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, 2016

Contents

1. Introduction
2. Field observations
3. Petrography and geochemistry
4. Crystal chemistry
5. Hydrothermal experiments and stability
6. Conclusions

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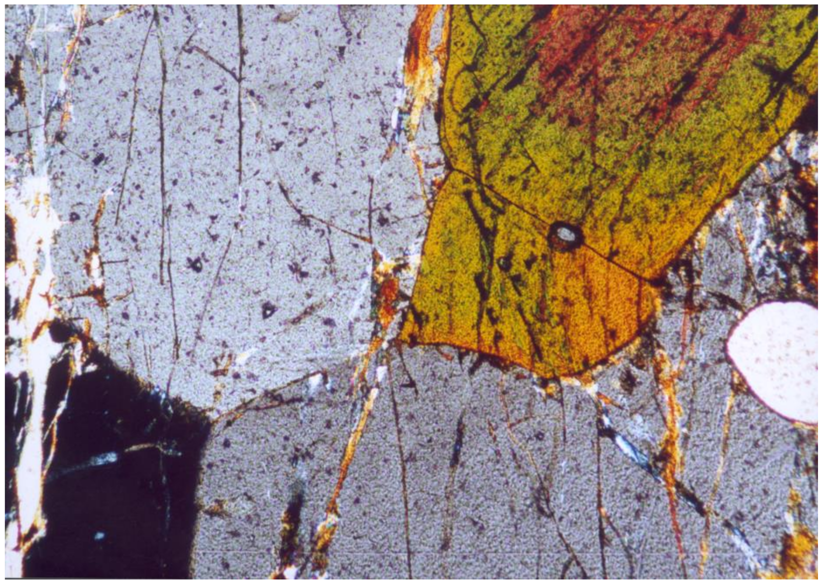
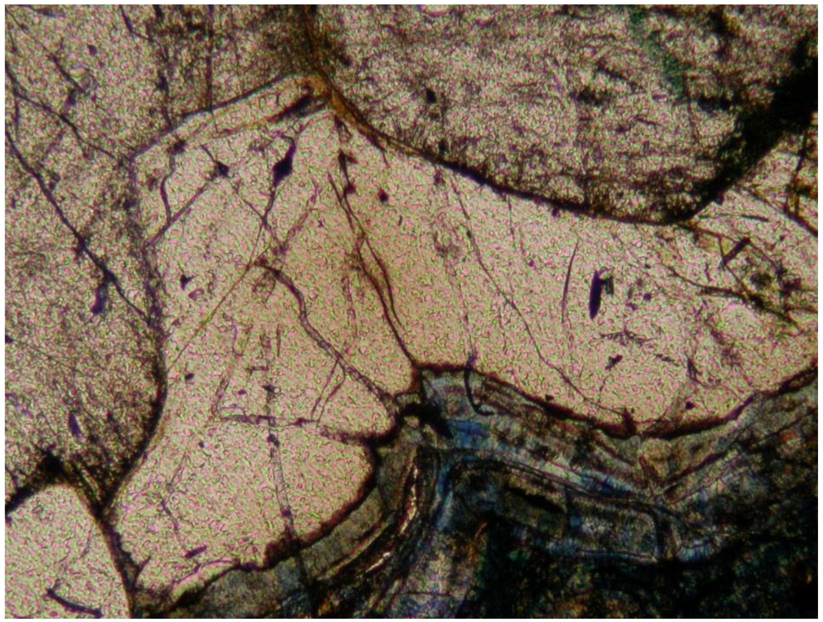
Occurrence

- Granitic pegmatites
- Metamorphic rocks
- Meteorites

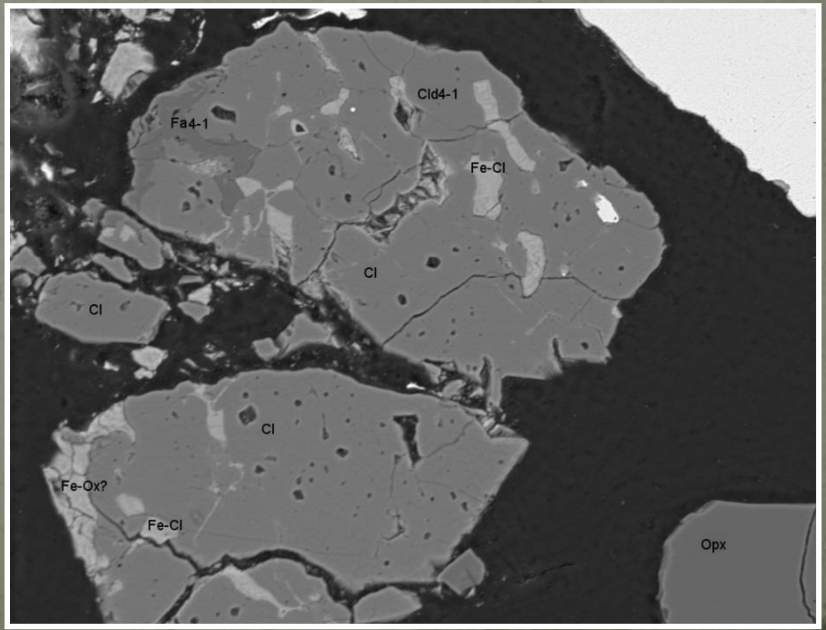


Fillowite + alluaudite, Kabira pegmatite, Uganda

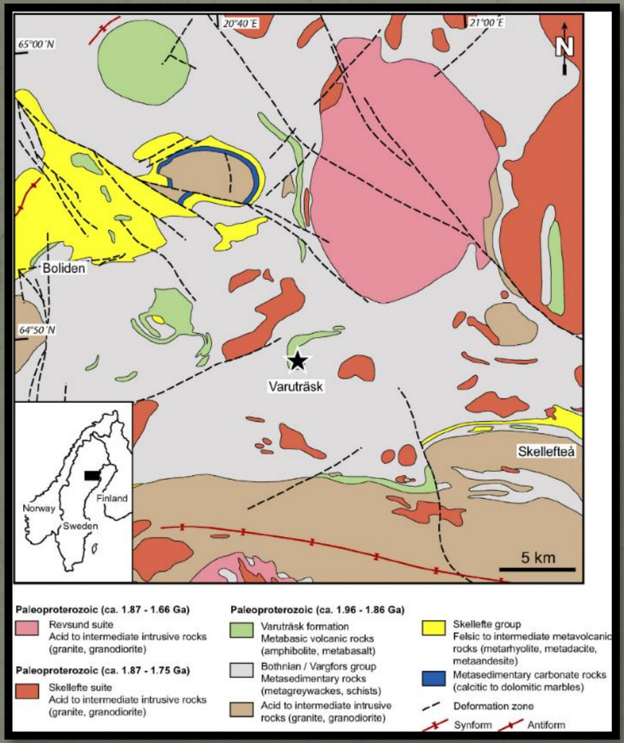


Johnsomervilleite, Loch Quoich, Scotland

Chladniite, GRA 95209 meteorite



The Varuträsk pegmatite



Percy Quensel (1881-1966)

Brian Mason (1917-2009)

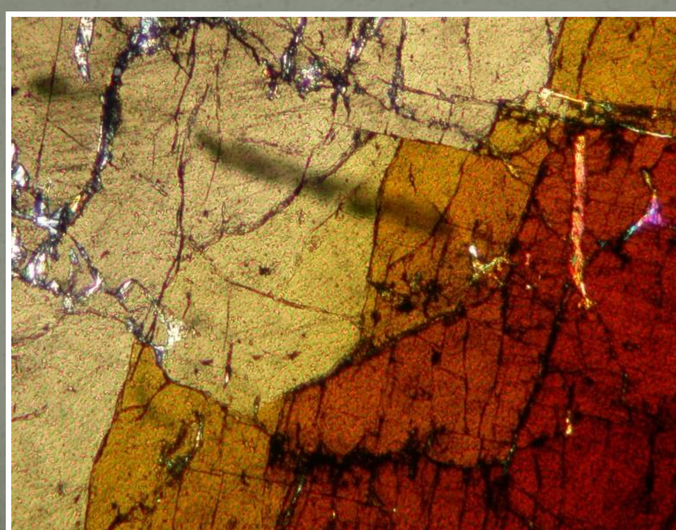
The triphylite group

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

(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

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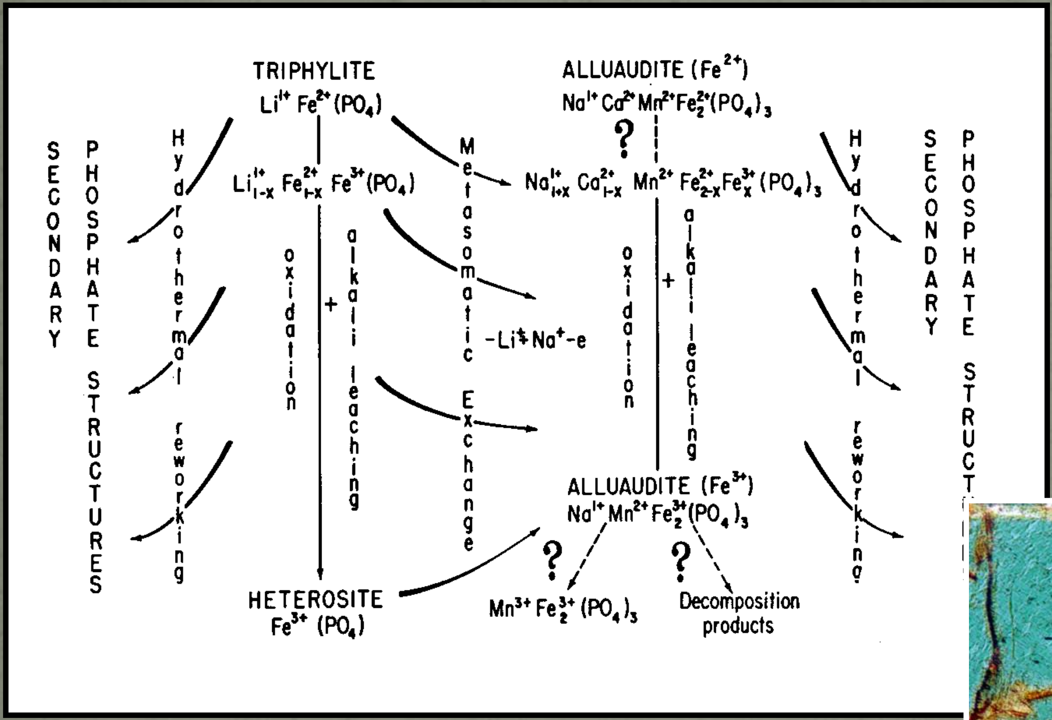
Varulite, $Na_2Mn_2Fe^{3+}(PO_4)_3$
Varuträsk, Sweden

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

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

Augustin-Alexis Damour
(1808-1902)

