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

Pegmatite phosphates: from the field to the lab.

Prof. Frédéric Hatert

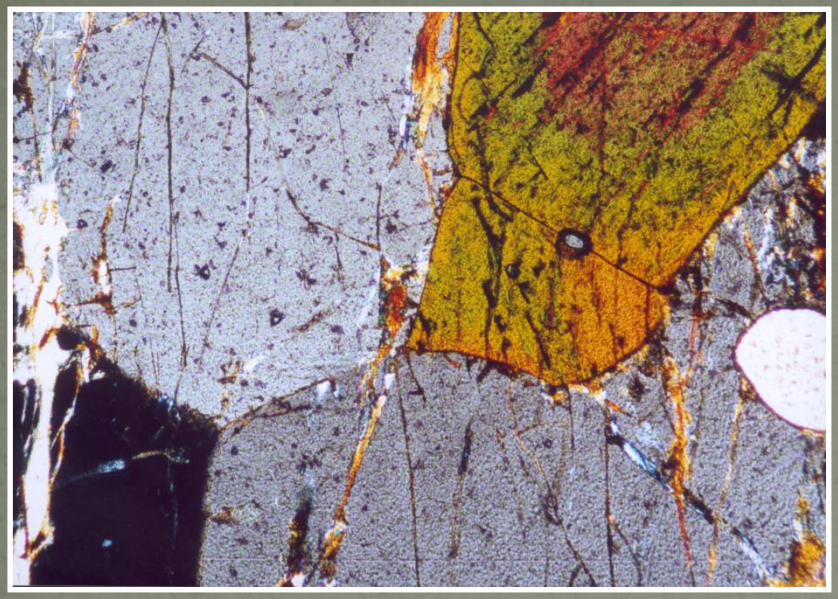
Pegmatite Workshop, 2022

Contents

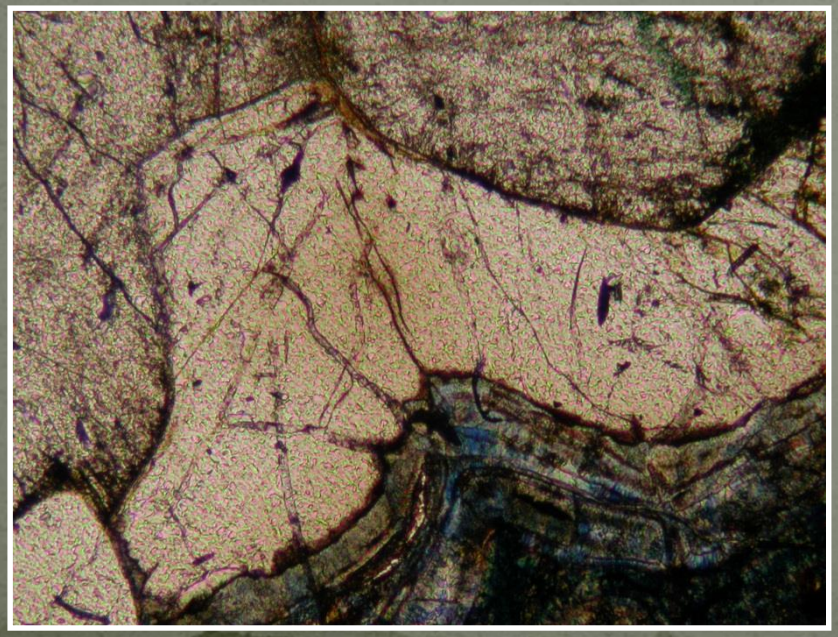
1. Introduction
2. Field observations
3. Petrography
4. Crystal chemistry and nomenclature
5. Hydrothermal experiments and stability
6. Conclusions

Occurrence

- -Granitic pegmatites
- -Metamorphic rocks
- -Meteorites

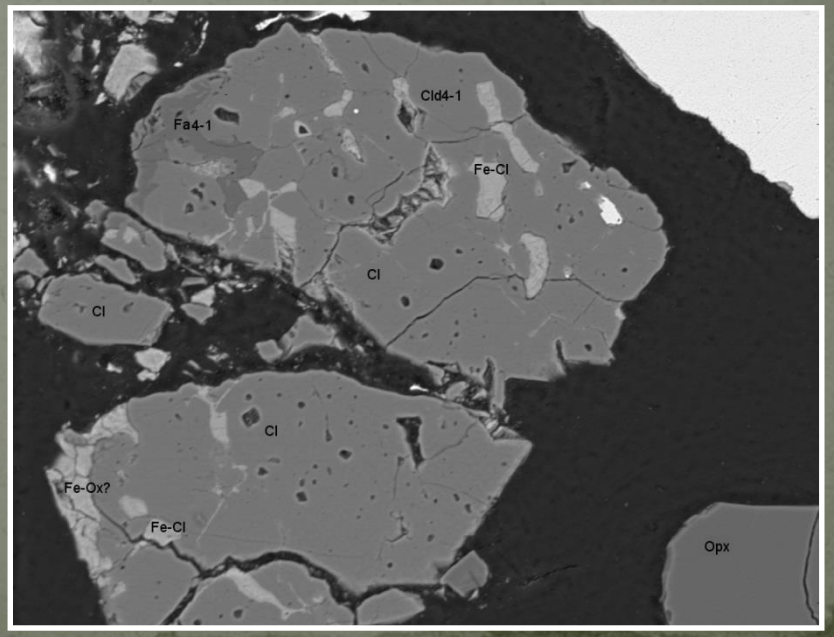


Fillowite + alluaudite, Kabira pegmatite, Uganda

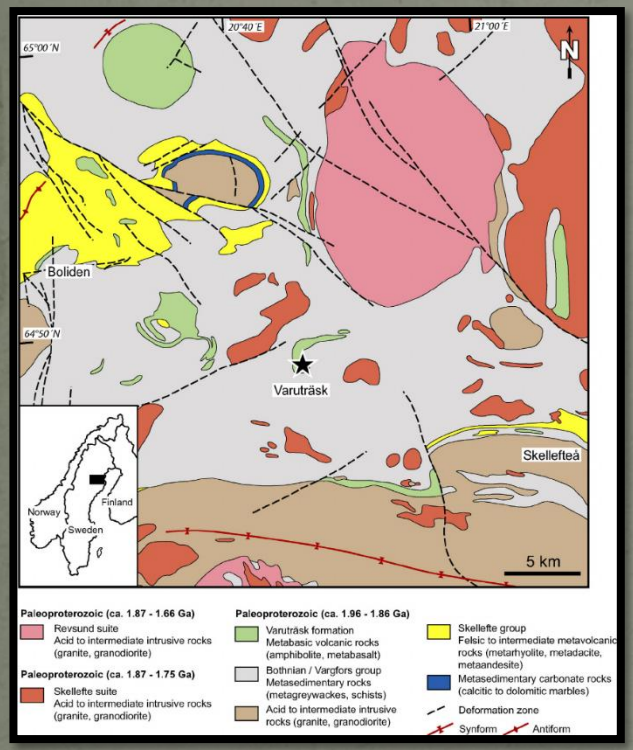


Johnsomervilleite, Loch Quoich, Scotland

Chladniite, GRA 95209 meteorite



The Varuträsk pegmatite



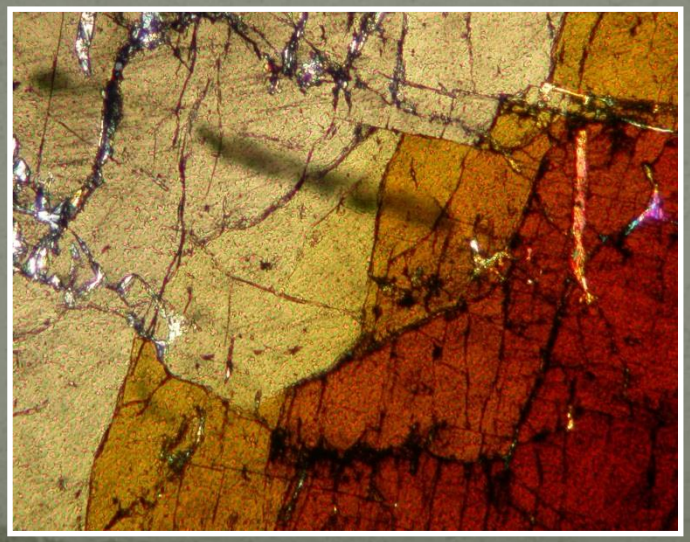
Percy Quensel (1881-1966)

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)

