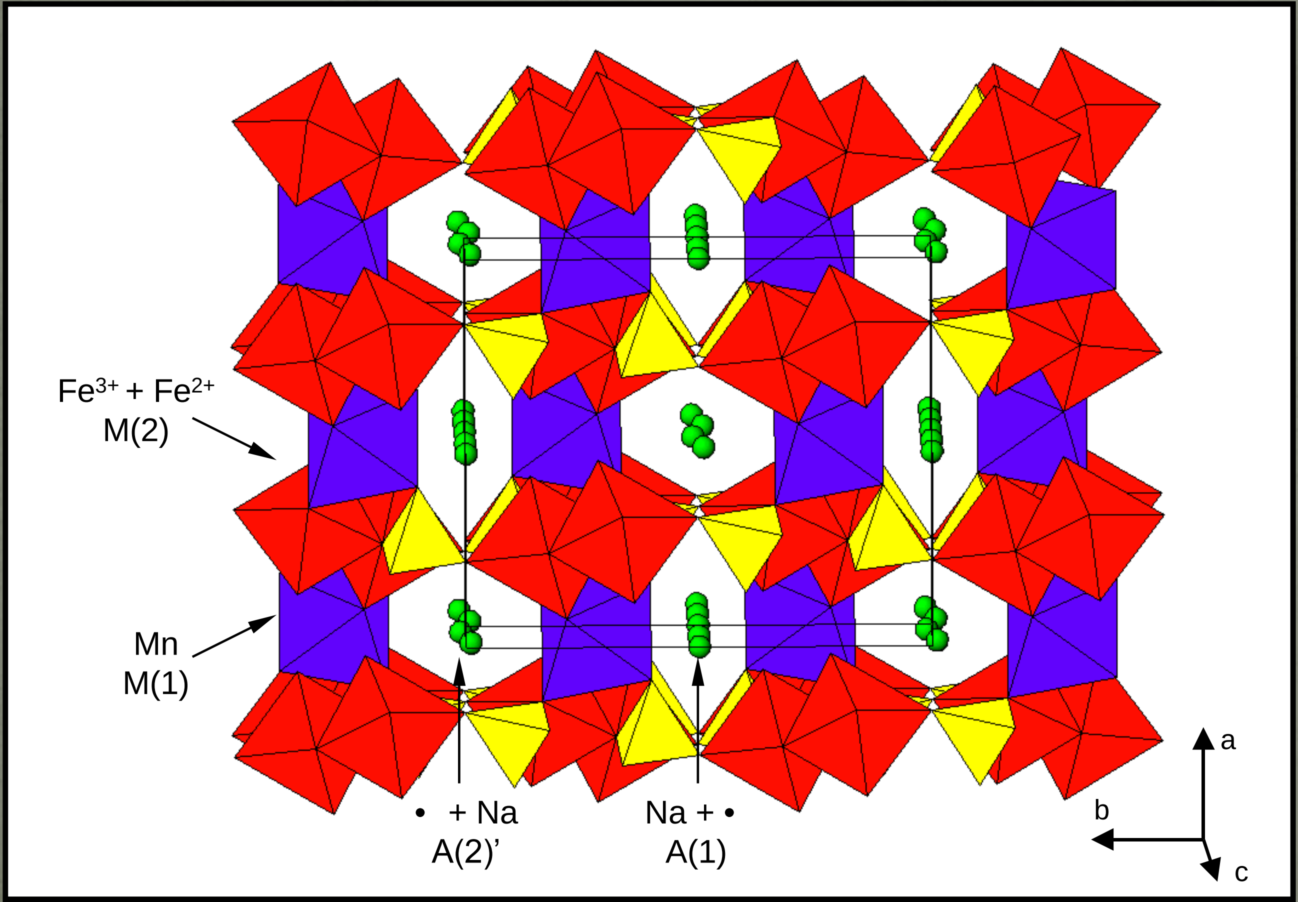
Triphylite
a = 5.987 Å
b = 10.286 Å
c = 4.690 Å
S.G. *Pmnb*



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

The alluaudite structure

A(2)’: gable disphenoid
A(1): distorted cube
M(1): very distorted octahedron
M(2): distorted octahedron