Genesis of alluaudites

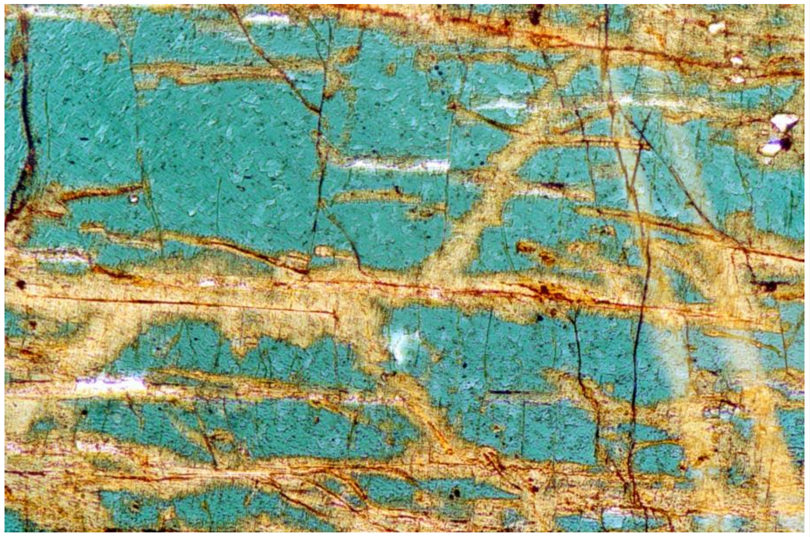


- **Secondary origin**
- **Primary origin**

Oxidation mechanism

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

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



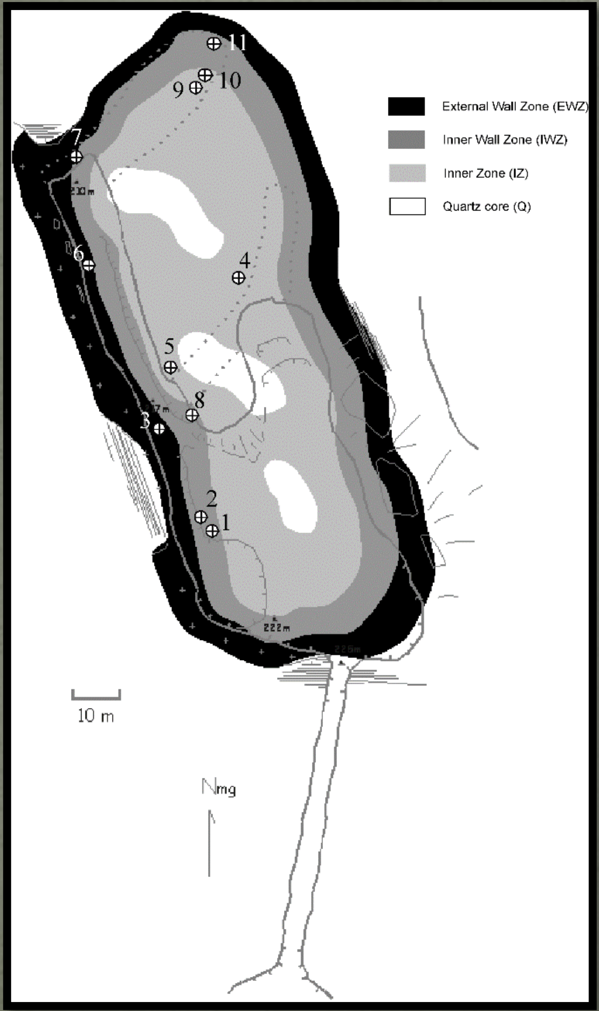
Alluaudite, Kibingo pegmatite, Rwanda

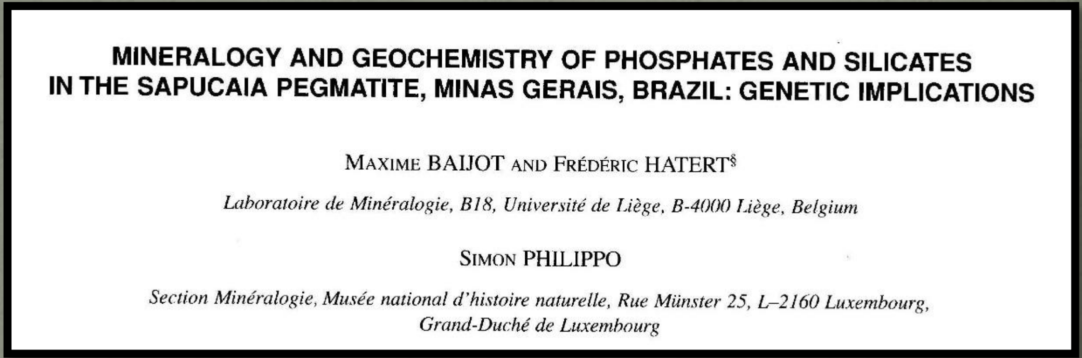
Let's go to the field!

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

Thin sections

Al phosphates

The triphylite + sarcopside assemblage

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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

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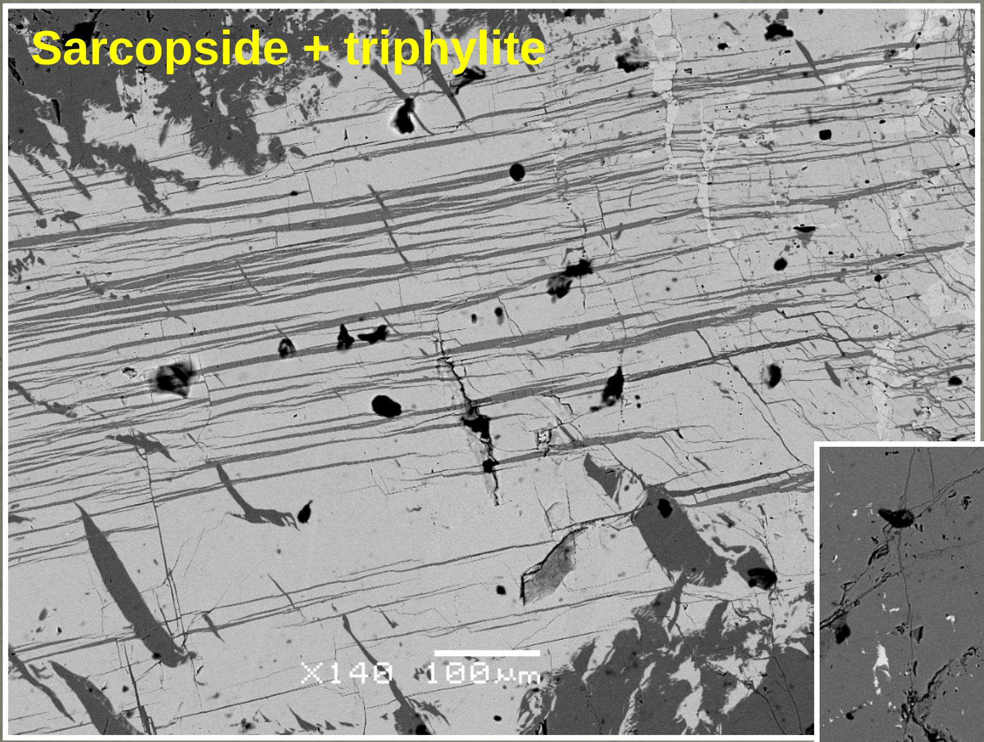
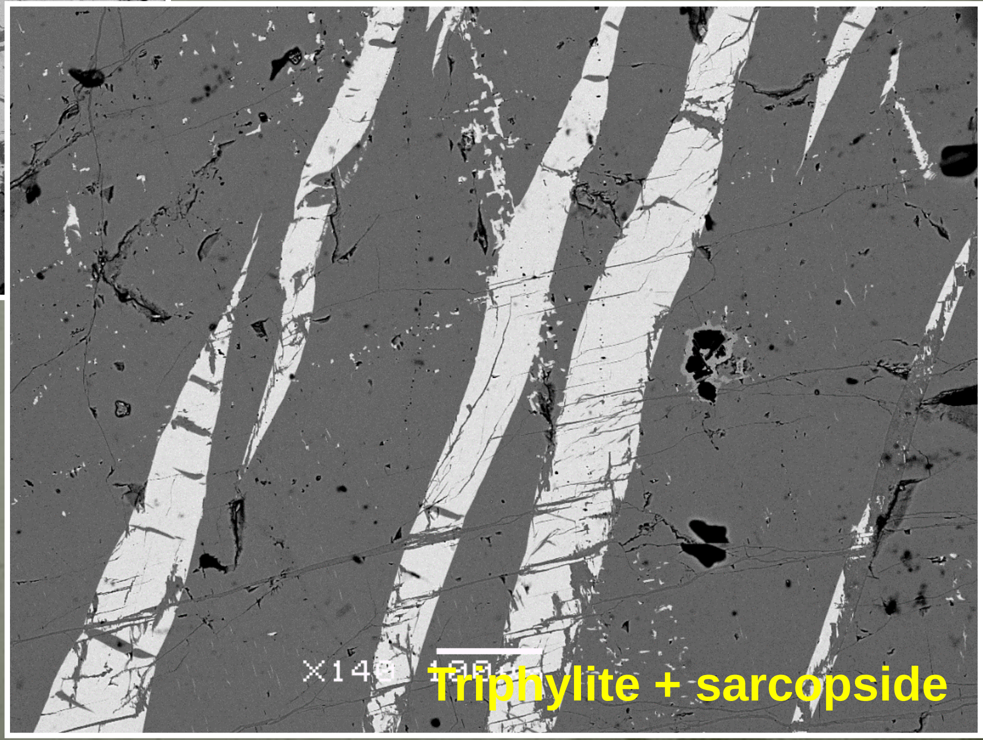


