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Stability of the alluaudite + triphylite paragenesis in granitic pegmatites, and first experimental evidence of sodium incorporation into triphylite

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ELBA-2005

Marina di Campo, May 24th 2005

Alluaudite, Buranga pegmatite, Rwanda

Alluaudite-type structure (*C2/c*)

(Moore, 1971; Hatert *et al.*, 2000)

$Na_2MnFe^{2+}Fe^{3+}(PO_4)_3 \Rightarrow \square NaMnFe^{3+}{}_2(PO_4)_3$
(Hagendorfite) (Alluaudite)

$Na_2Fe^{2+}{}_2Fe^{3+}(PO_4)_3 \Rightarrow \square NaFe^{2+}Fe^{3+}{}_2(PO_4)_3$
(Ferrohagendorfite) (Ferroalluaudite)

Olivine-type structure (*Pmnb*)

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

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

Genesis of alluaudites

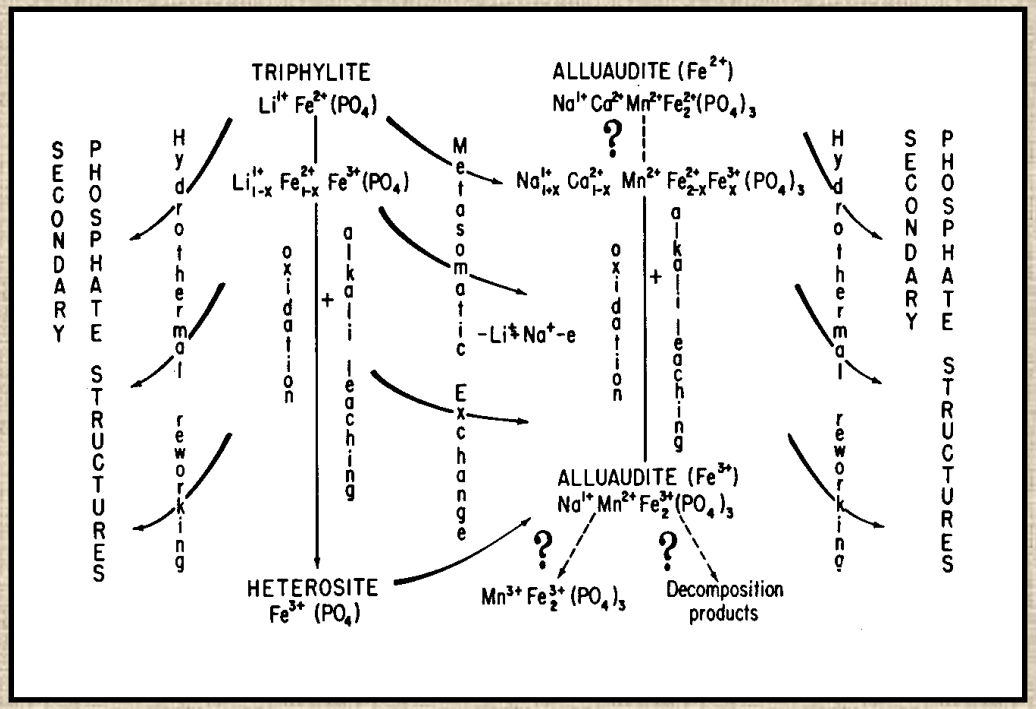
- **Quensel (1957)**:

  Varulite and « hühnerkobelite » crystallize between 400 and 600°C ⇒ PRIMARY

- **Moore (1971)**:

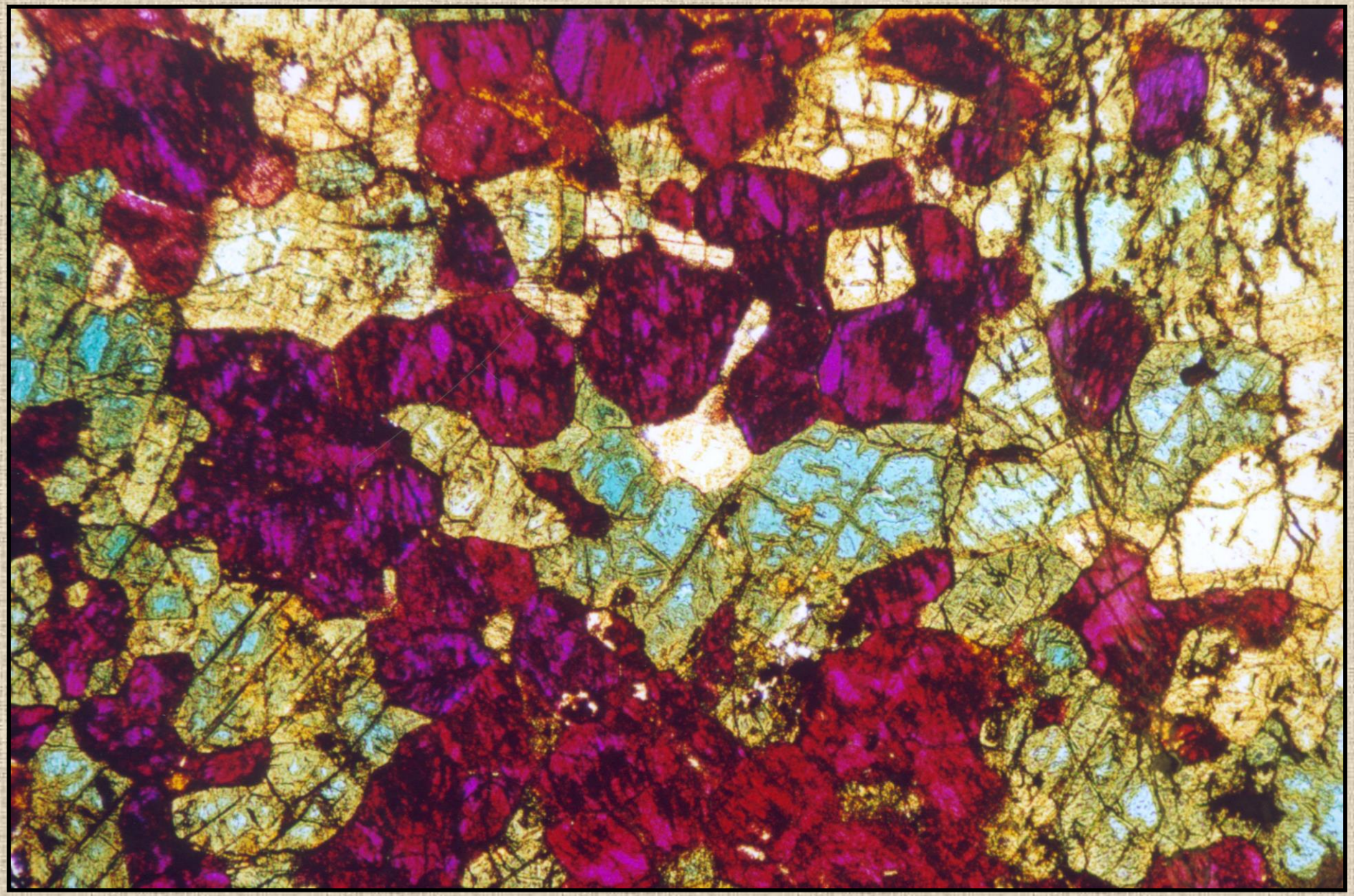
  Alluaudites are produced by oxidation and Li → Na exchange, starting from triphylite-lithiophilite

  ⇒ SECONDARY



- **Fransolet *et al.* (1994, 1997, 1998, 2004)**:

  Observation of PRIMARY alluaudite + ferrisicklerite + heterosite, alluaudite + arrojadite, and alluaudite + fillowite paragenesis