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

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

Université de Liège

Crystal chemistry of natural alluaudites

- **Moore & Ito (1979)**

***A*(2)' ⇒ Na^{+}, •, K^{+}**
***A*(1) ⇒ Na^{+}, Mn^{2+}, Ca^{2+}, •**
***M*(1) ⇒ Mn^{2+}, Fe^{2+}, Ca^{2+}, Mg^{2+}**
***M*(2) ⇒ Fe^{3+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Li^{+}**

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

Oxidation mechanism:

Na^{+} + Fe^{2+} ⇒ • + Fe^{3+}

$Na_2MnFe^{2+}Fe^{3+}(PO_4)_3$ ⇒ •$NaMnFe^{3+}_2(PO_4)_3$
$Na_2Fe^{2+}_2Fe^{3+}(PO_4)_3$ ⇒ •$NaFe^{2+}Fe^{3+}_2(PO_4)_3$

Université de Liège

Crystal chemistry of synthetic alluaudite-type compounds

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

→ Na-Mn-Fe^{3+} (+ PO_4) system
→ Role of Li^+
→ Role of Cd^{2+} and Zn^{2+}
→ Role of In^{3+} and Ga^{3+}

Experimental

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

→ Na-Mn-Fe^{2+}-Fe^{3+} (+ PO_4) system

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]

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

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

Solid-state synthesis and hydrothermal experiments

X-ray structure refinements

Crystal chemistry of the divalent cation in alluaudite-type phosphates: A structural and infrared spectral study of the $Na_{1.5}(Mn_{1-x}M_x^{2+})_{1.5}Fe_{1.5}(PO_4)_3$ 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

Hydrothermal experiments

Université de Liège

Gold tubes

Hydrothermal lab

Hydrothermal bomb

Opened gold capsules

Université de Liège

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?**

Preliminary hydrothermal experiments

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

High Temperature Metasomatic Alteration

Triphylite-lithiophilite
$Li(Fe^{2+},Mn^{2+})PO_4$

~ 500°C - 300°C

Non-oxidizing conditions

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

Addition of Al^{3+}
Griphite, Scorzalite

Addition of Ca^{2+}
Whitlockite

Addition of Na^+
Natrophilite

Oxidizing conditions

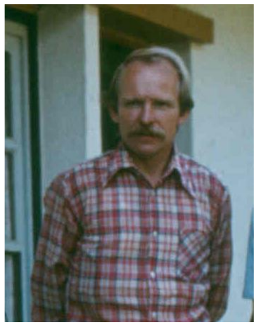
Oxidation of Fe^{2+} to Fe^{3+}
Ferrisicklerite-sicklerite