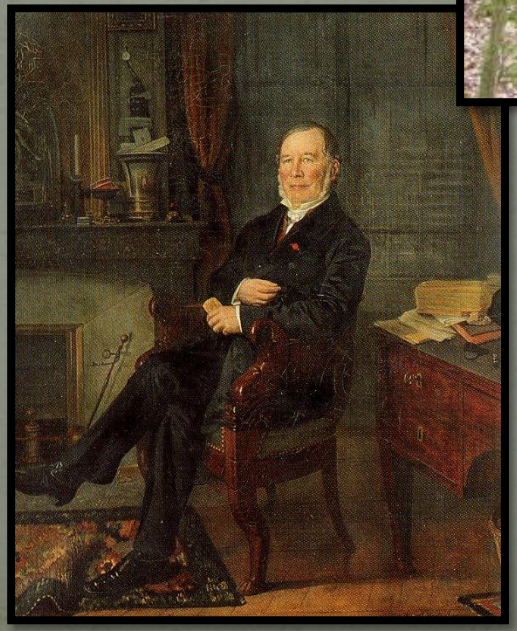
$Li(Fe^{2+},Mn^{2+})PO_4 \Rightarrow Li_{1-x}(Fe^{3+},Mn^{2+})PO_4 \Rightarrow [](Fe^{3+},Mn^{3+})PO_4$
(Triphylite) (Ferrisicklerite) (Heterosite)



The alluaudite group

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

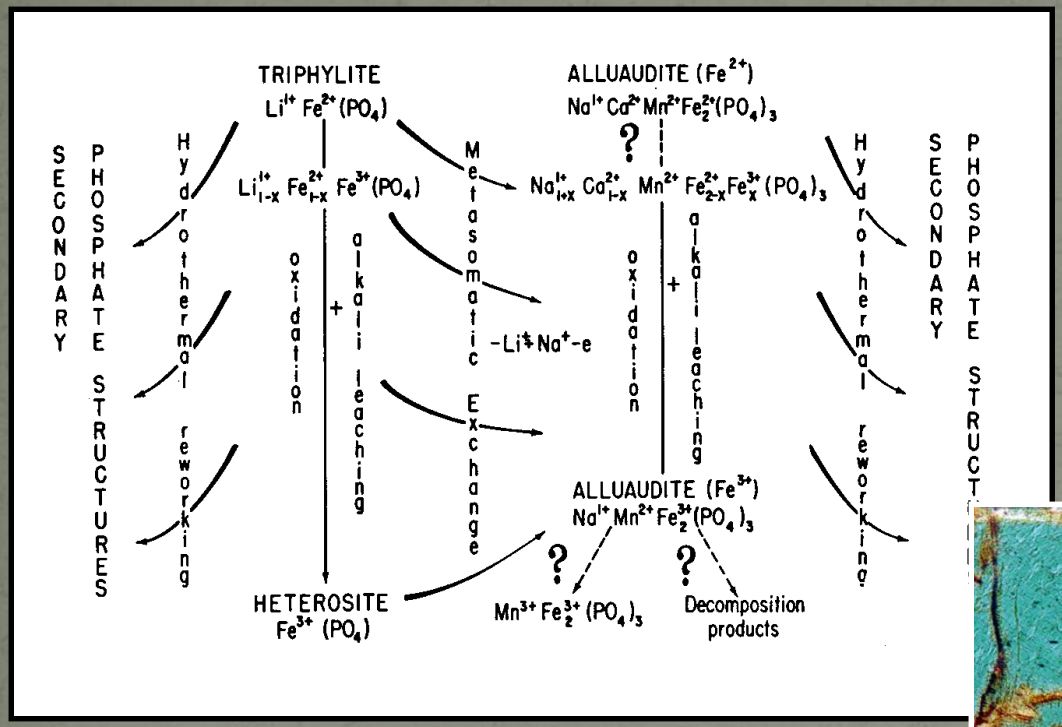
Chanteloube pegmatite
Alluaudite, $NaMnFe^{3+}{}_2(PO_4)_3$



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

Augustin-Alexis Damour
(1808-1902)

Genesis of alluaudites

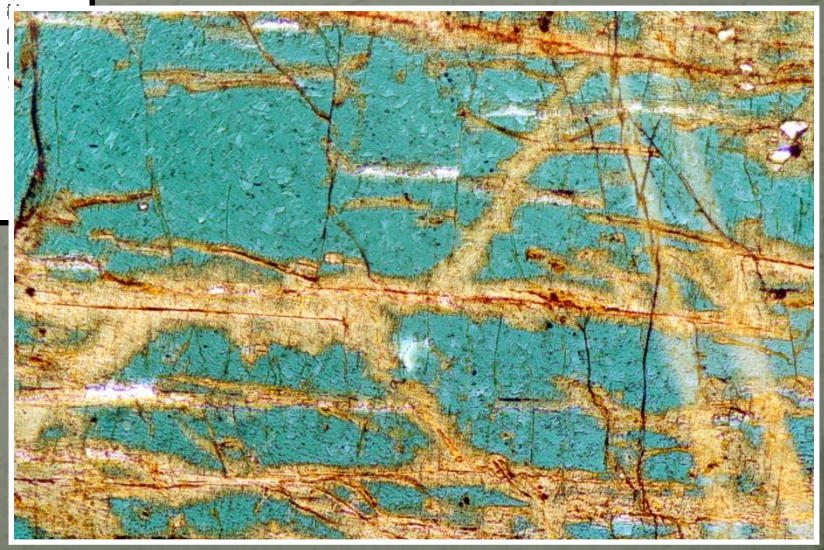


- Secondary origin
- Primary origin

Oxidation mechanism

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

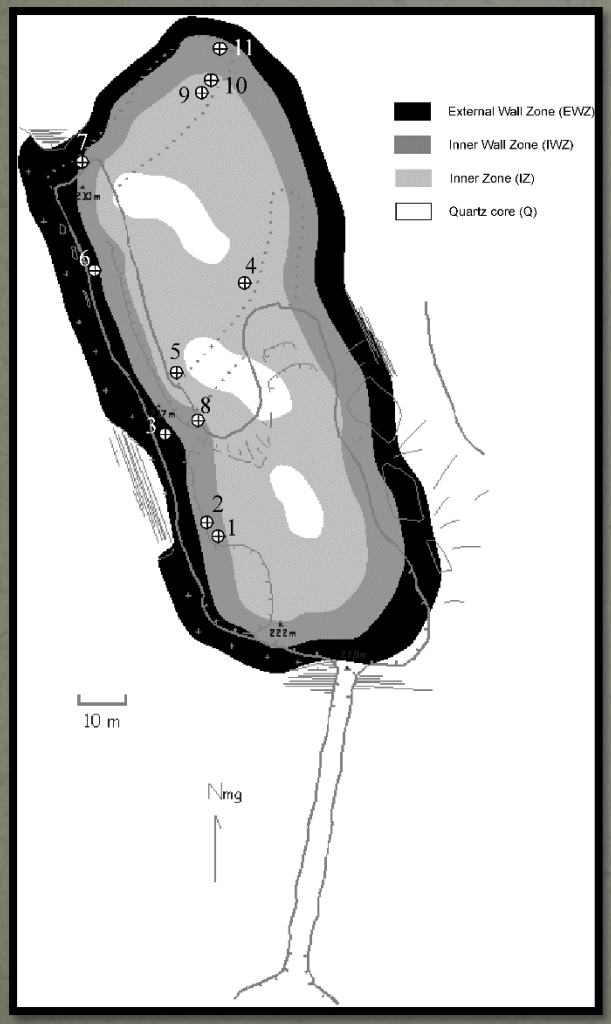
$$Na^{+} + Fe^{2+} \Rightarrow [] + Fe^{3+}$$



Alluaudite, Kibingo pegmatite, Rwanda

Let's go to the field!