Hagendorfite, alluaudite and heterosite, Kibingo pegmatite, Rwanda

Experimental

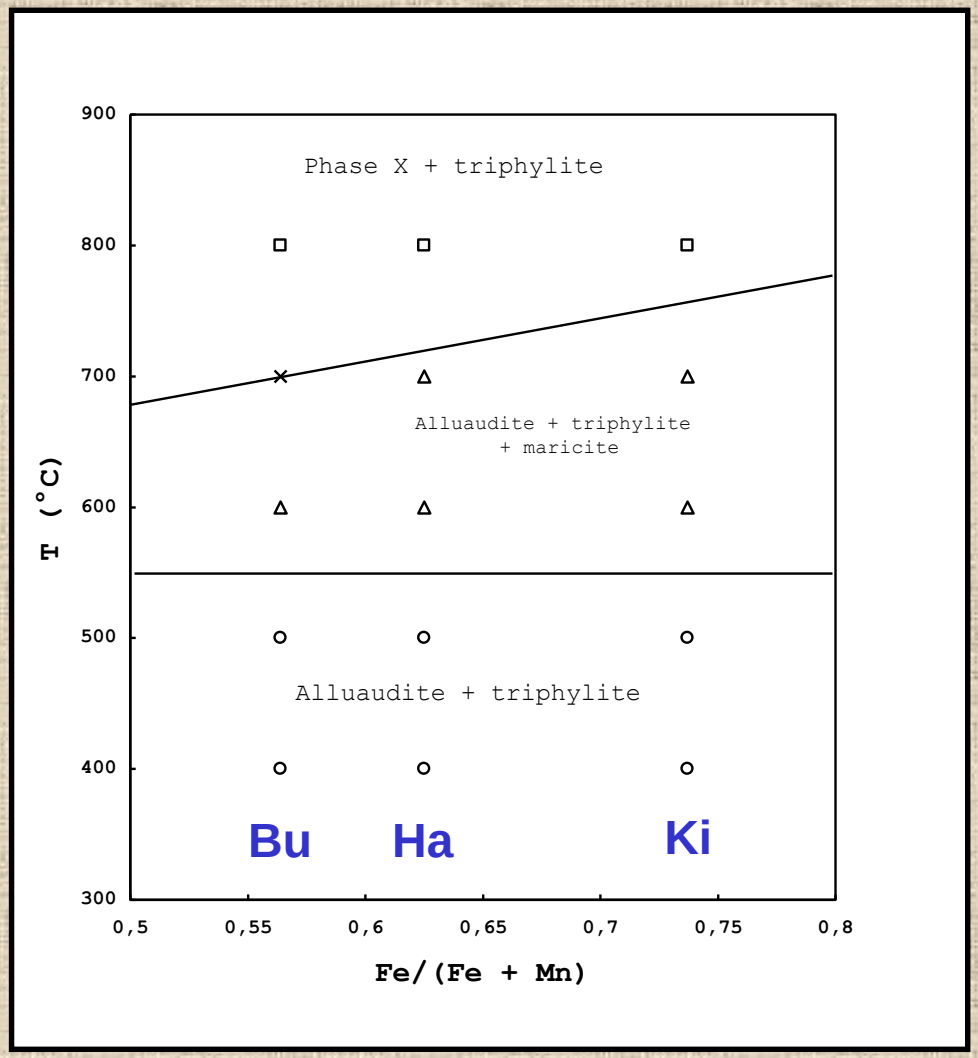
Buranga: $LiNa_2Mn_{1.745}Fe^{2+}_{1.255}Fe^{3+}(PO_4)_4$

Hagendorf-Süd: $LiNa_2Mn_{1.502}Fe^{2+}_{1.498}Fe^{3+}(PO_4)_4$

Kibingo: $LiNa_2Mn_{1.054}Fe^{2+}_{1.946}Fe^{3+}(PO_4)_4$

- Hydrothermal synthesis
- Tuttle-type cold-seal bombs
- T = 400-800 °C
- P = 1 kbar
- Double capsule method (Au 4 mm, $Ag_{70}Pd_{30}$ 2 mm)
- Oxygen fugacity: Ni/NiO (NNO)