Cañada pegmatite, Spain

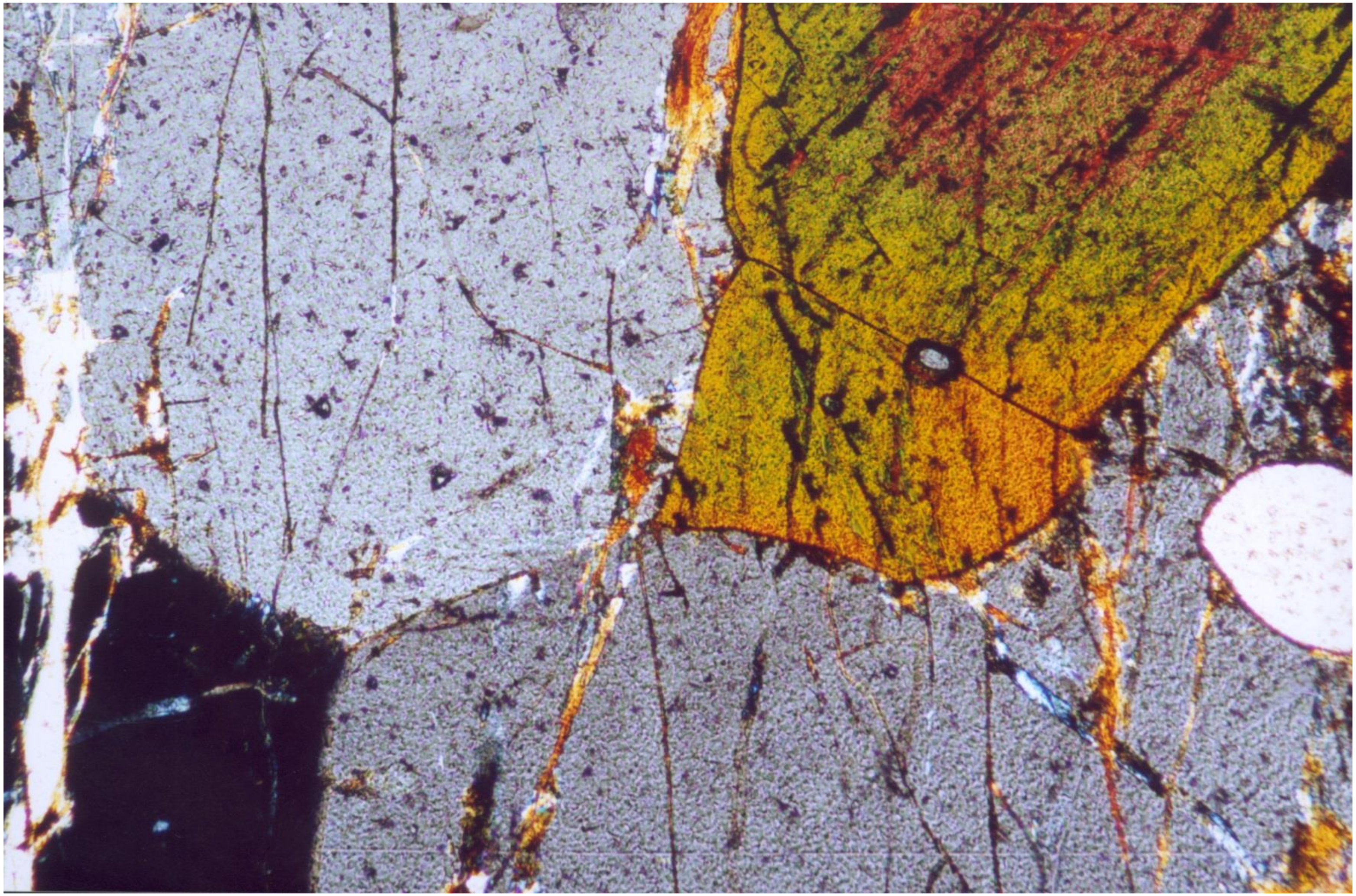


Lamellar textures

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

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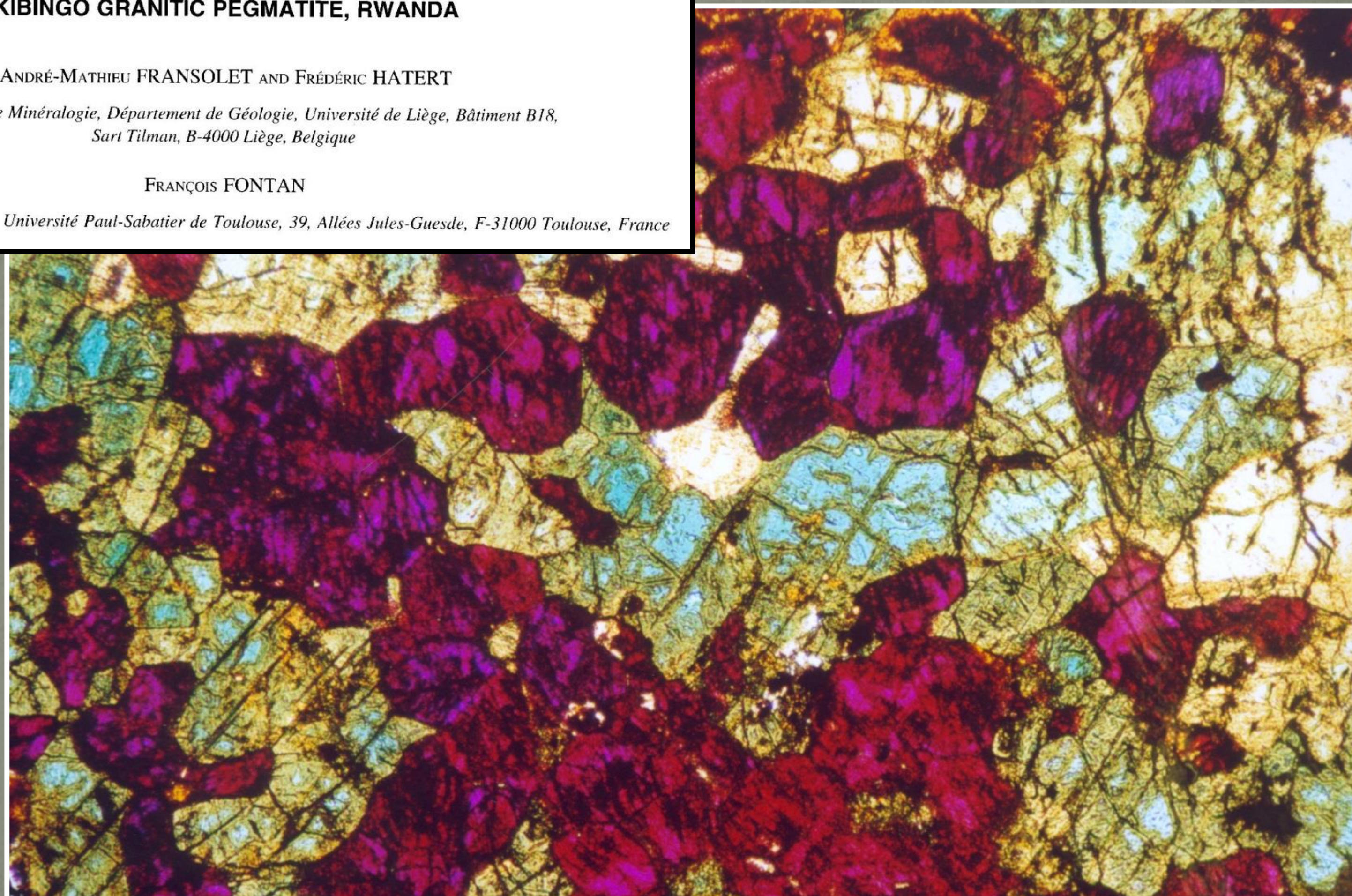
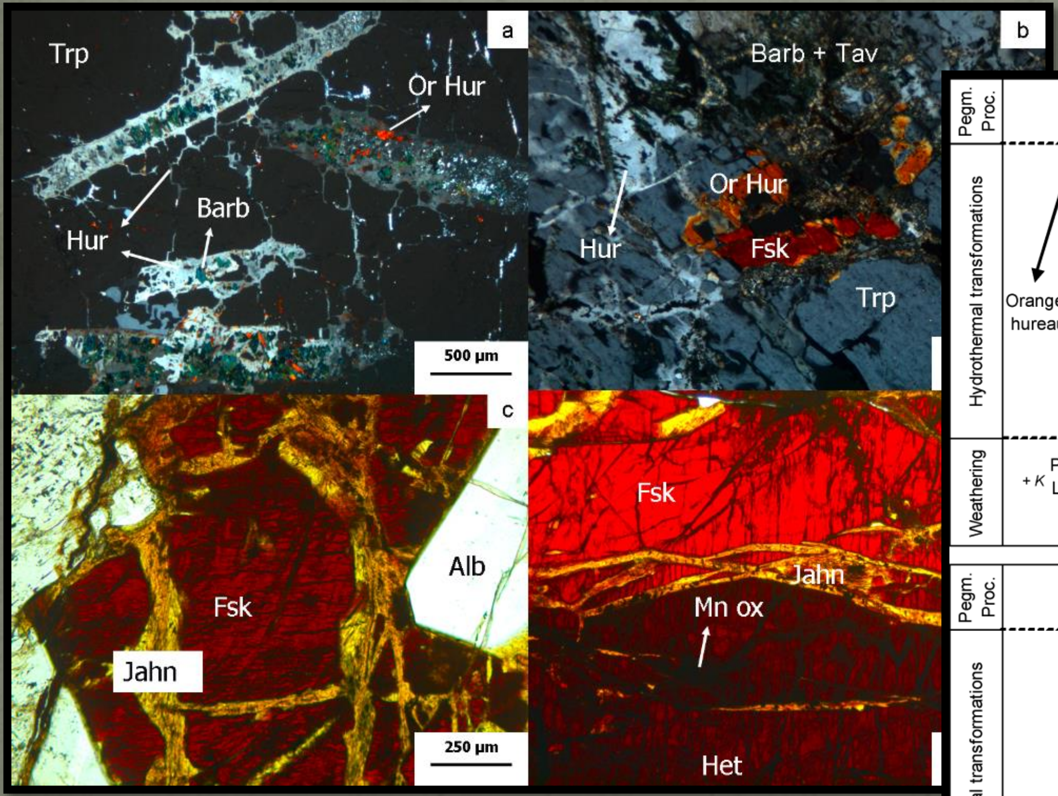
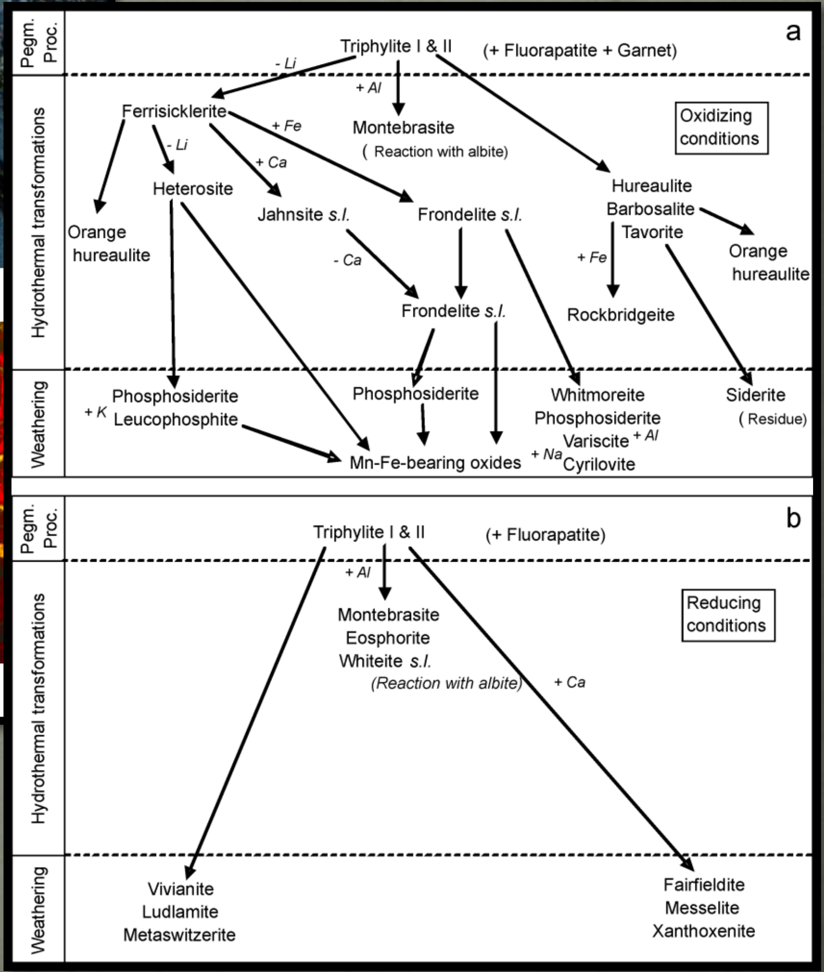


Hagendorfite, alluaudite, and heterosite, Kibingo pegmatite, Rwanda

Complex assemblages from Sapucaia



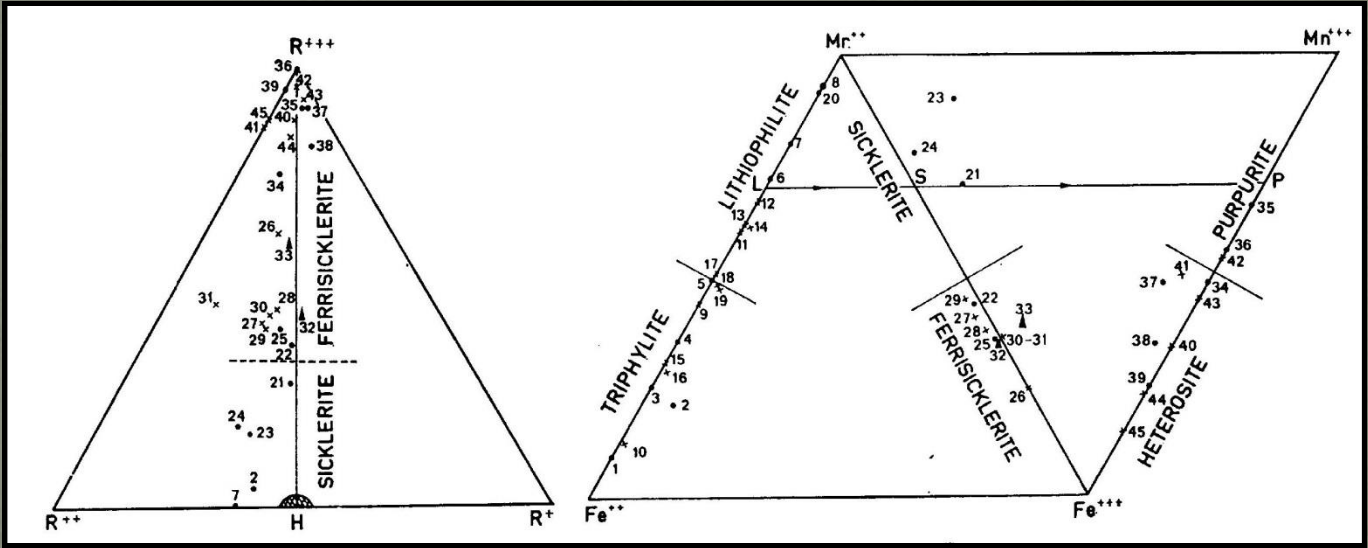


Electron-microprobe analyses

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!