Leaching of Li^+
Heterosite-purpurite

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

Simmons *et al.* 2003

Triphylite cubes

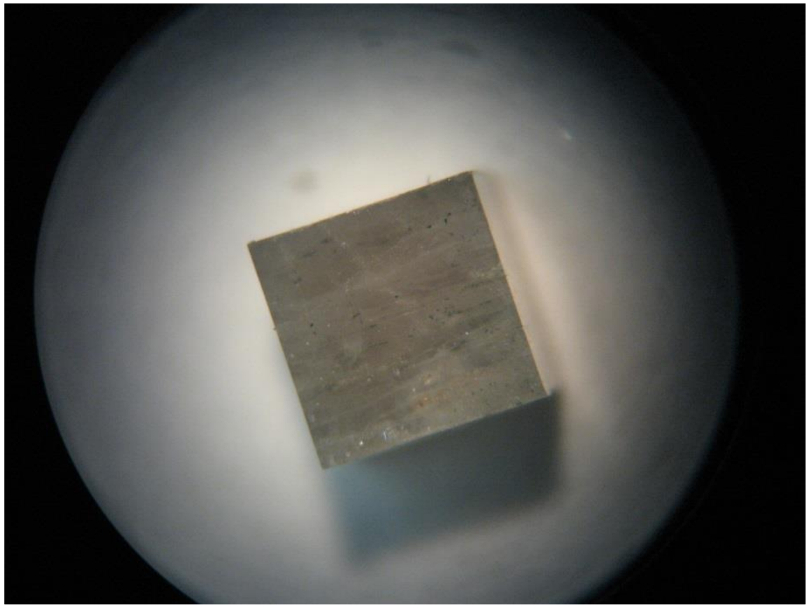


Sample 9706.41, Palermo, N.H., USA
Collection Paul Keller, Stuttgart

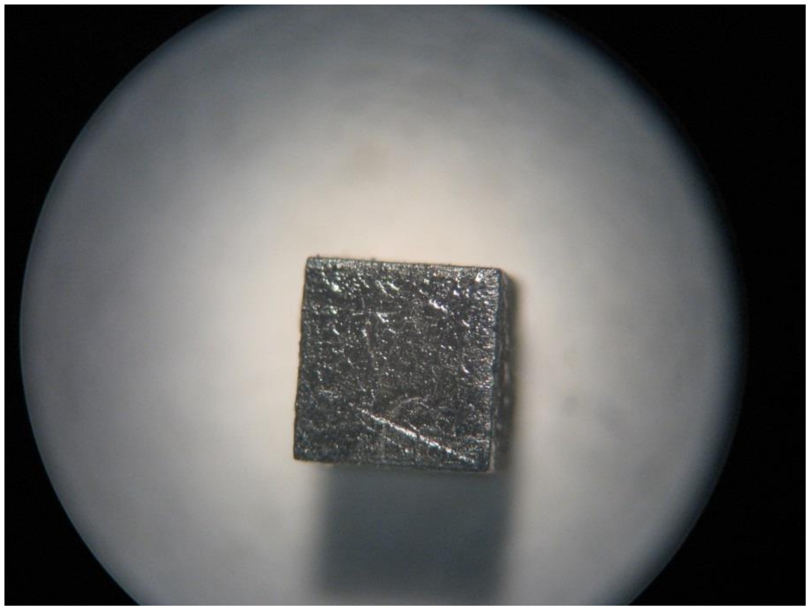
X $LiFePO_4$ = 0.74(1) 100% Fe^{2+}
X $LiMnPO_4$ = 0.21(1)
X $LiMgPO_4$ = 0.05(1)