Stability of the alluaudite + triphylite paragenesis

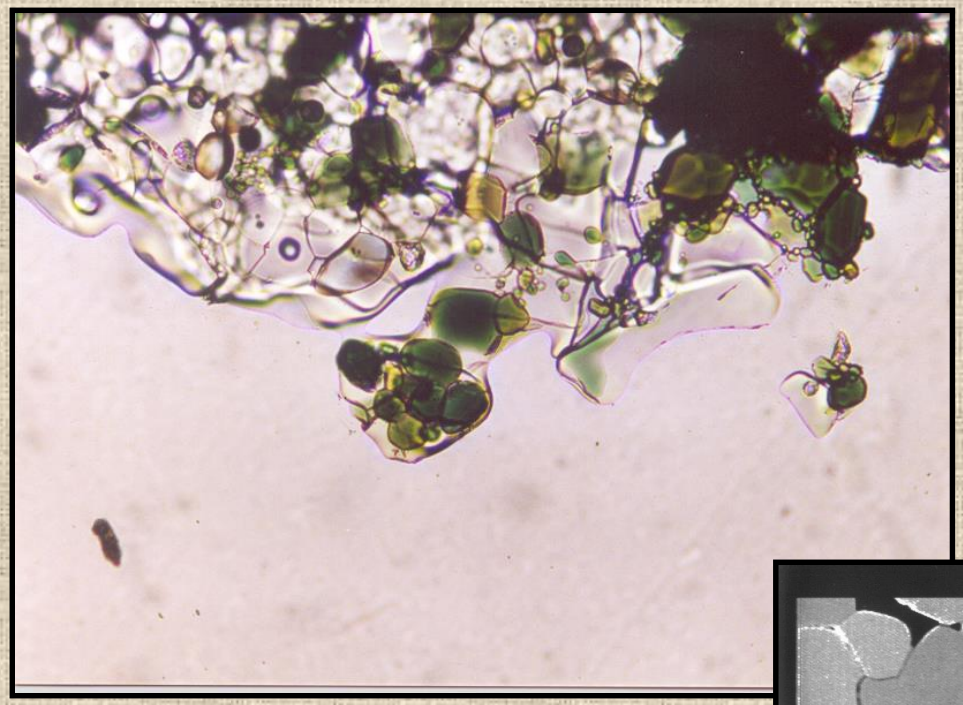


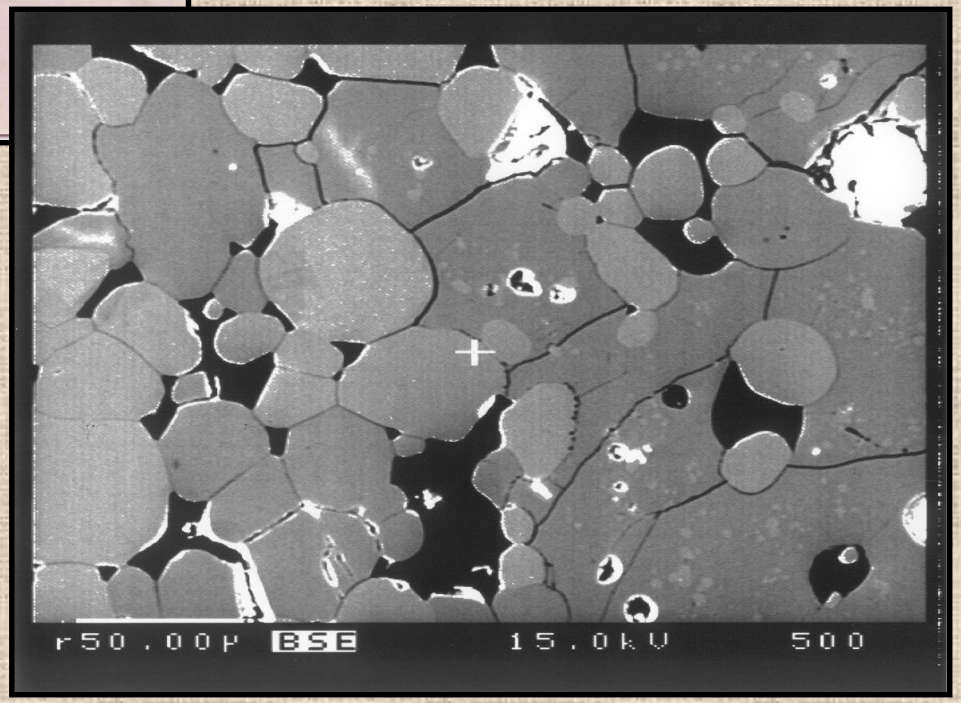
No maricite in pegmatites

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

Maricite: $Na(Fe^{2+},Mn)(PO_4)$