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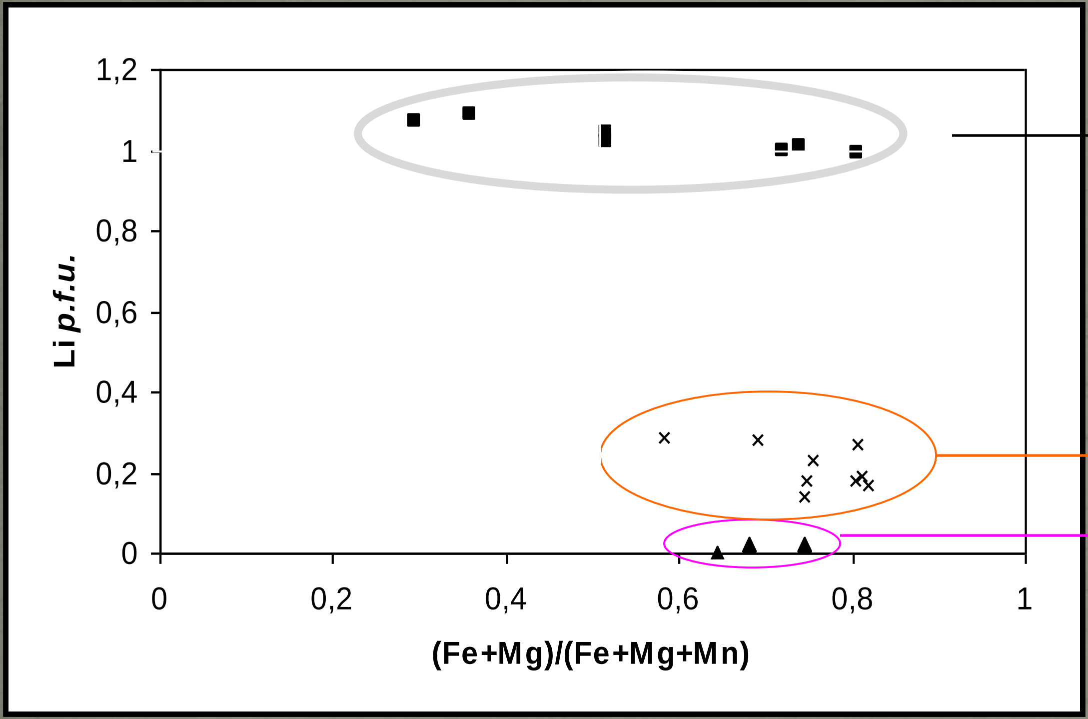
SIMS analyses of Li contents

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!

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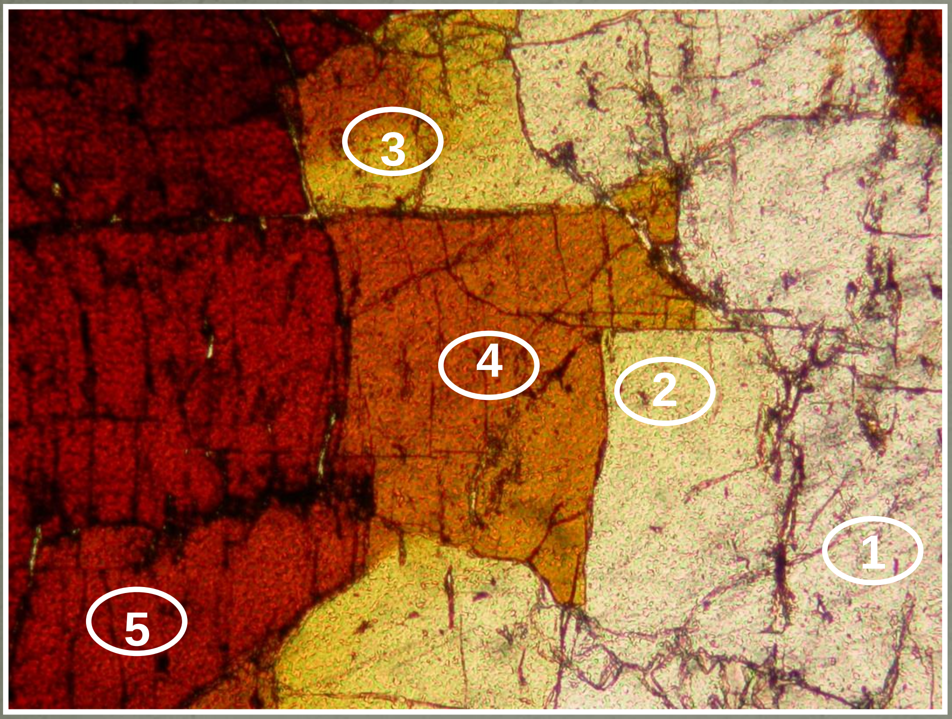
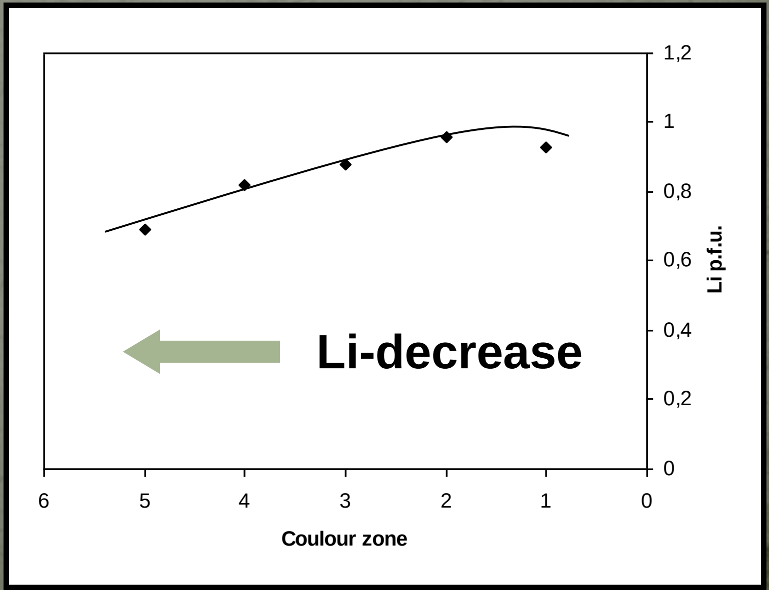
Oxidation of sicklerite

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: $Li_{0.69}(Fe^{3+}_{0.16}Mn^{2+}_{0.62}Mn^{3+}_{0.19})(PO_4)$

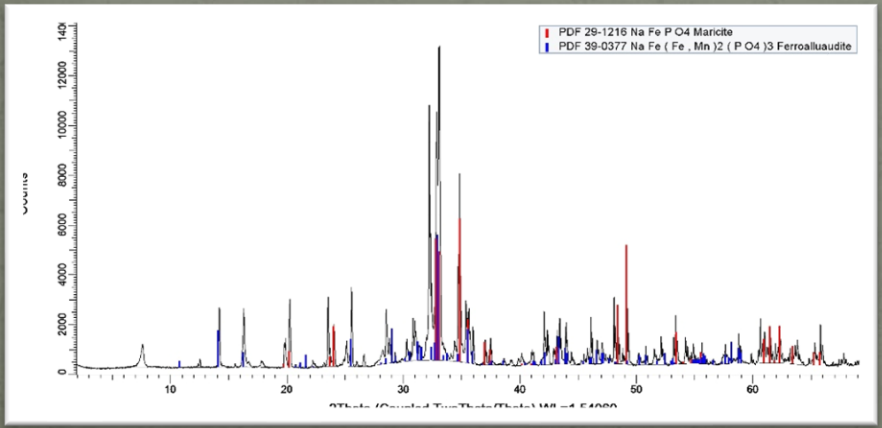


- **The transition from lithiophilite to sicklerite is progressive**
- **The change in colour is due to the presence of Mn^{3+}**