0.1n HCl, 21mg $KMnO_4$, 120°C, 28 d

Before run

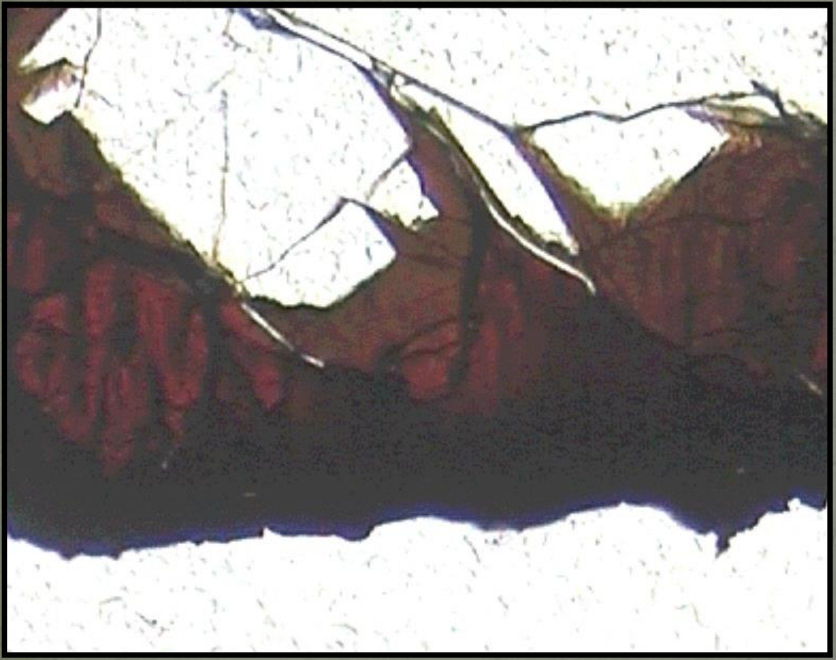


After run



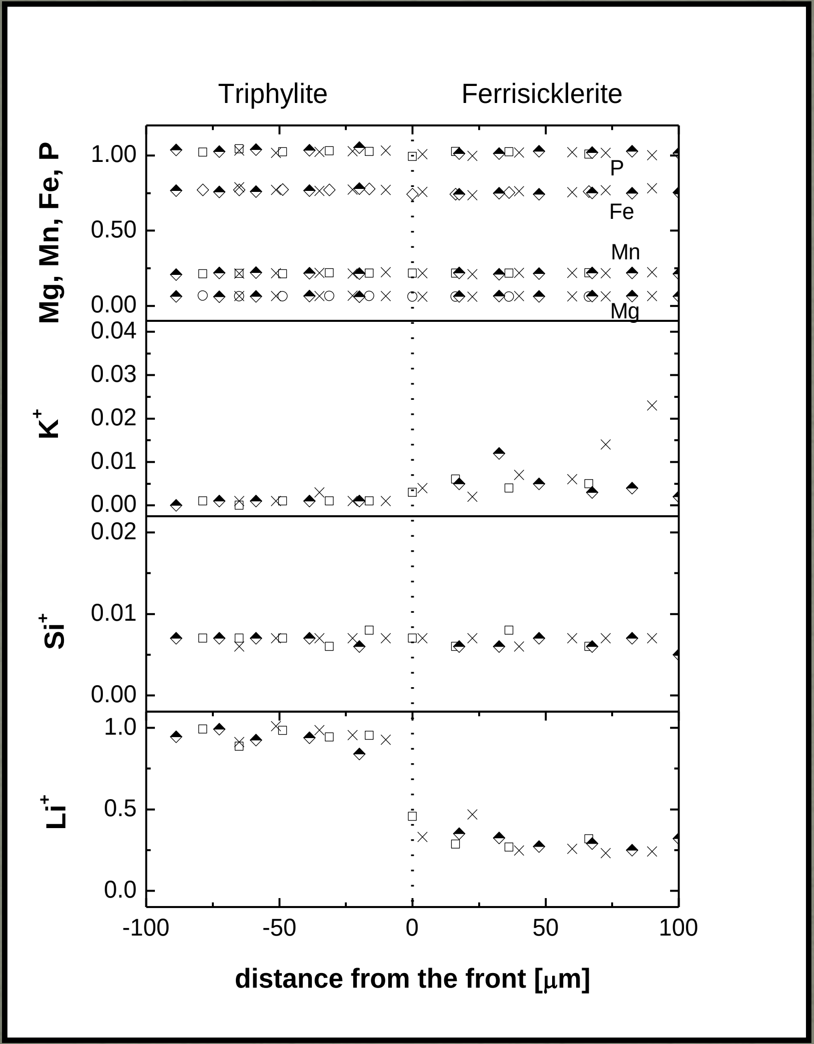
Oxidation to ferrisicklerite

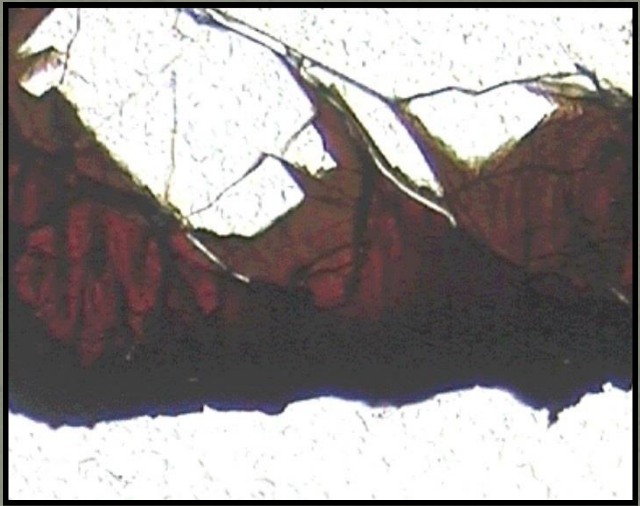
- First hydrothermal synthesis of ferrisicklerite
- At very low temperature
- Under a very high fO_2

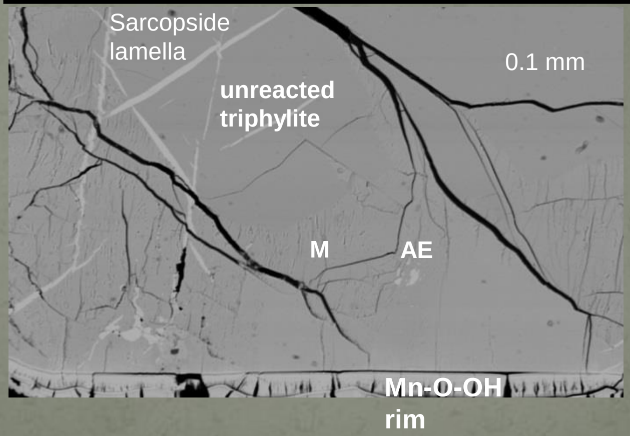


Ferrisicklerite is a low temperature metasomatic alteration mineral (?)