Pegmatite zoning



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

MAXIME BAIJOT AND FRÉDÉRIC HATERT§

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SIMON PHILIPPO

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

Fe-Mn phosphates in pegmatites

Palermo #1 pegmatite, NH

Buranga pegmatite, Rwanda

Sapucaia pegmatite, Brazil

Back to the lab…

Fe-Mn phosphates

Petrography

Thin sections

Al phosphates

The triphylite + sarcopside assemblage

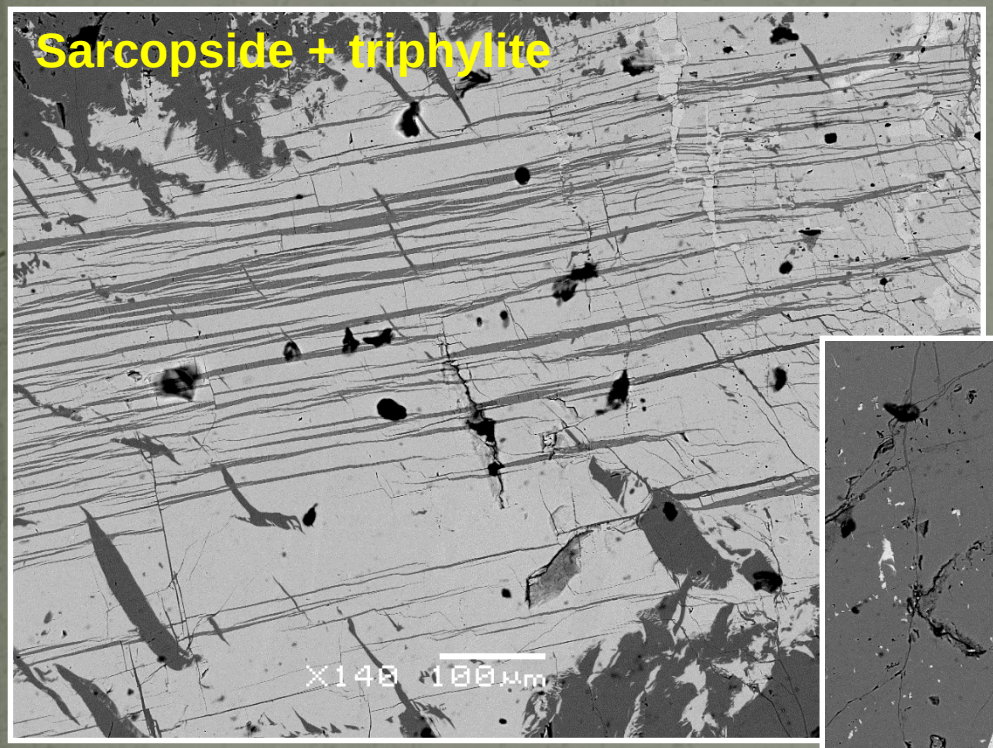
Intercroissances et inclusions
dans les associations graftonite-sarcopside-triphylite

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

Fransolet, 1977

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

The triphylite + sarcopside assemblage



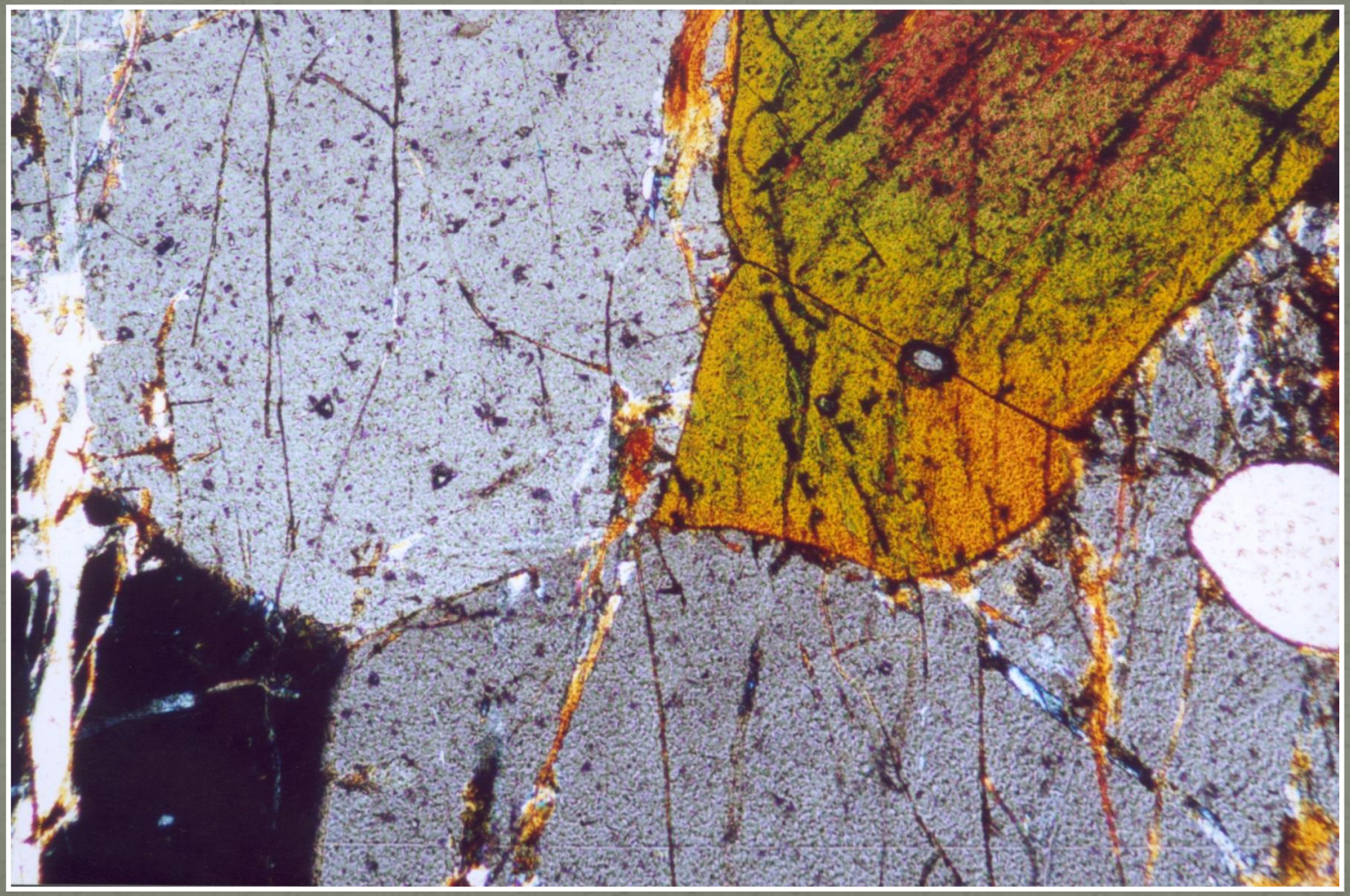
Cañada pegmatite, Spain

Lamellar textures

EXSOLUTION!!