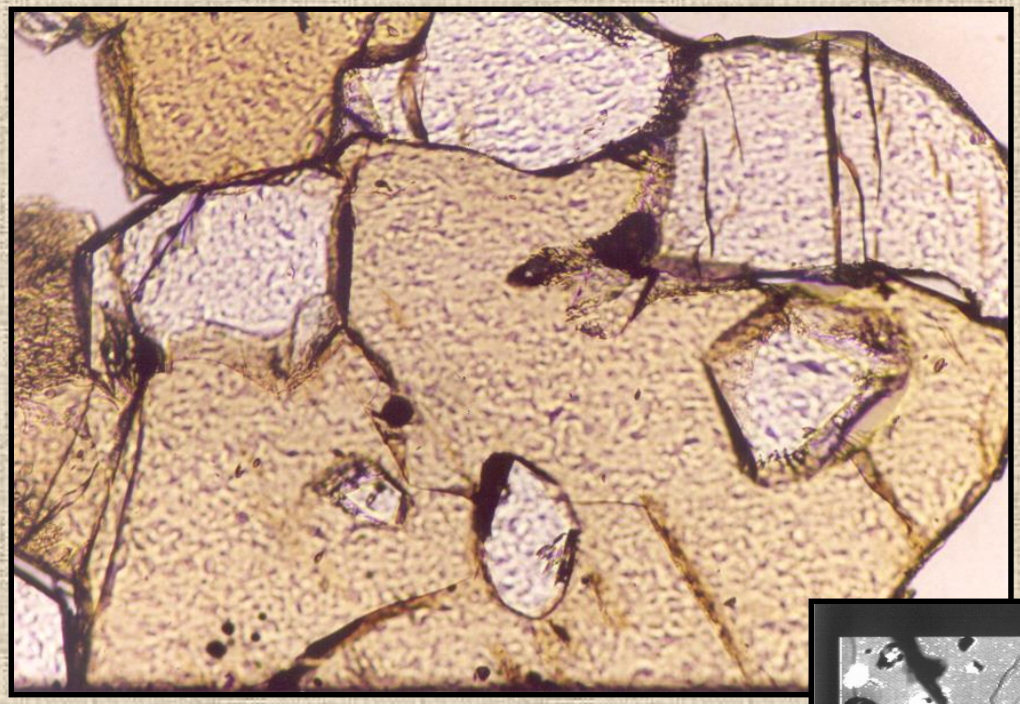
Bu = Buranga, Rwanda
Ha = Hagendorf-Süd, Germany
Ki = Kibingo, Rwanda





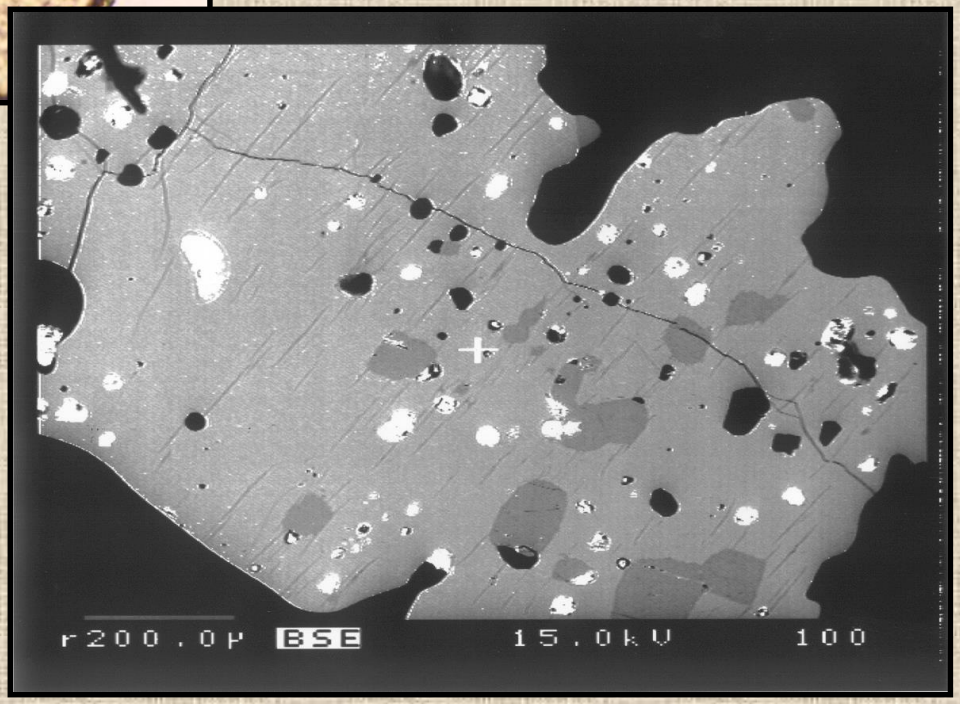
700°C

Alluaudite + triphylite + maricite



800°C

X-phase + triphylite



X-phase:

Pnma or $Pna2_1$

a = 25.892(4) Å

b = 14.792(5) Å

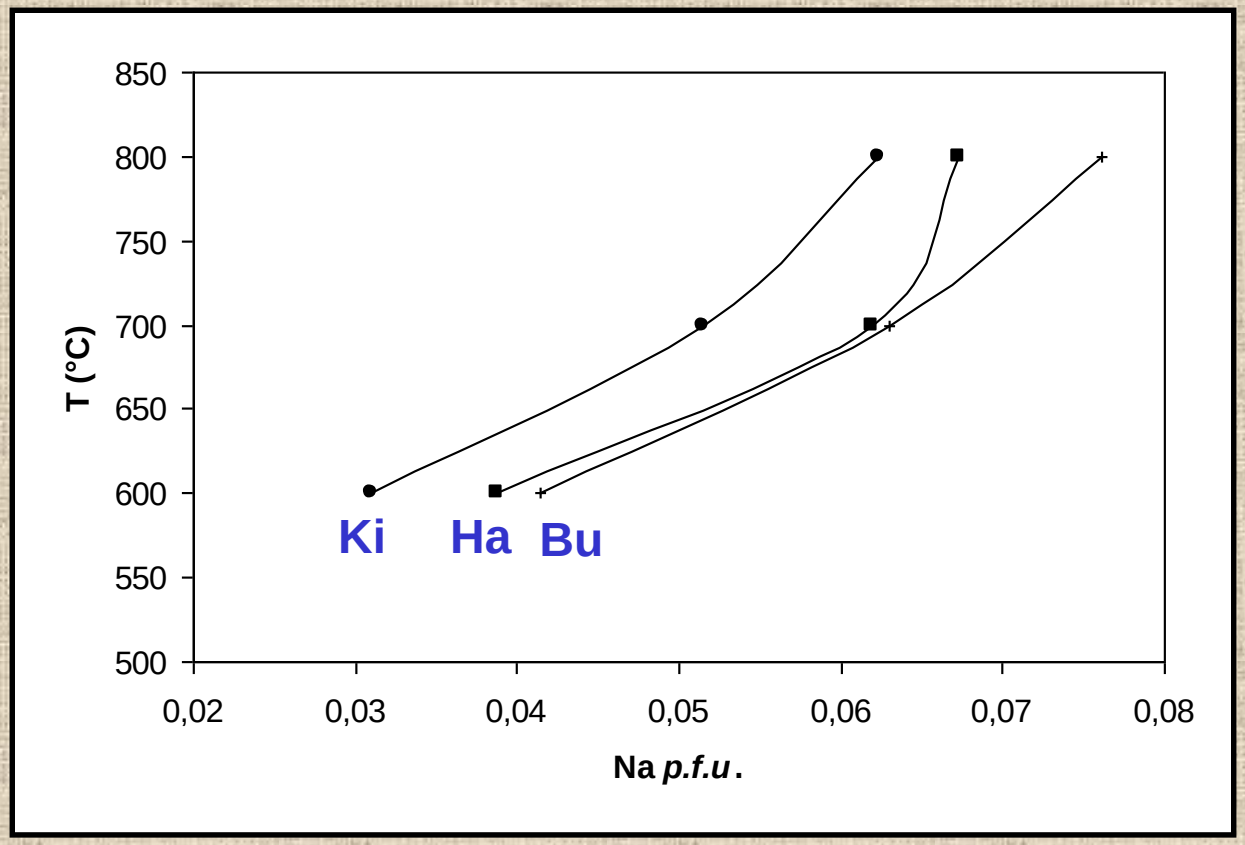
c = 10.364(2) Å

Microprobe analyses of synthetic phosphates

	600°C		700°C		800°C
	% Na_2O triphylite	% Li_2O maricite	% Na_2O triphylite	% Li_2O maricite	% Na_2O triphylite
Buranga	0.81	0.48	1.23	0.86	1.45
Hagendorf-Süd	0.76	0.42	1.21	0.72	1.30
Kibingo	0.61	0.58	0.97	0.47	1.19