Decrease of the Li content

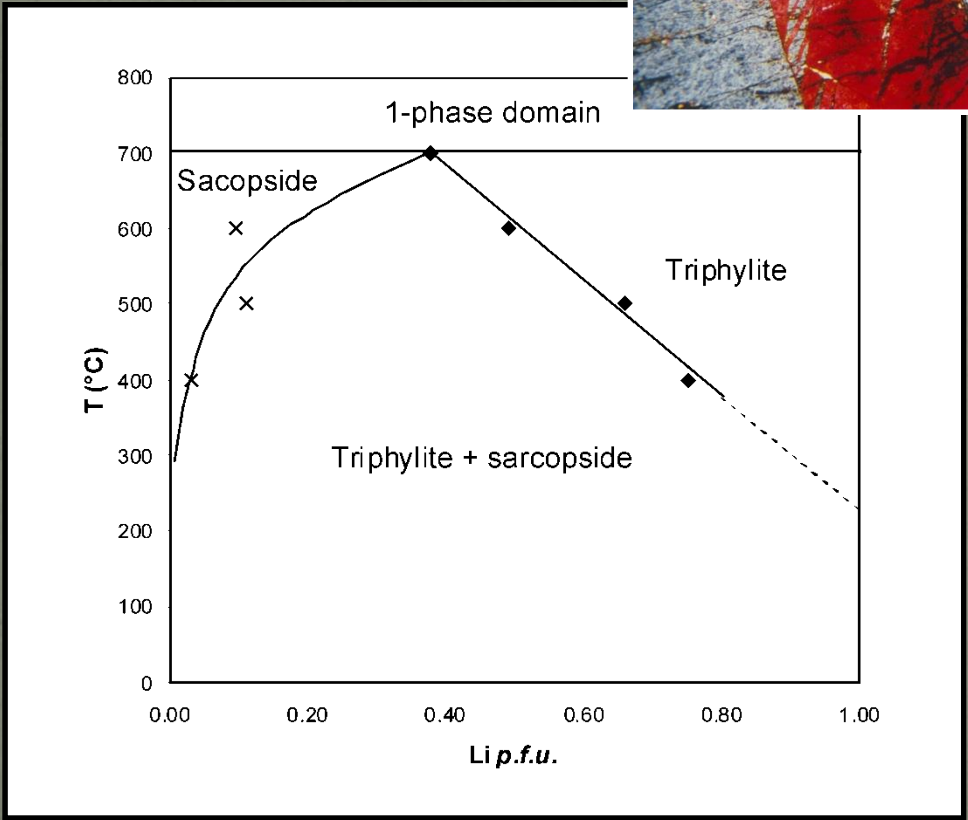






Sharp contact between triphylite and ferrisicklerite!

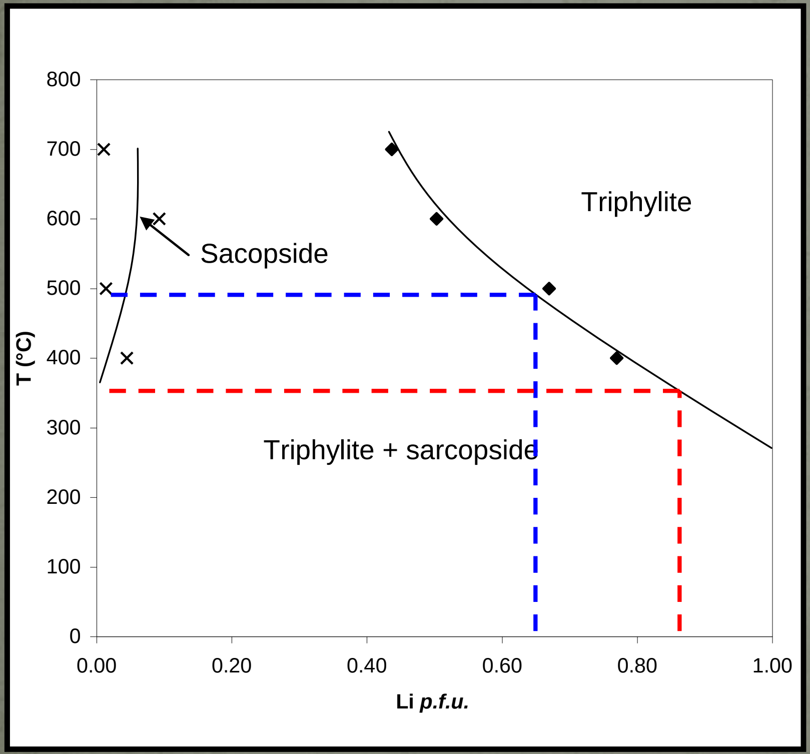
Stability of the triphylite + sarcopside assemblage