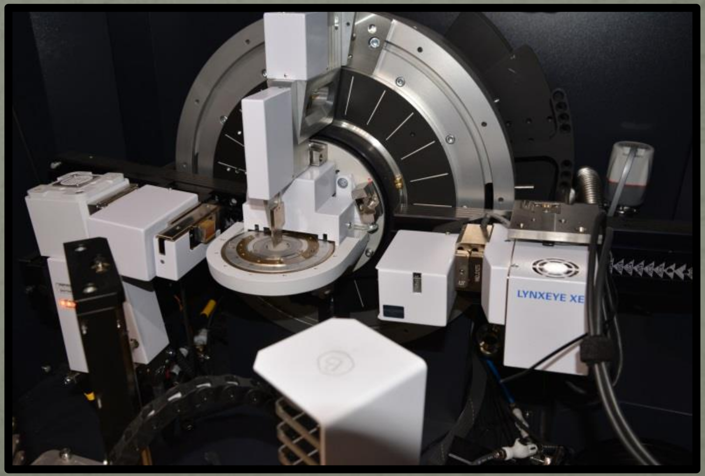
X-ray powder diffraction

Sample preparation

Sample holder



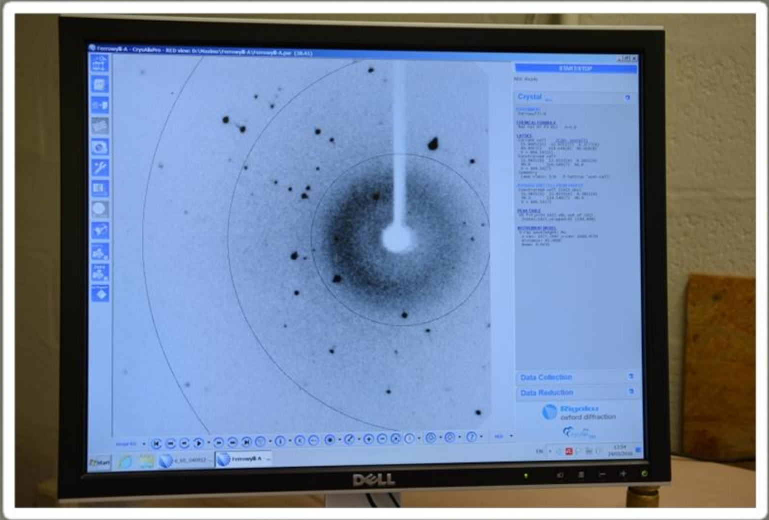
Powder pattern



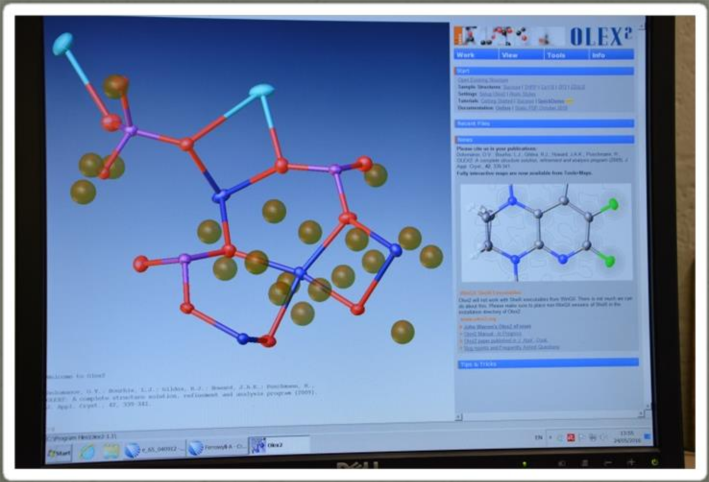
Powder diffractometer

Single-crystal X-ray diffraction

4-circle diffractometer



Diffraction spots



Structure determination

The triphylite structure

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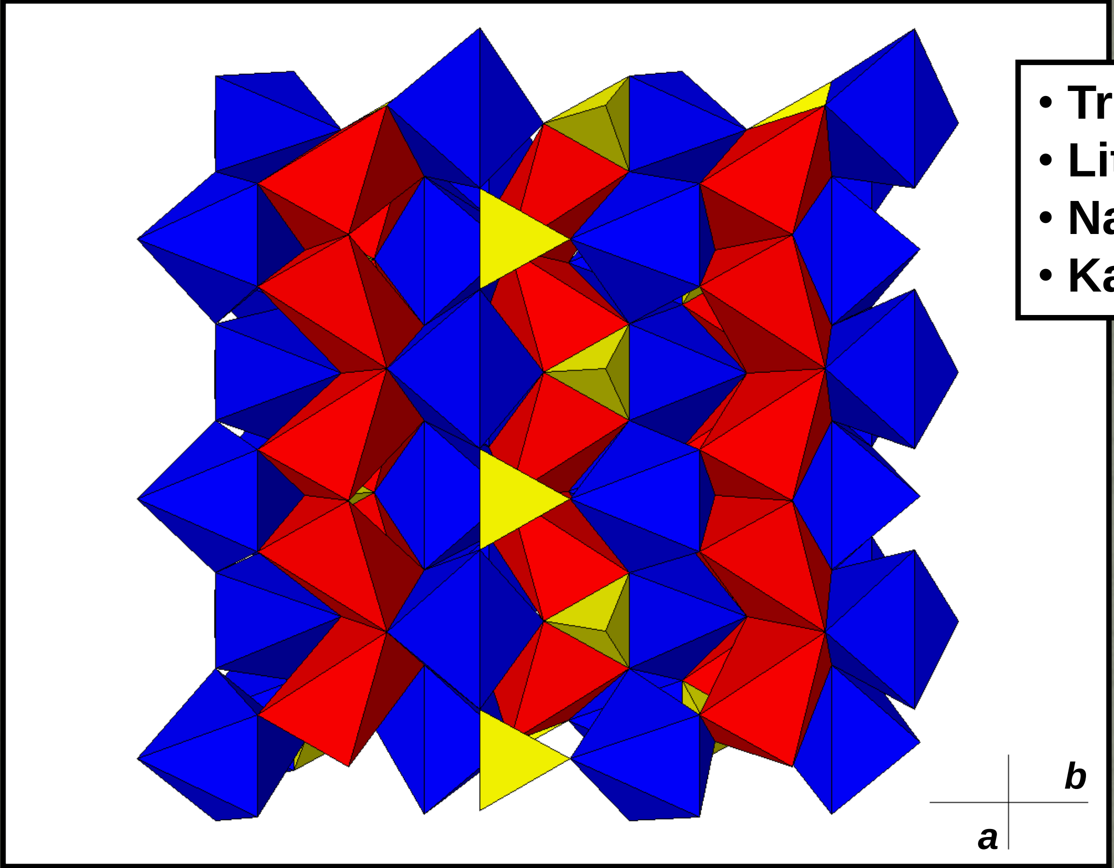


- Triphylite, $LiFe^{2+}(PO_4)$
- Lithiophilite, $LiMn(PO_4)$
- Natrophilite, $NaMn(PO_4)$
- Karenwebberite, $NaFe^{2+}(PO_4)$

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 ULg

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

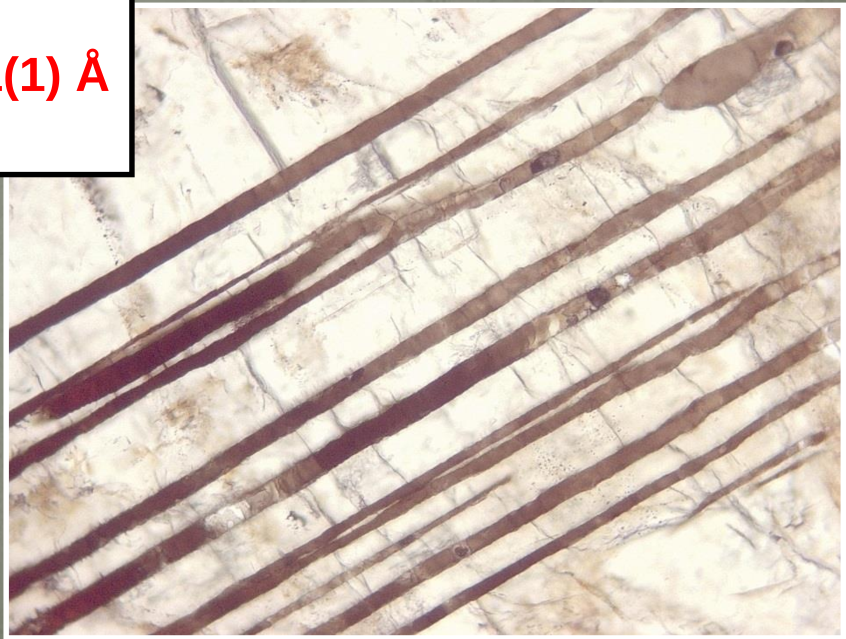
Karenwebberite, $Na(Fe^{2+},Mn^{2+})PO_4$, a new member of the triphylite group from the Malpensata pegmatite, Lecco Province, Italy

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

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

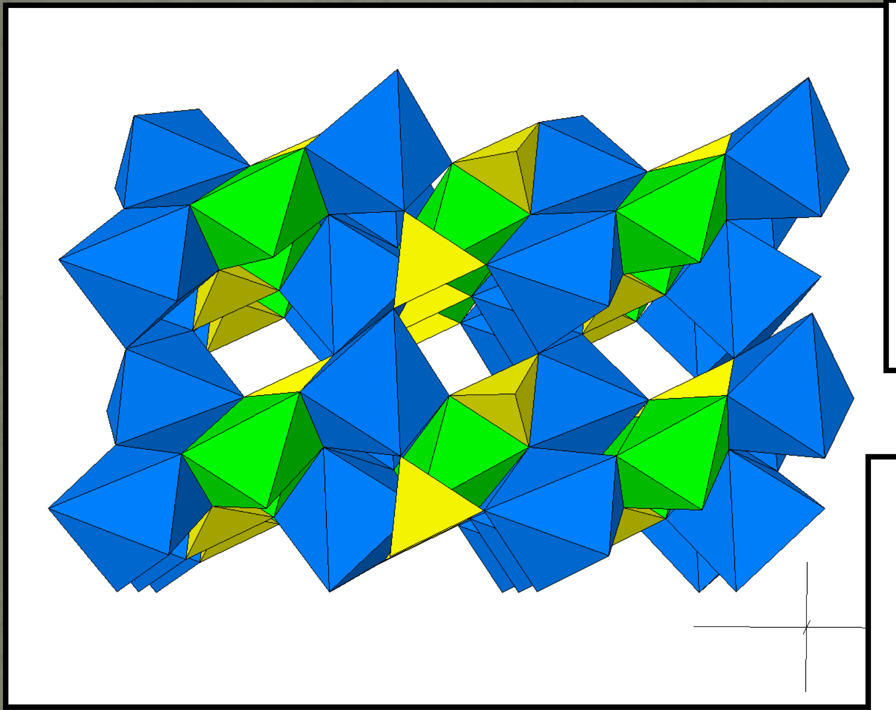
Departimento de Mineralogía y Petrología, Universidad del País Vasco/EHU, Apdo. 644, E–48080 Bilbao, Spain