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

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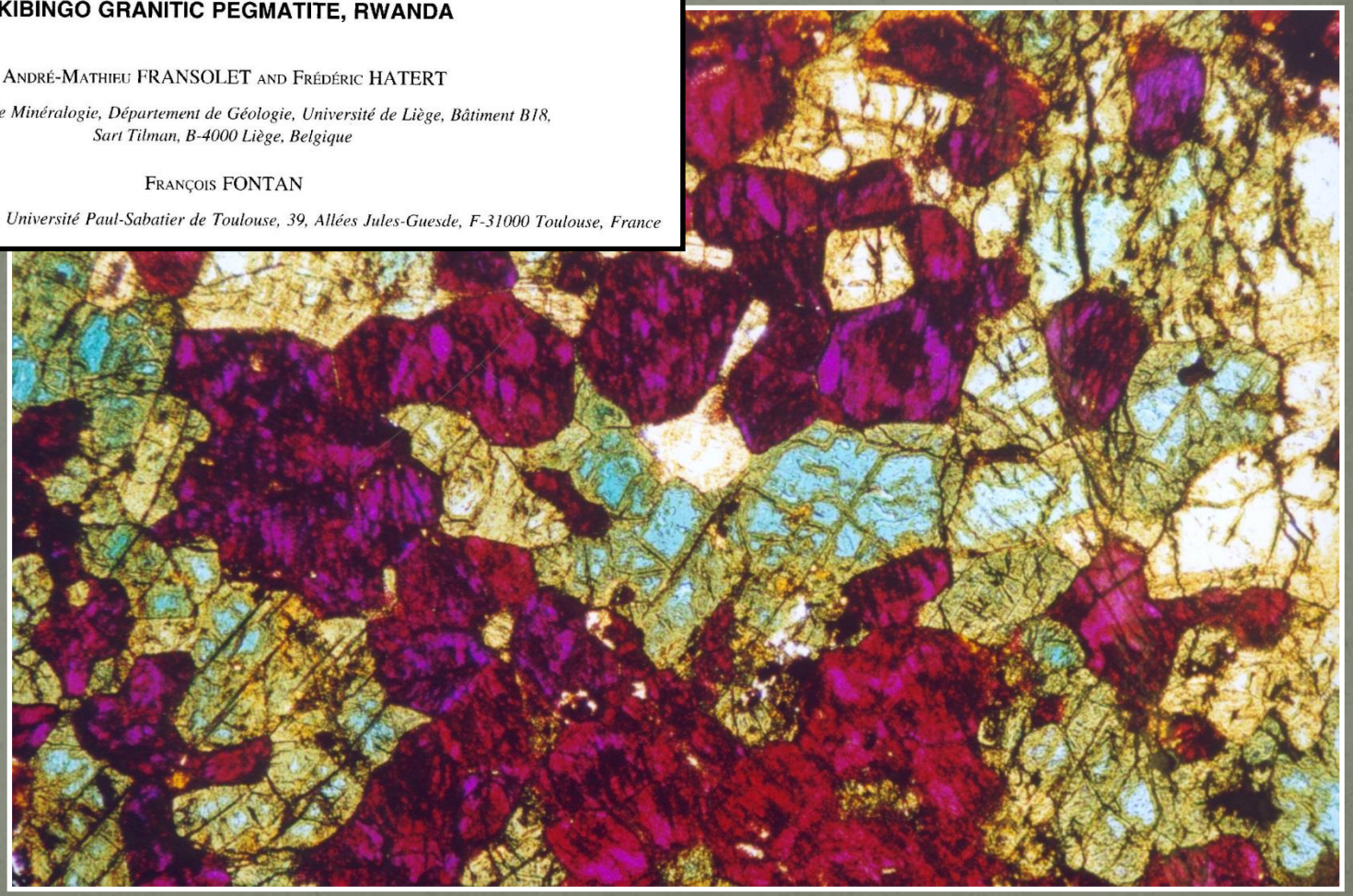
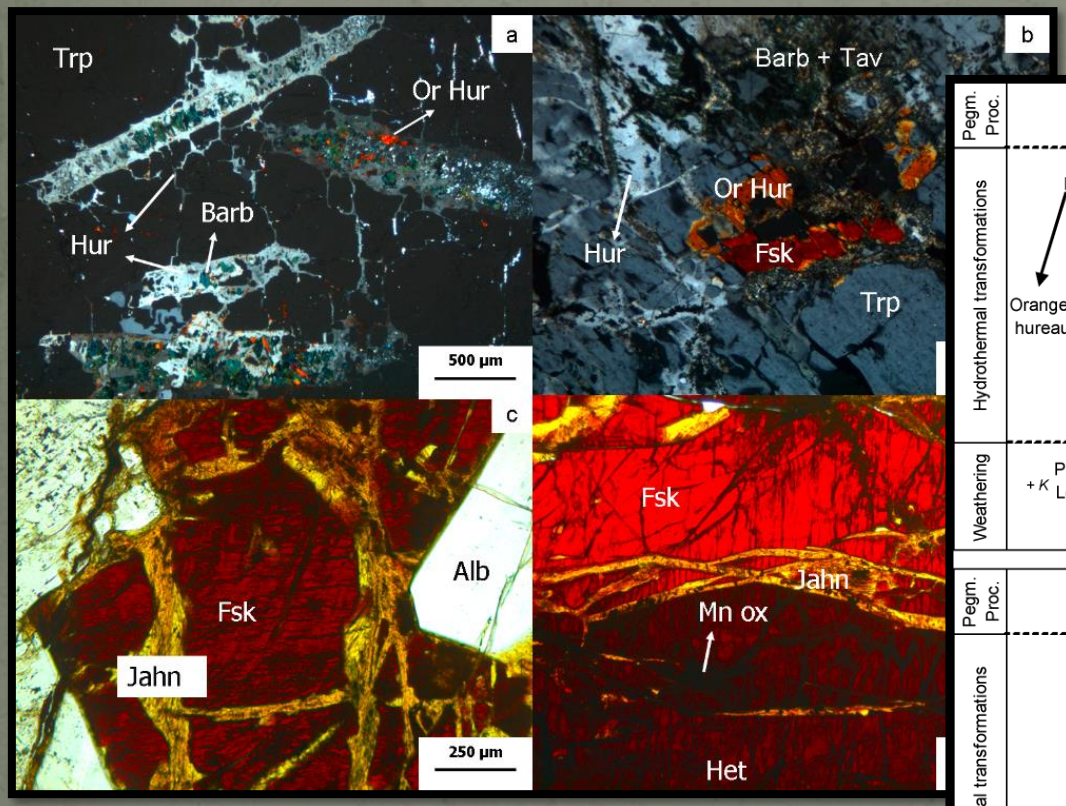
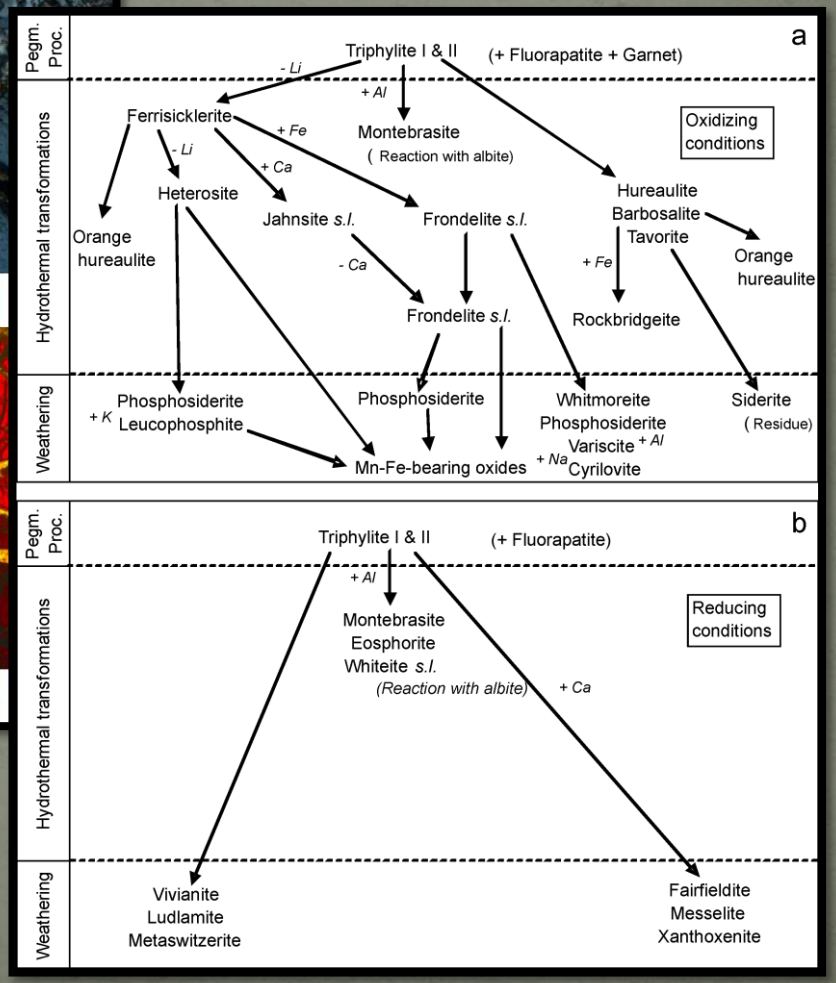
Laboratoire de Minéralogie, Université Paul-Sabatier de Toulouse, 39, Allées Jules-Guesde, F-31000 Toulouse, France