$LiFe^{2+}_{2.5}(PO_4)_2$

- 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

Calculation of crystallisation temperatures for natural assemblages



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

Phase diagram for the $LiMn_{0.5}Fe^{2+}{}_2(PO_4)_3$ starting composition

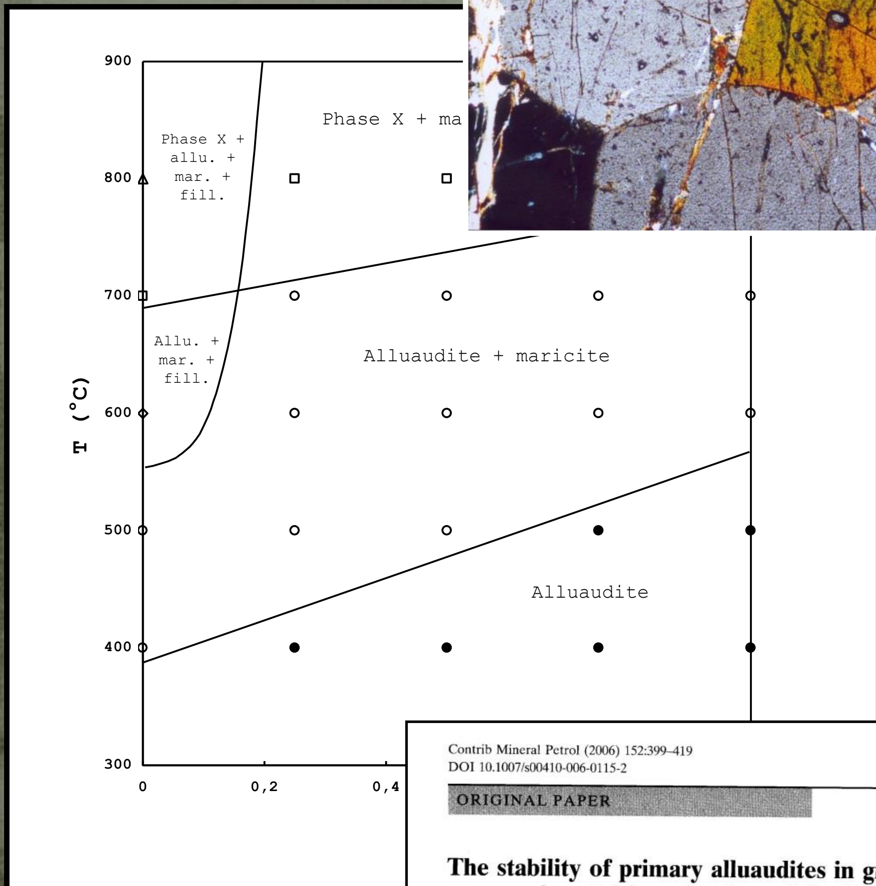
Cañada

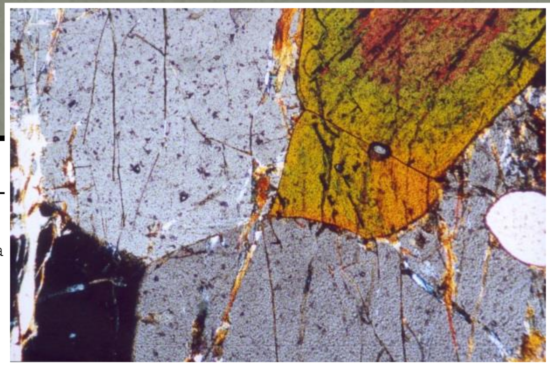
35 % sarcopside and 65 % triphylite
T ~ 500°C