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

$Mn_3(PO_4)_2$

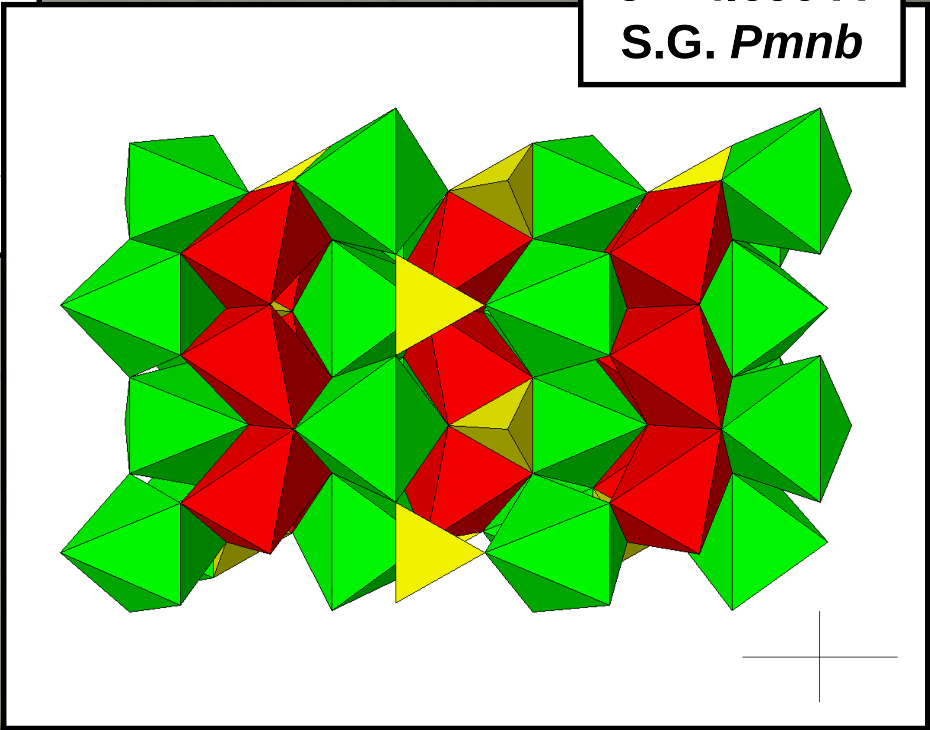
Florencia Márquez Zavalía

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. $P2_1/c$

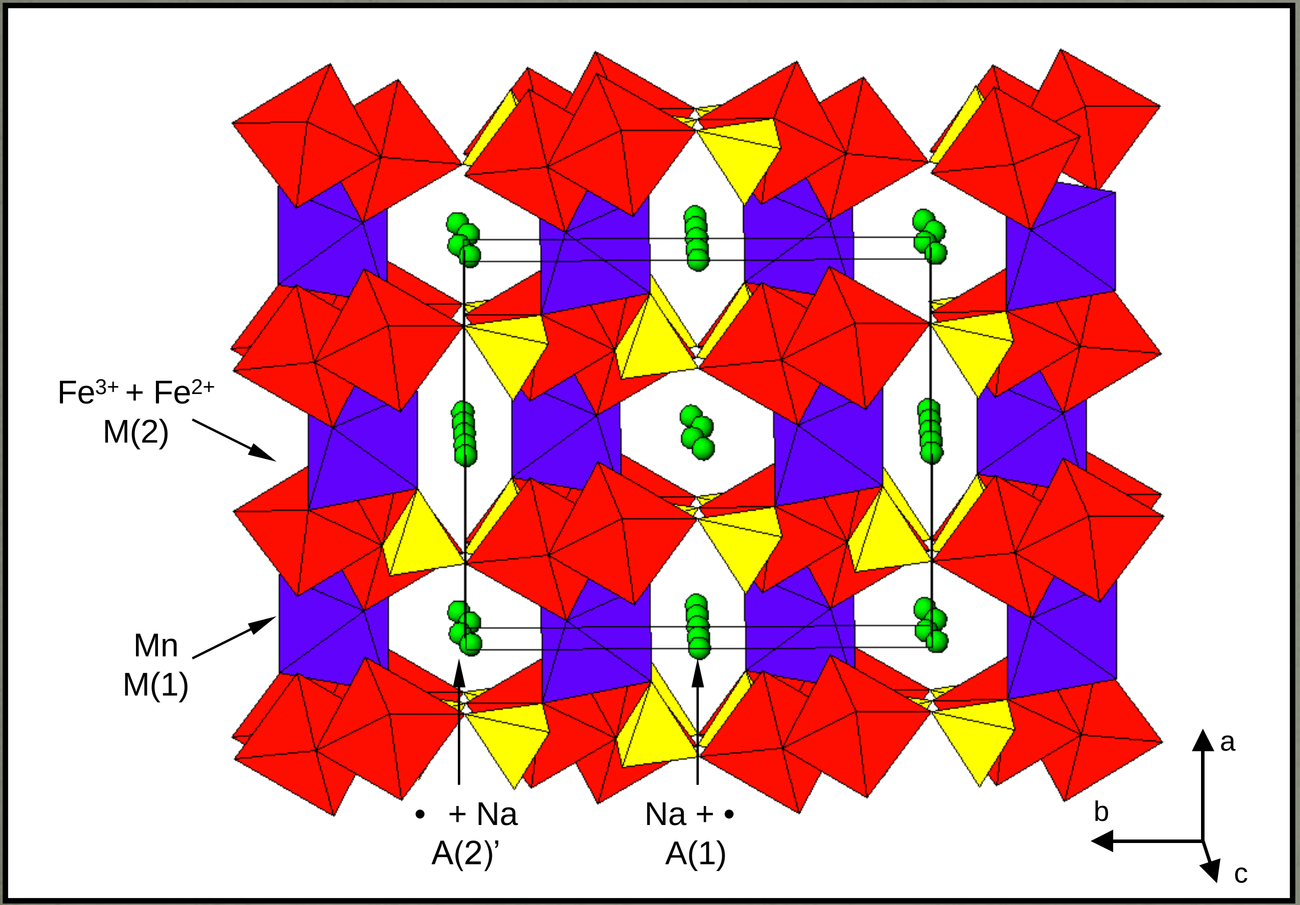
Triphylite
a = 5.987 Å
b = 10.286 Å
c = 4.690 Å
S.G. *Pmnb*



- 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



$C2/c$, $Z = 4$

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

Crystal chemistry of natural alluaudites

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- **Moore & Ito (1979)**

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

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

Oxidation mechanism:

$Na^{+} + Fe^{2+} \Rightarrow$ • $+ Fe^{3+}$

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

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Crystal chemistry of synthetic alluaudite-type compounds

Experimental

- 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+}

- 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) [VI]	Ionic radius (Å) [VIII]	Site *A*(2)'	Site *A*(1)	Site *M*(1)	Site *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 $Na_{1.5}(Mn_{1-x}M^{2+}_{x})_{1.5}Fe_{1.5}(PO_4)_3$ solid solutions ($x = 0$ to 1, $M^{2+} = Cd^{2+}, Zn^{2+}$)

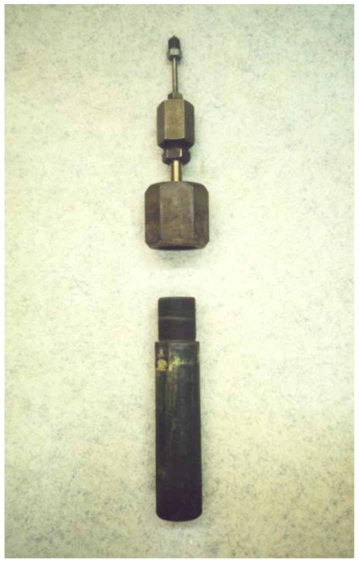
Frédéric Hatert *
Laboratoire de Minéralogie, Université de Liège, Bâtiment B18, B-4000 Liège, Belgium

Hydrothermal experiments

Hydrothermal lab

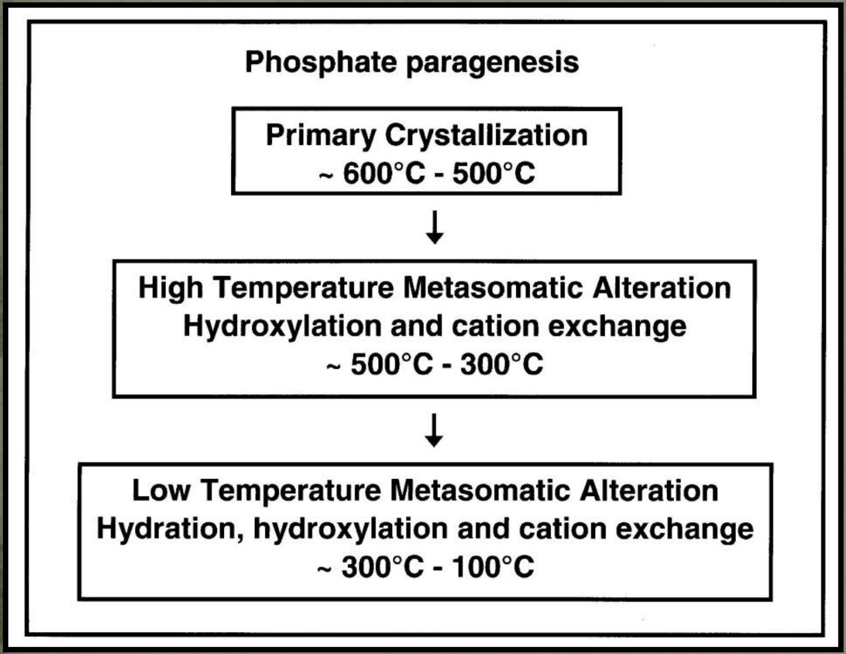
Gold tubes

Hydrothermal bomb

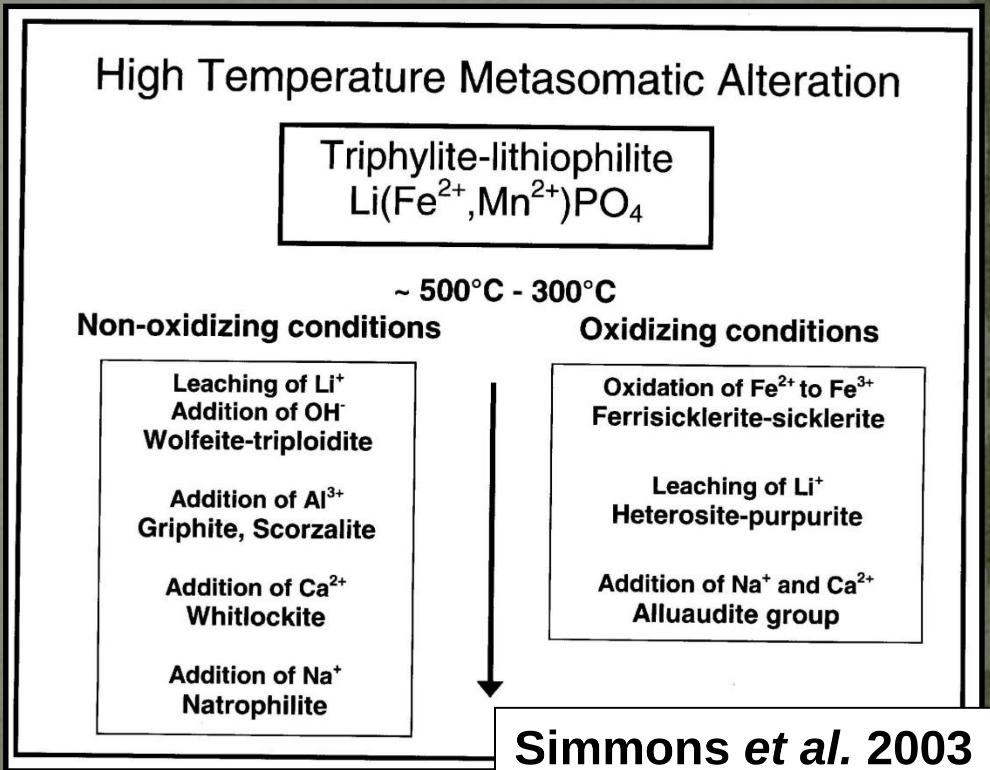


Opened gold capsules

The stability of ferrisicklerite



- **Crystallization temperatures of ferrisicklerite?**
- **Degree of oxidation?**

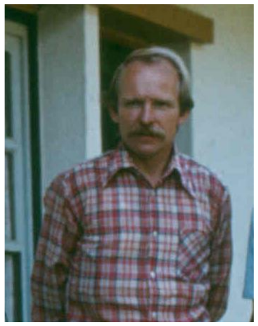


Simmons *et al.* 2003

Preliminary hydrothermal experiments

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

Triphylite cubes

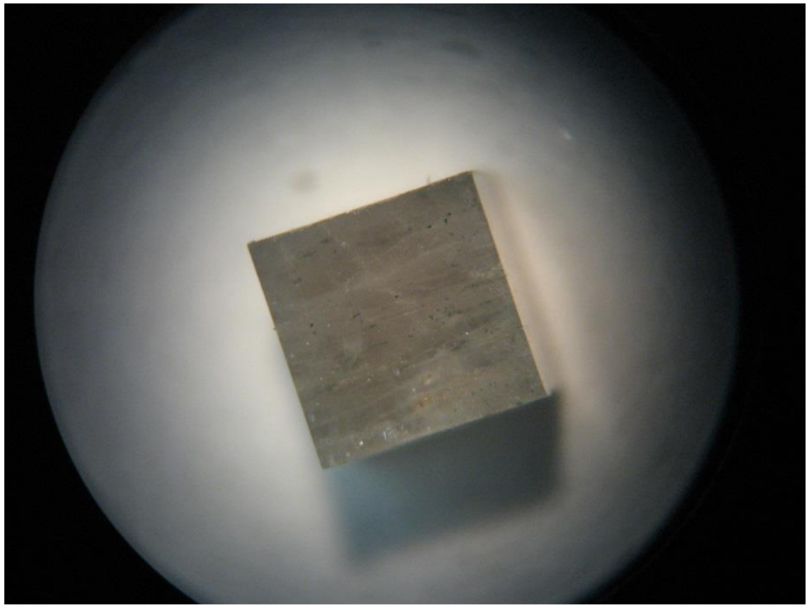


Sample 9706.41, Palermo, N.H., USA
Collection Paul Keller, Stuttgart

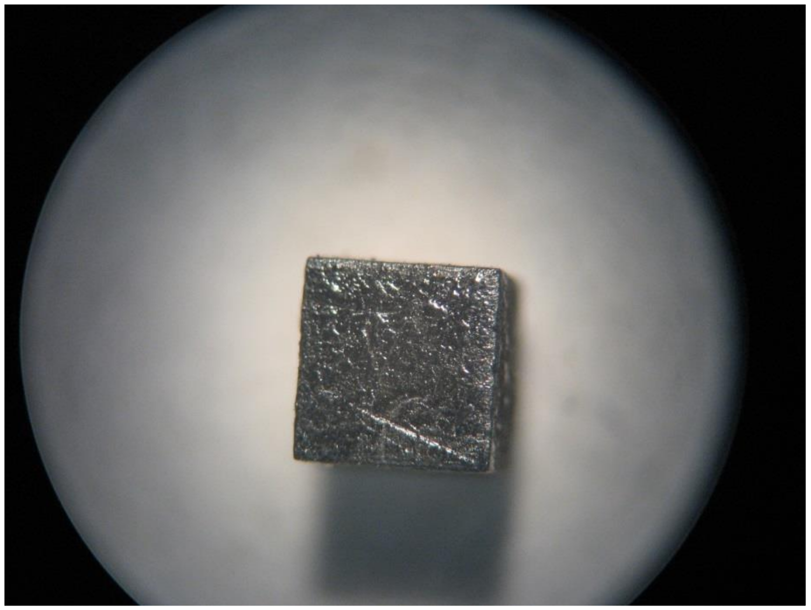
X $LiFePO_4$ = 0.74(1) 100% Fe^{2+}
X $LiMnPO_4$ = 0.21(1)
X $LiMgPO_4$ = 0.05(1)