Hagendorfite, alluaudite, and heterosite, Kibingo pegmatite, Rwanda

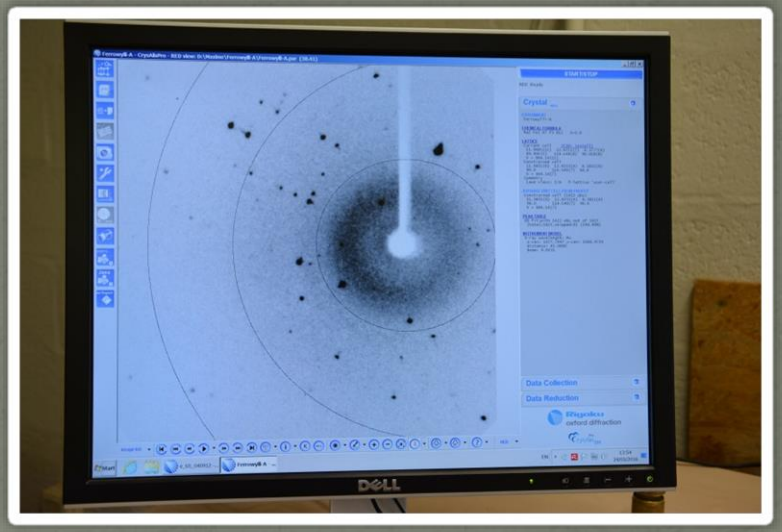
Complex assemblages from Sapucaia



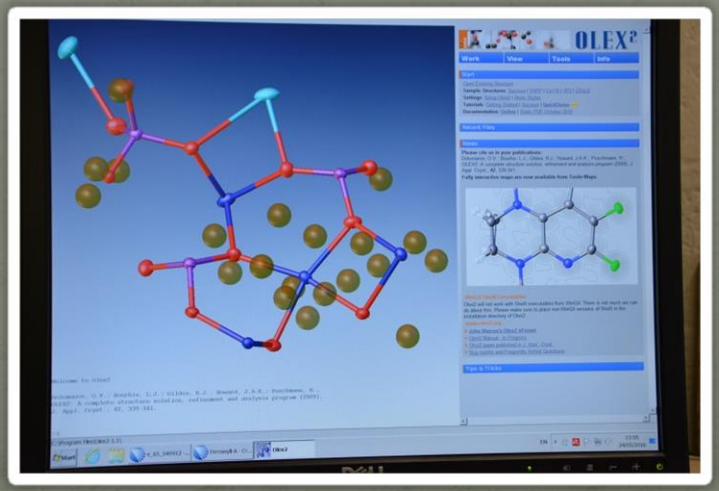


Single-crystal X-ray diffraction

4-circle diffractometer

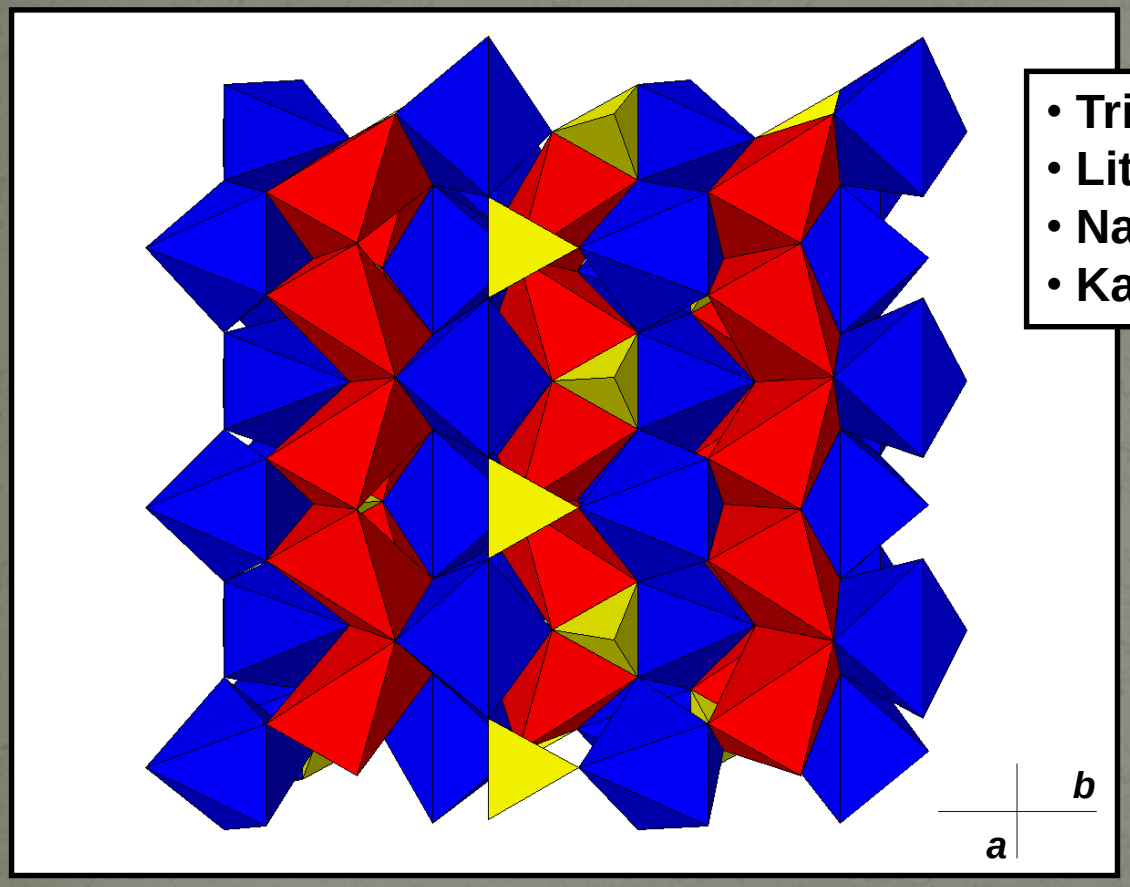


Diffraction spots



Structure determination

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...

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

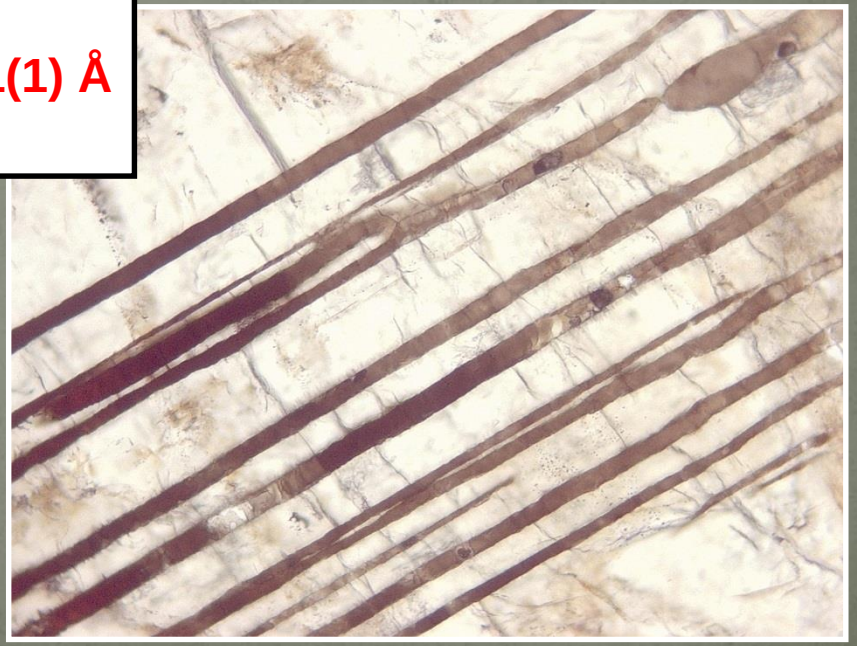
PIETRO VIGNOLA,[1] FRÉDÉRIC HATERT,[2,*] ANDRÉ-MATHIEU FRANSOLET,[2] OLAF MEDENBACH,[3] VALERIA DIELLA,[1] AND SERGIO ANDÒ[4]

$NaFe^{2+}PO_4$

***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

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ENCARNACIÓN RODA-ROBLES

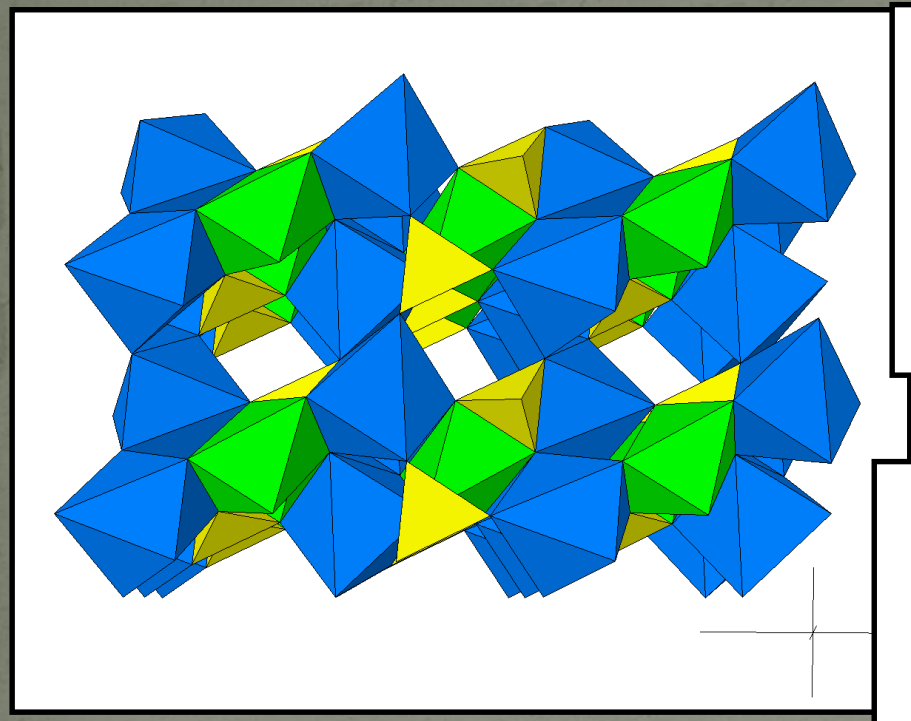
Departimento de Mineralogía y Petrología, Universidad del País Vasco/EHU, Apdo. 644, E–48080 Bilbao, Spain