Tsoabismund

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

Stability of alluaudites





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

Université de Liège

- **Low T ⇒ alluaudite**
- **High T ⇒ "X-phase"**
- **Mn ⇒ fillowite [$NaMn_4(PO_4)_3$]**

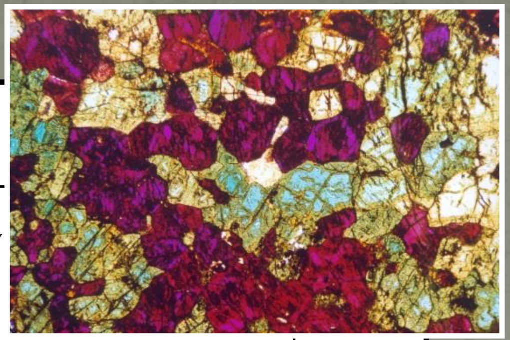
No maricite [$NaFePO_4$] in pegmatites

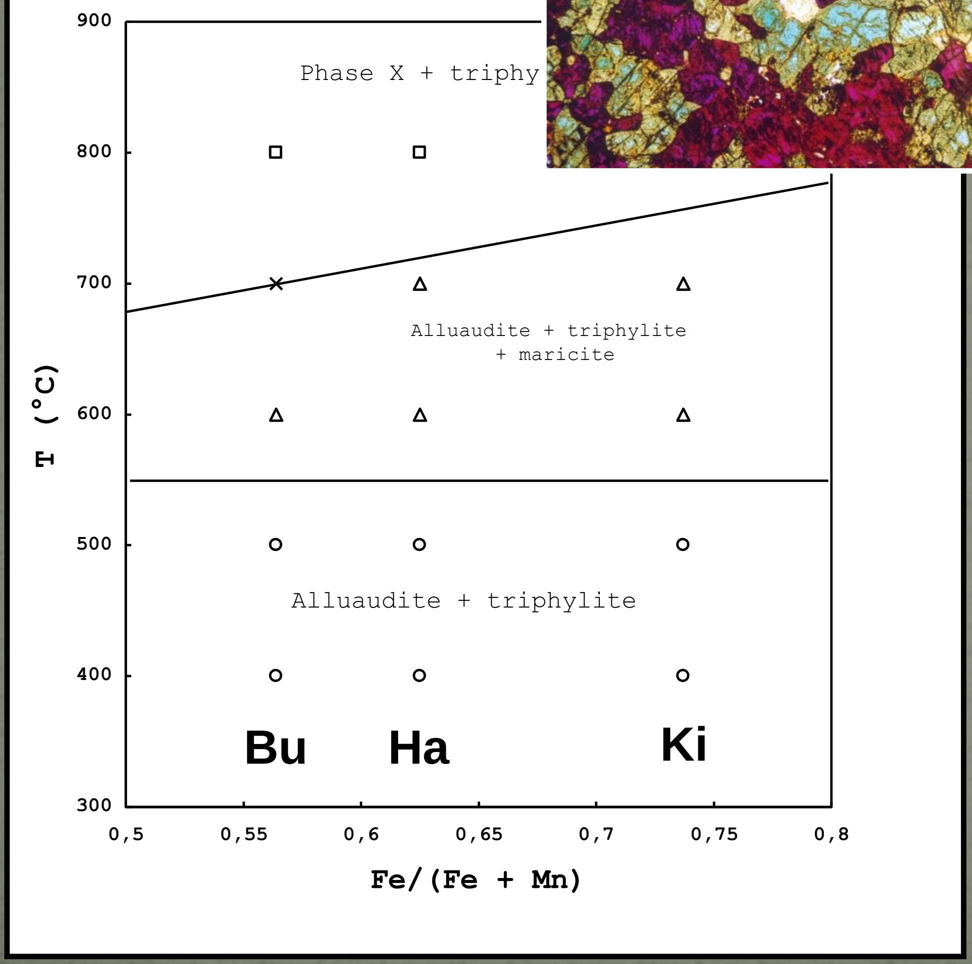
Varulite
$Na_2Mn_2Fe^{3+}(PO_4)_3$
350-400°C