0.1n HCl, 21mg $KMnO_4$, 120°C, 28 d

Before run

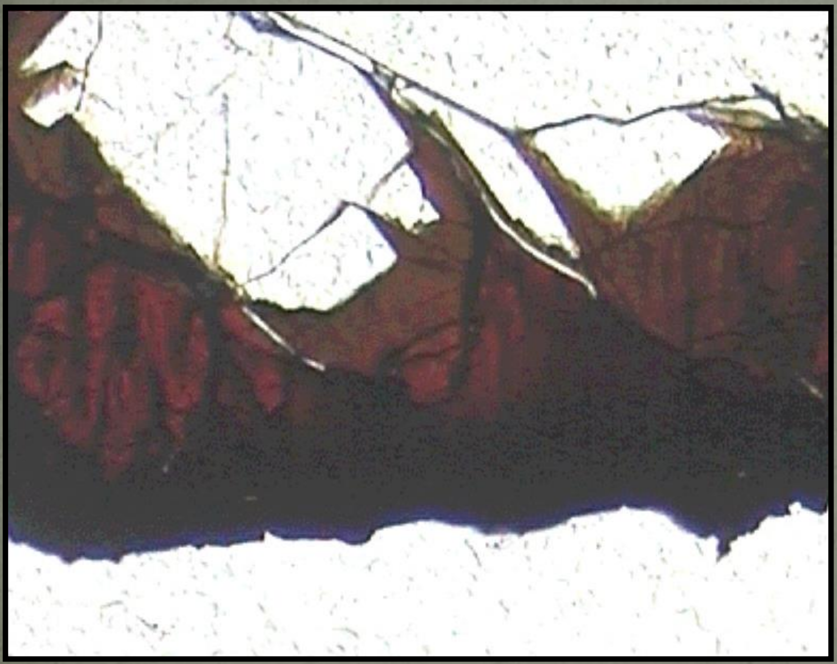


After run



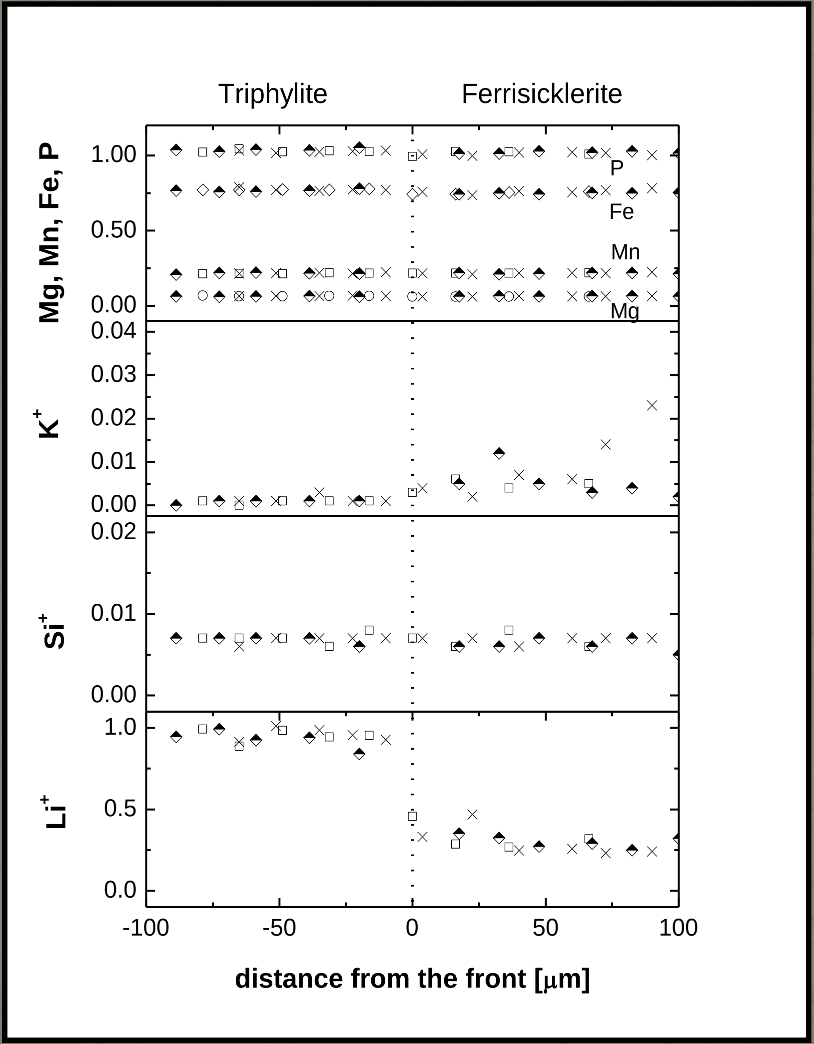
Oxidation to ferrisicklerite

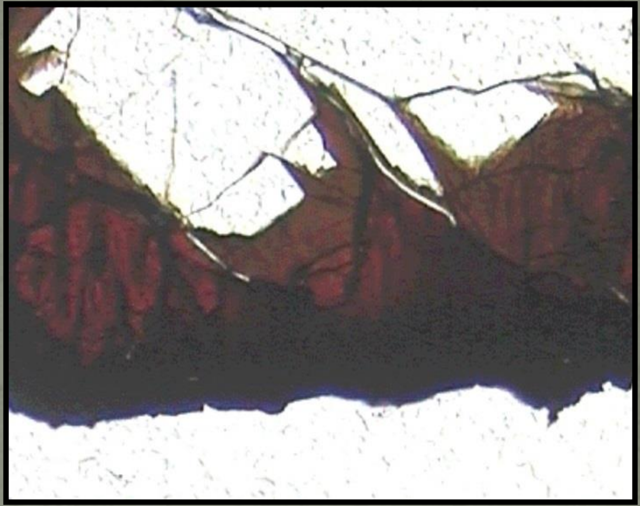
- **First hydrothermal synthesis of ferrisicklerite**
- **At very low temperature**
- **Under a very high *f*O_2**

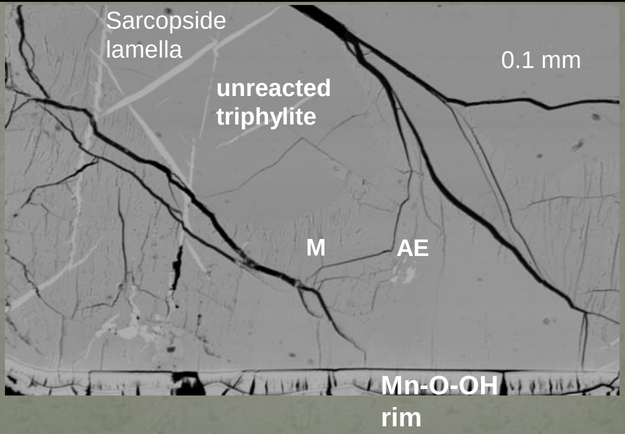


Ferrisicklerite is a low temperature metasomatic alteration mineral (?)

Decrease of the Li content

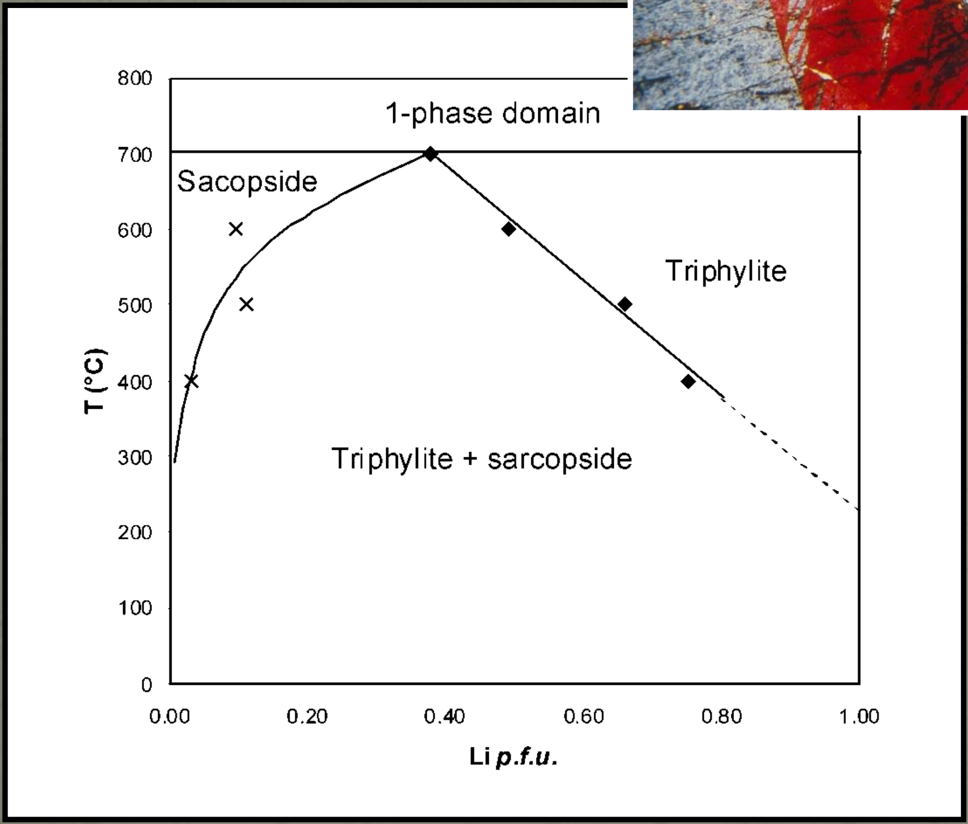






Sharp contact between triphylite and ferrisicklerite!