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

$Mn_3(PO_4)_2$

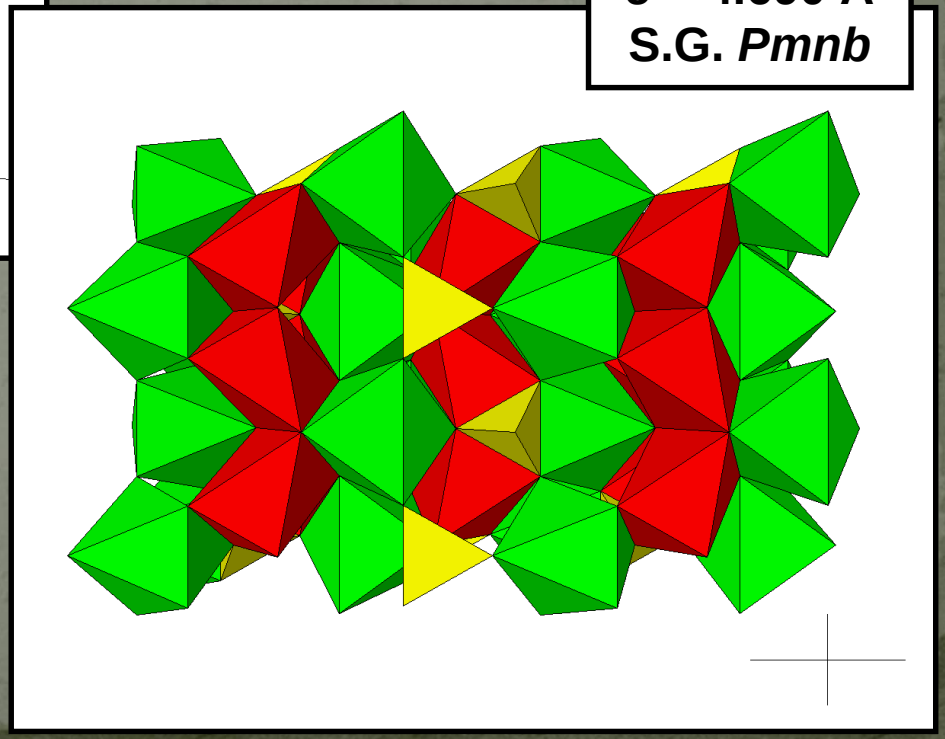
Florencia Márquez Zavalía

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. ***P*2$_1$*/c***

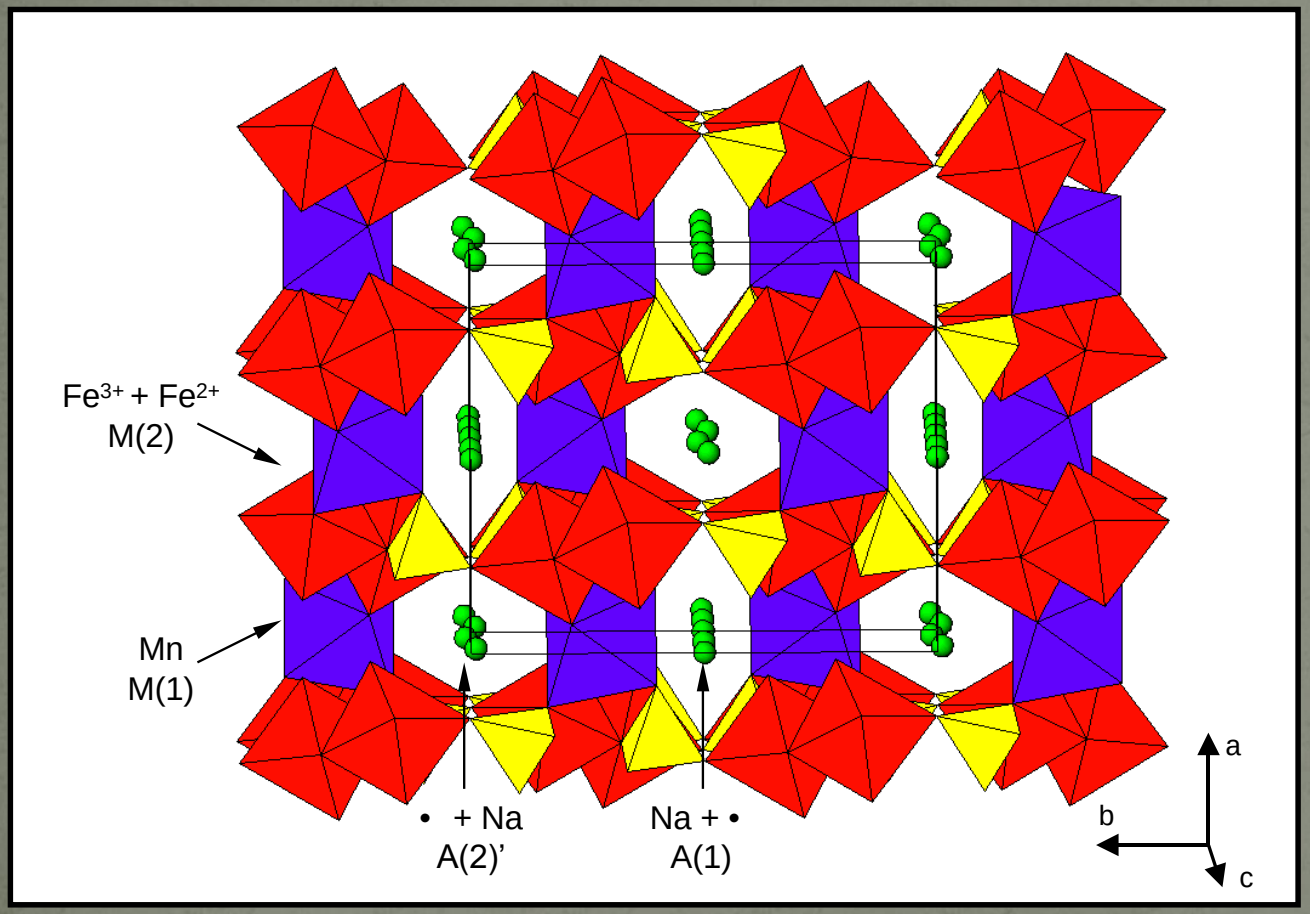
Triphylite
a **= 5.987 Å**
b **= 10.286 Å**
c **= 4.690 Å**
S.G. ***Pmnb***



- **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

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

Crystal chemistry of natural alluaudites

- **Moore & Ito (1979)**

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

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

Oxidation mechanism:

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

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

New nomenclature for alluaudites

Eur. J. Mineral.
2019, **31**, 807–822
Published online 8 July 2019

To Christian Chopin, for 30 years of dedicated service to EJM

A new nomenclature scheme for the alluaudite supergroup

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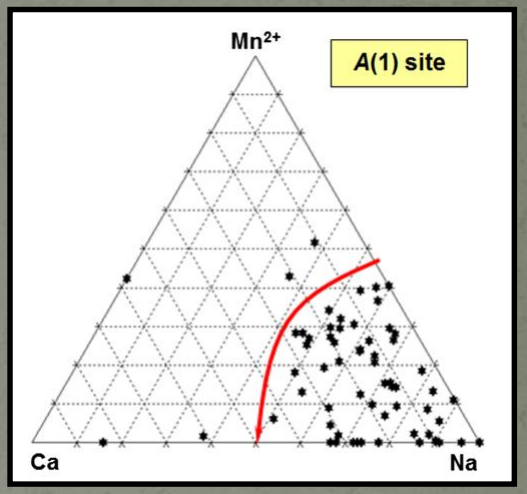
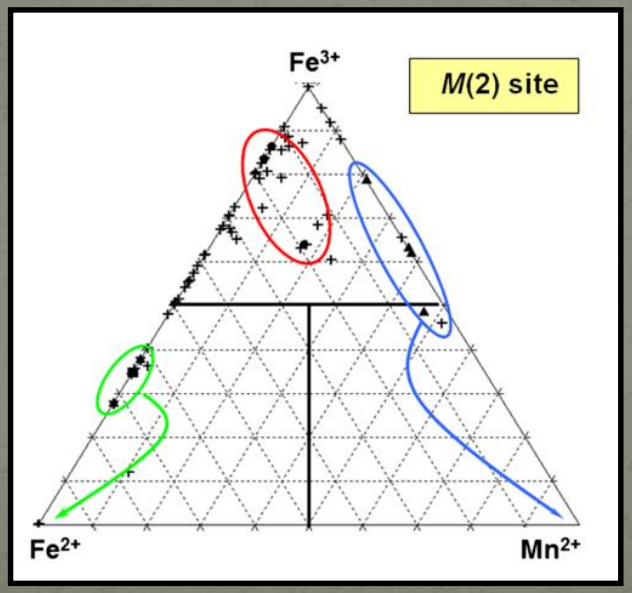
*Corresponding author, e-mail: fhatert@uliege.be





Type 1: $^{M(2)}M^{2+} < 0.5$

- $\square Na M^{2+} Fe^{3+}_2(PO_4)_3$: ALLUAUDITES
- $\square Na M^{2+} Mn^{3+}_2(PO_4)_3$: ROOT1

Type 2: $0.5 < {}^{M(2)}M^{2+} < 1.5$

- $Na_2 M^{2+} Fe^{2+} Fe^{3+}(PO_4)_3$: HAGENDORFITES
- $Na_2 M^{2+} Mn^{2+} Fe^{3+}(PO_4)_3$: VARULITES
- $Na_2 M^{2+} Mg Fe^{3+}(PO_4)_3$: ROOT2

Hydrothermal experiments

Hydrothermal lab

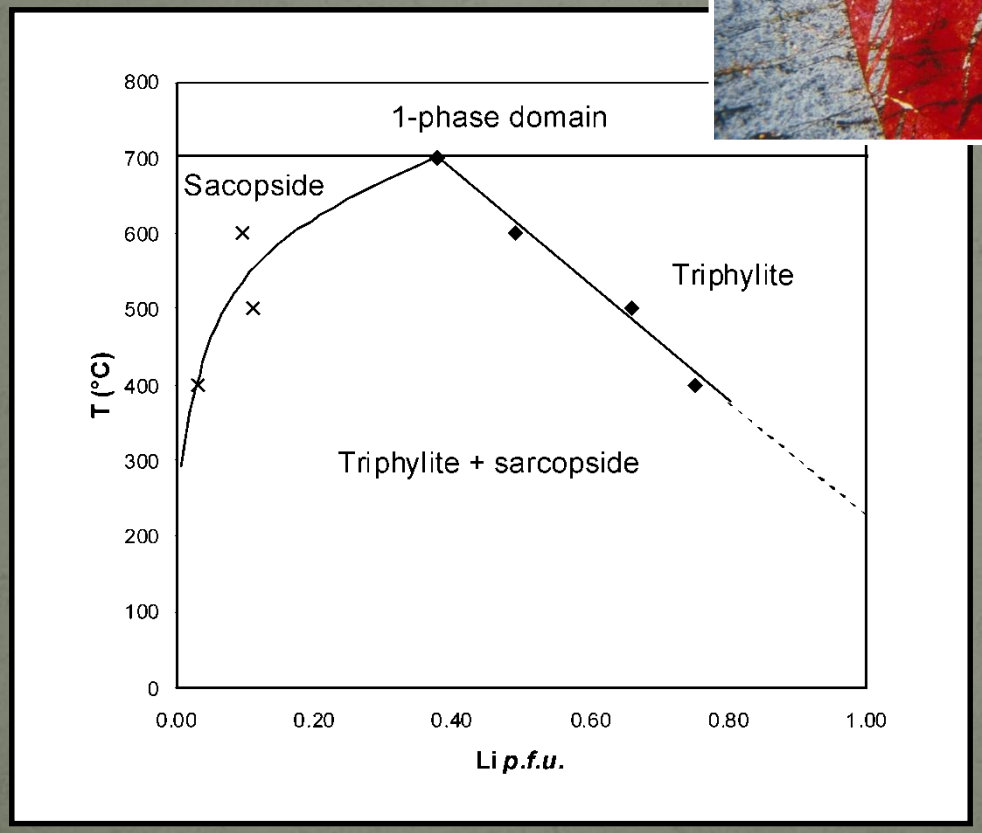
Gold tubes

Hydrothermal bomb

Opened gold capsules

P = 1 kbar
T = 400-800°C

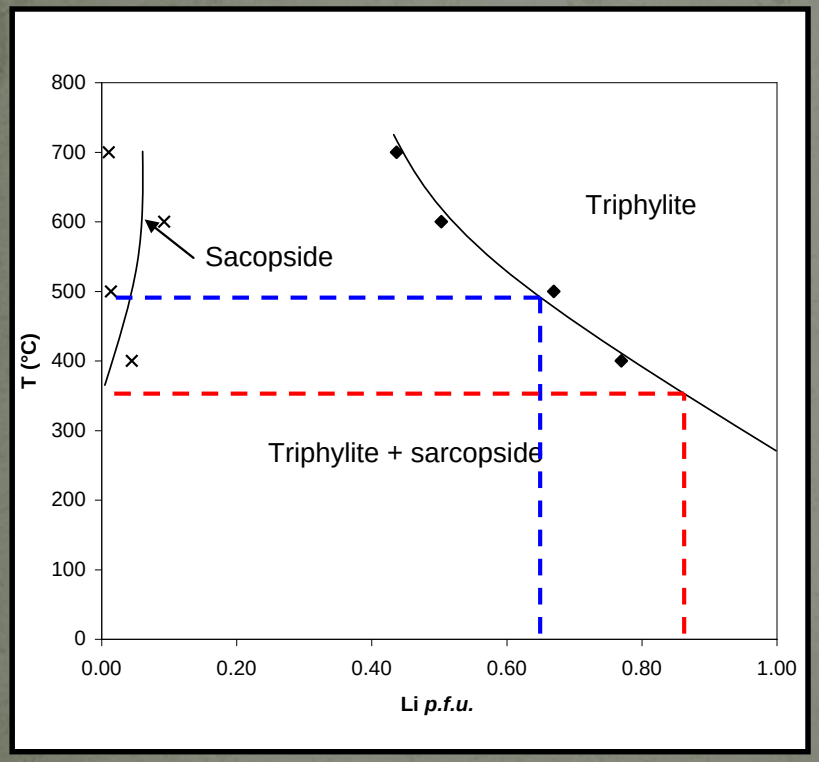
Stability of the triphylite + sarcopside assemblage