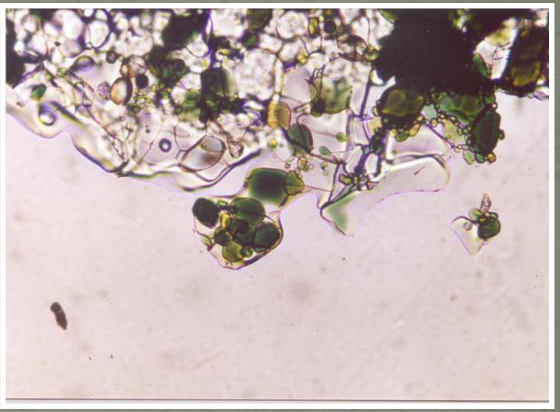
Hagendorfite
$Na_2MnFe^{2+}Fe^{3+}(PO_4)_3$
450-500°C

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

Stability of the triphylite + alluaudite asemblage





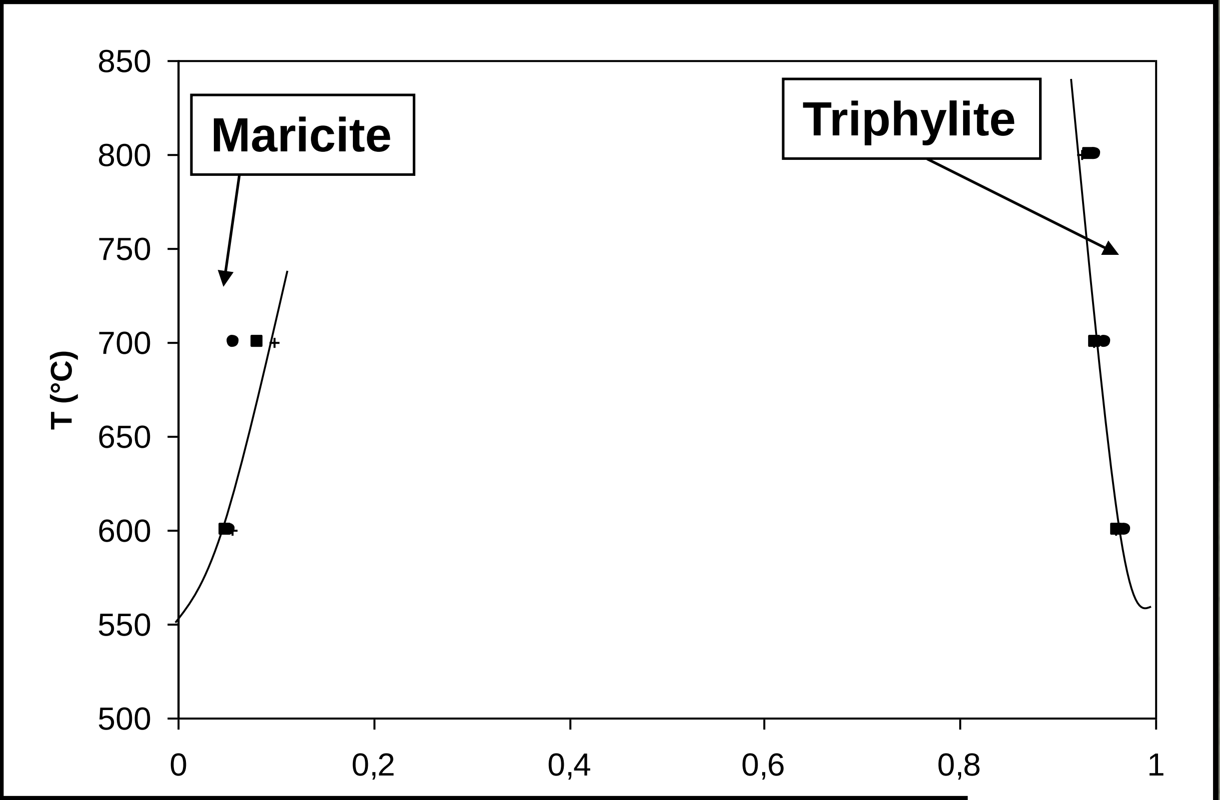


No maricite in pegmatites

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

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

The Na-in-triphylite geothermometer



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

Frederic Hatert · Luisa Ottolini · Peter Schmid-Beurmann

- **In triphylite, 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!**

Conclusions

Enjoy phosphates, and….

Let's have a beer!