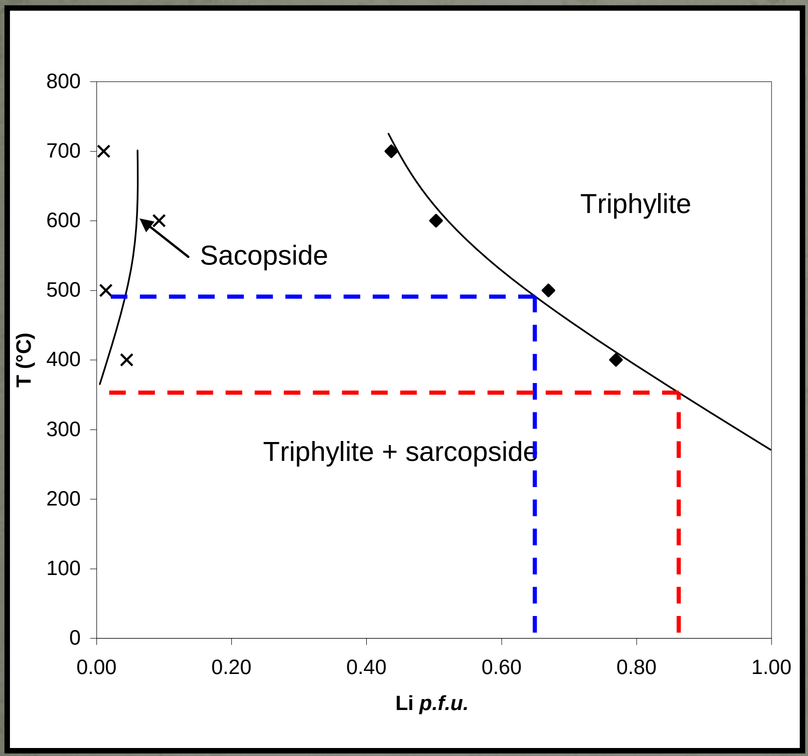
Stability of the triphylite + sarcopside assemblage



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

- **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

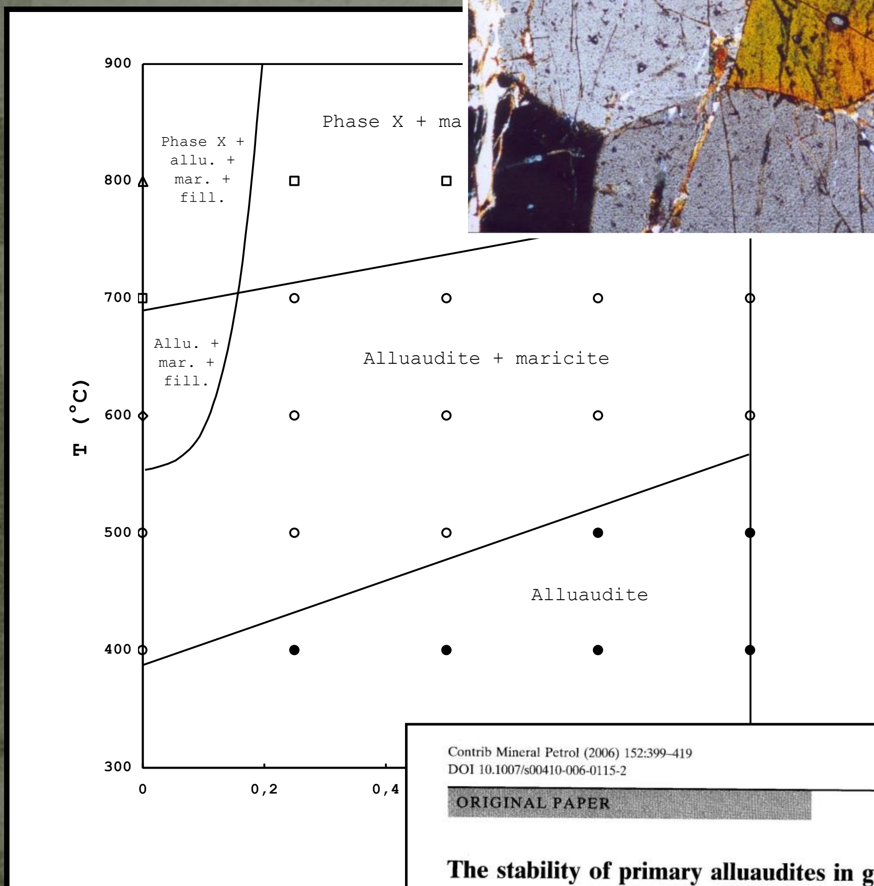
35 % sarcopside and 65 % triphylite
T ~ 500°C

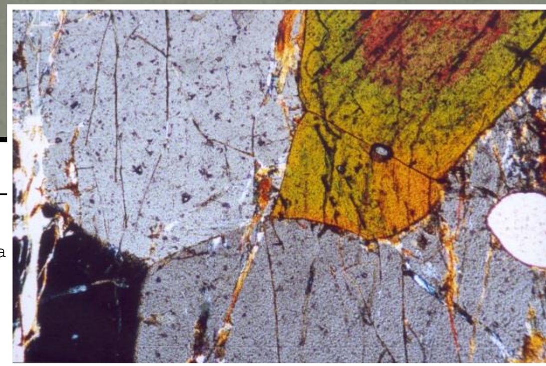
Tsoabismund

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

Stability of alluaudites

Université de Liège





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

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

No maricite [$NaFePO_4$] in pegmatites

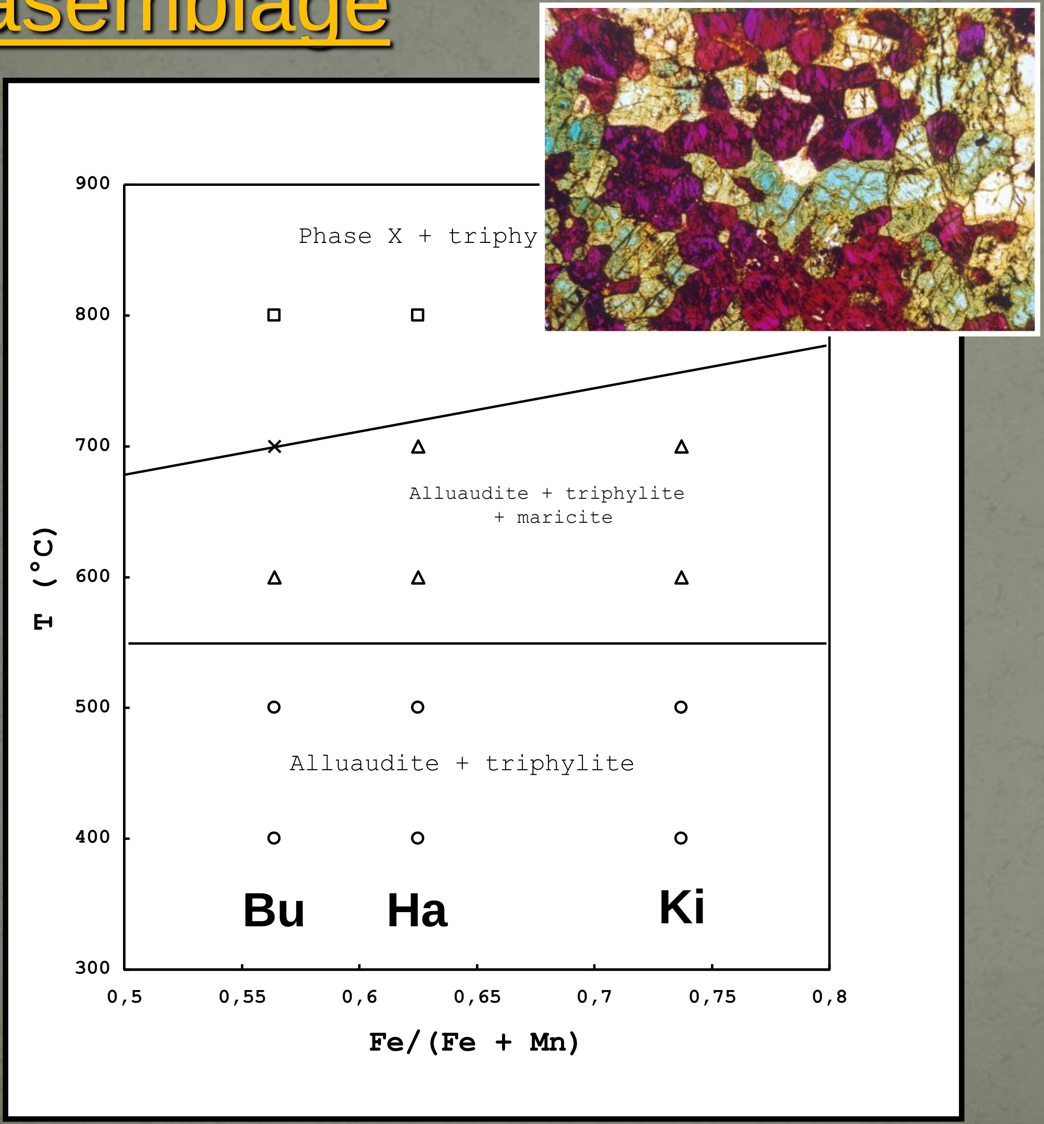
⇓

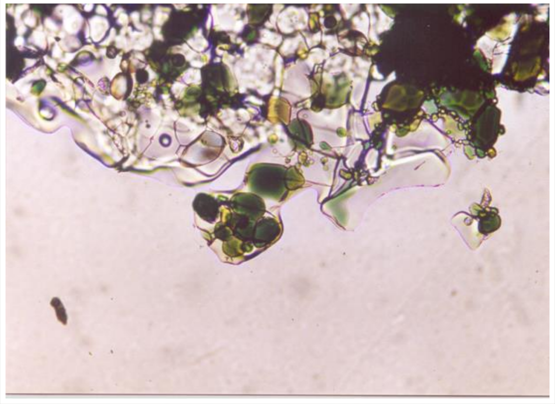
Varulite
$Na_2Mn_2Fe^{3+}(PO_4)_3$
350-400°C

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





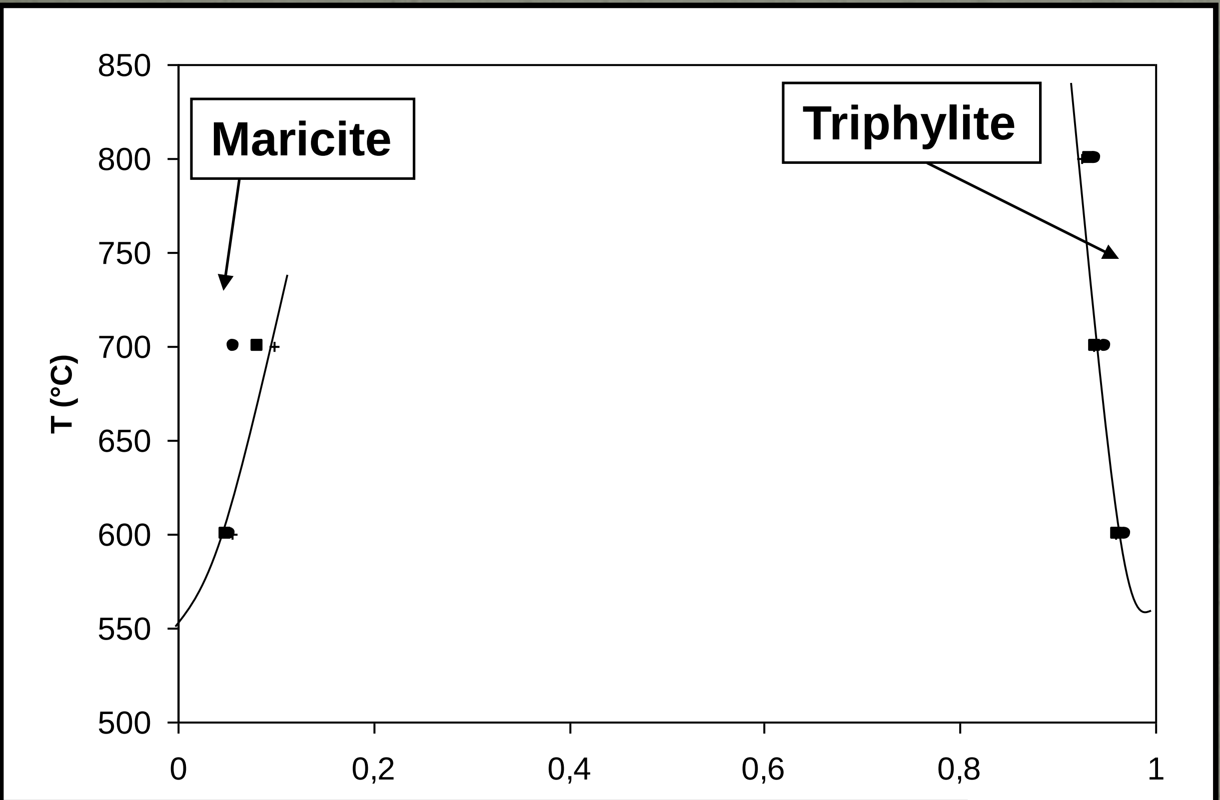
No maricite in pegmatites

↓

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!