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

- 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

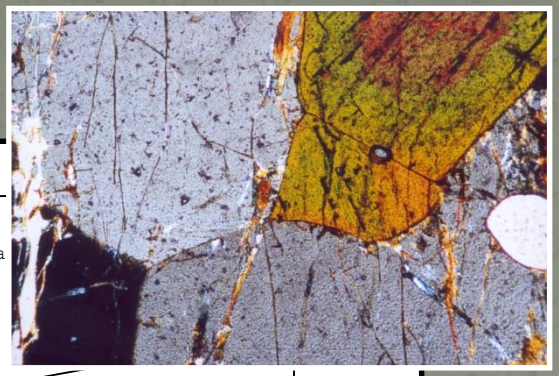
T ~ 500°C

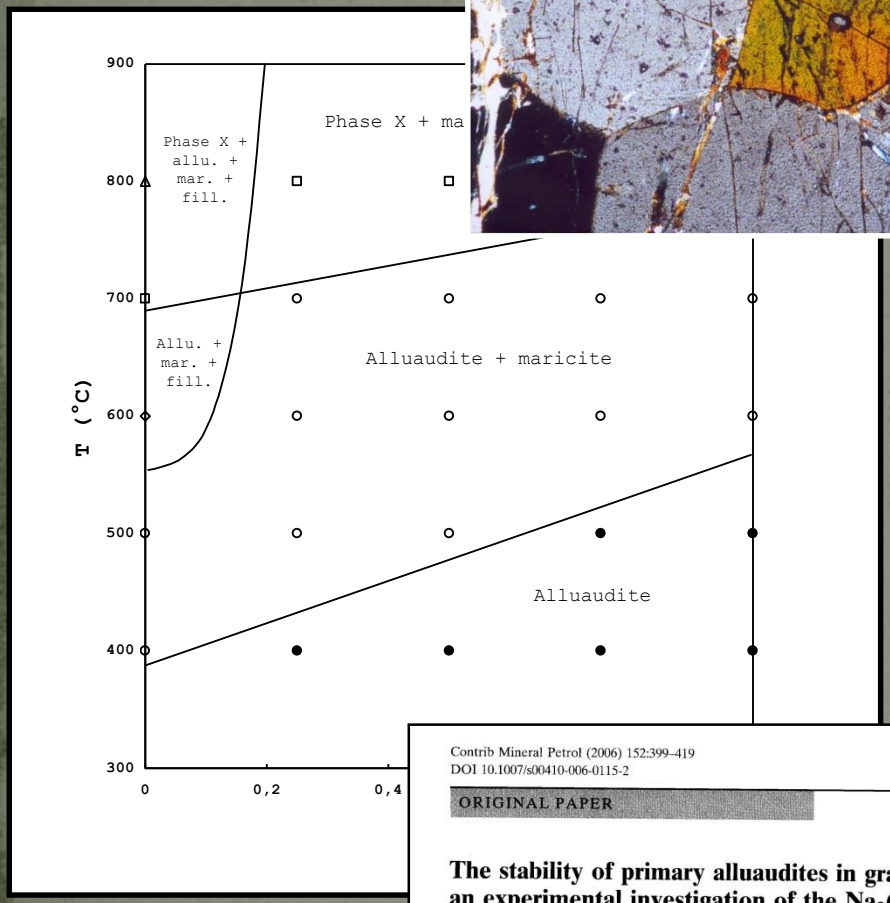
Tsoabismund

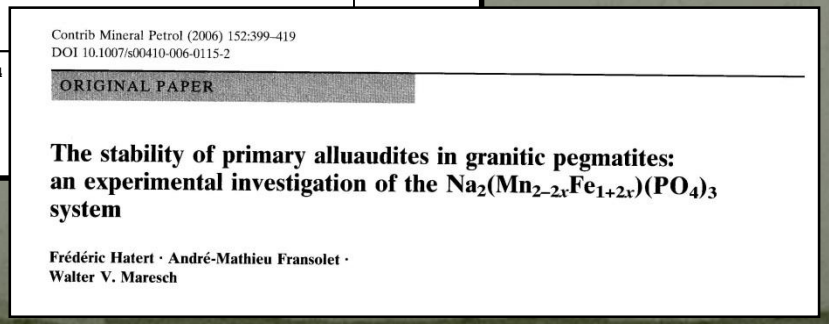
15 % sarcopside and 85 % triphylite

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

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

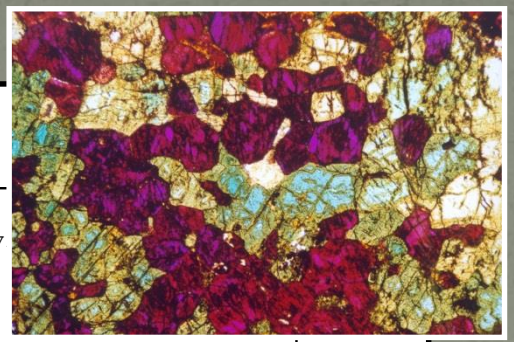
No maricite [$NaFePO_4$] in pegmatites

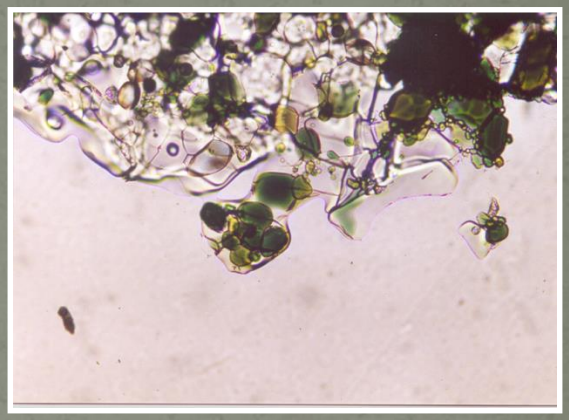
Varulite
$Na_2Mn_2Fe^{3+}(PO_4)_3$
350-400°C

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



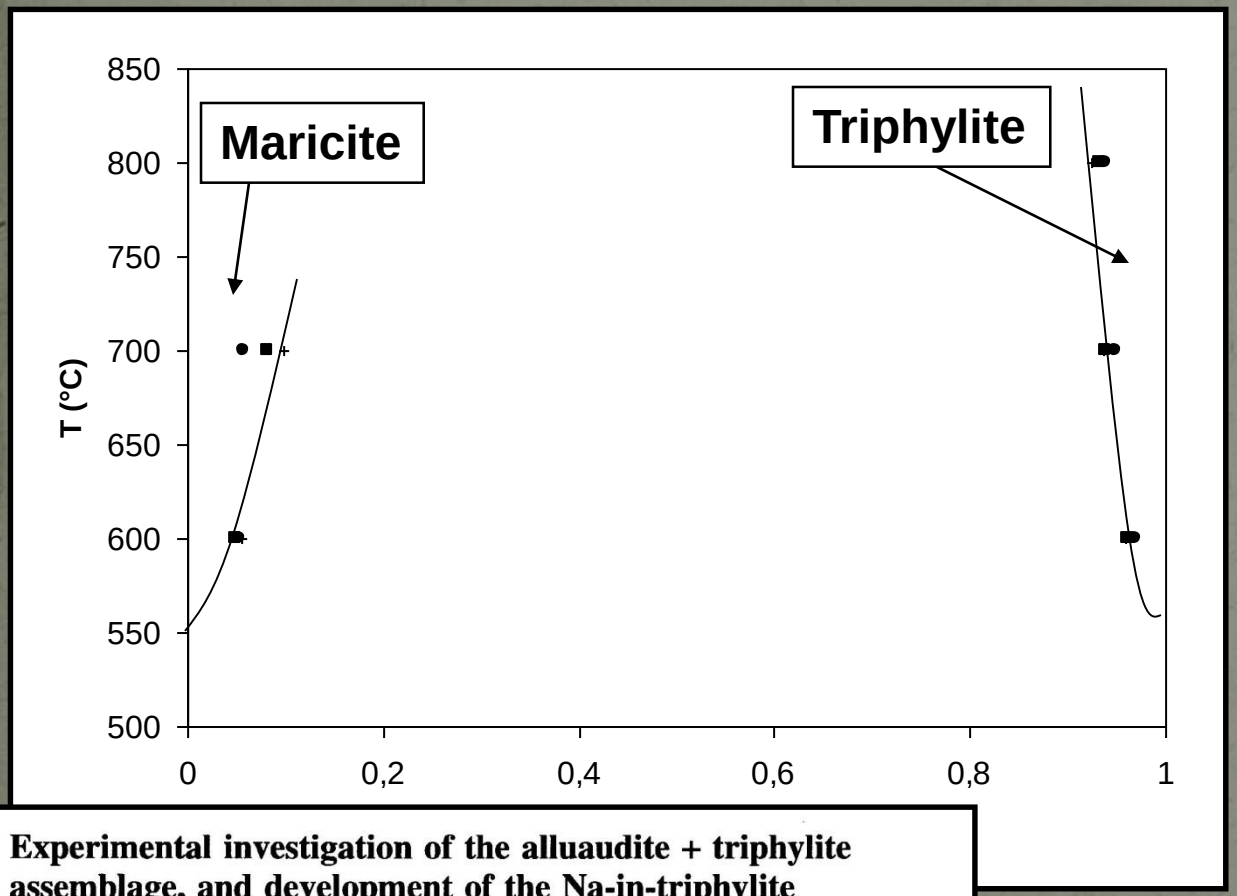


No maricite in pegmatites

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

• **Phosphates are « exotic » minerals, forming large masses in the most evolved parts of granitic pegmatites**

• **<u>They are of great interest for pegmatologists, to:</u>**

- ✓ **Understand pegmatite evolution during the post-magmatic stages (HT and LT hydrothermal, meteoric)**
- ✓ **Definine the T and oxygen fugacity conditions of pegmatites**

• **<u>For mineralogists and solid-state scientists:</u>**

- ✓ **They provide an infinite source of new mineral species**
- ✓ **Their exciting crystal structures are an inspiration for the development of new materials (alluaudites and triphylites in Li-ion batteries)**