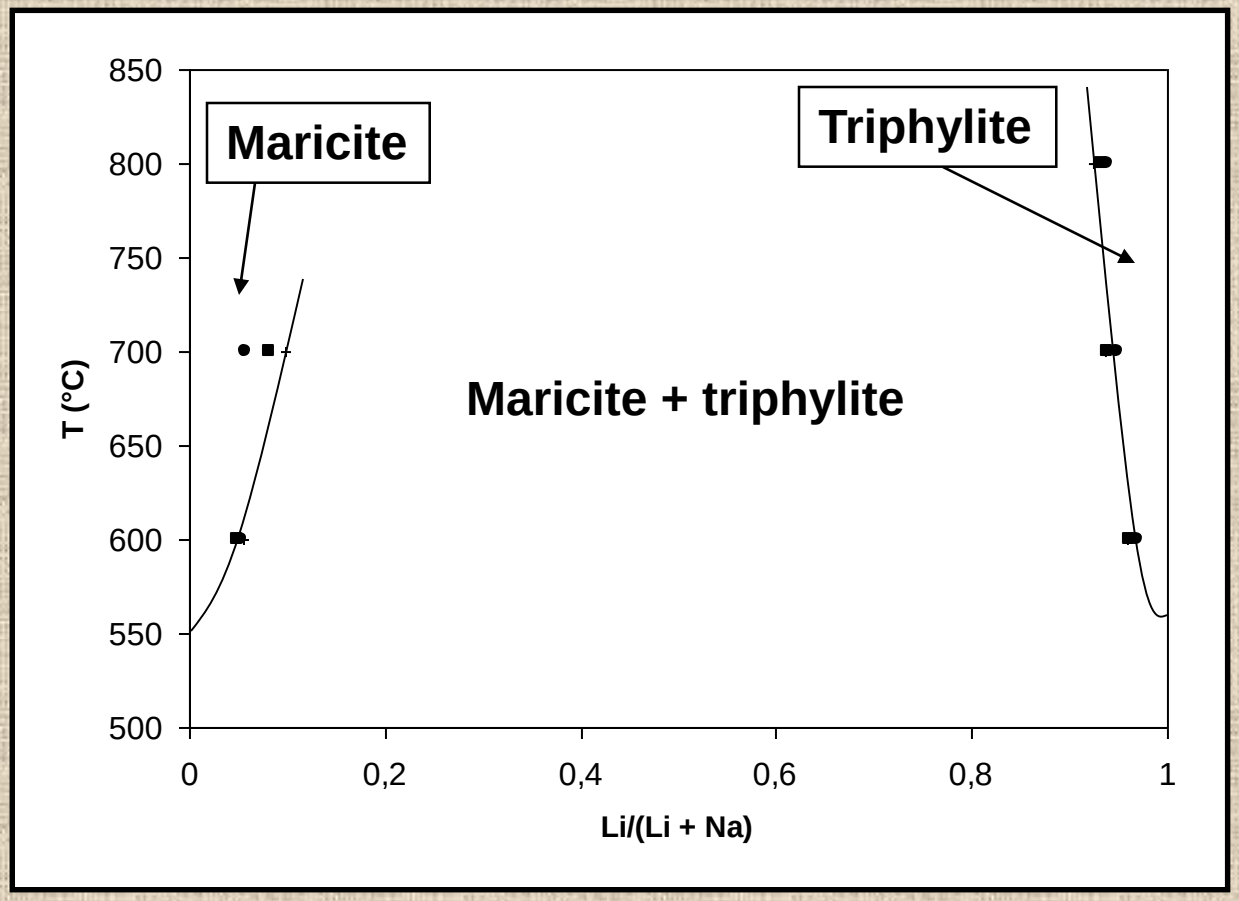
Partitioning of Li and Na between triphylite and maricite

Variations of Na-content of synthetic triphylites



- **Na-content increases with temperature**
- **When T is constant, Na is higher for the Mn-rich compositions**

Maricite-triphylite phase diagram



- **Na in triphylite can reach 0.08 *a.p.f.u.* at 800°C**
- **Li in maricite can reach 0.10 *a.p.f.u.* at 700°C**
- **No partitioning below ca. 550°C**

Occurrence of secondary triphylite

Triphylite-I

1.45 wt. % Na_2O

0.08 *a.p.f.u.* Na

T = 800°C

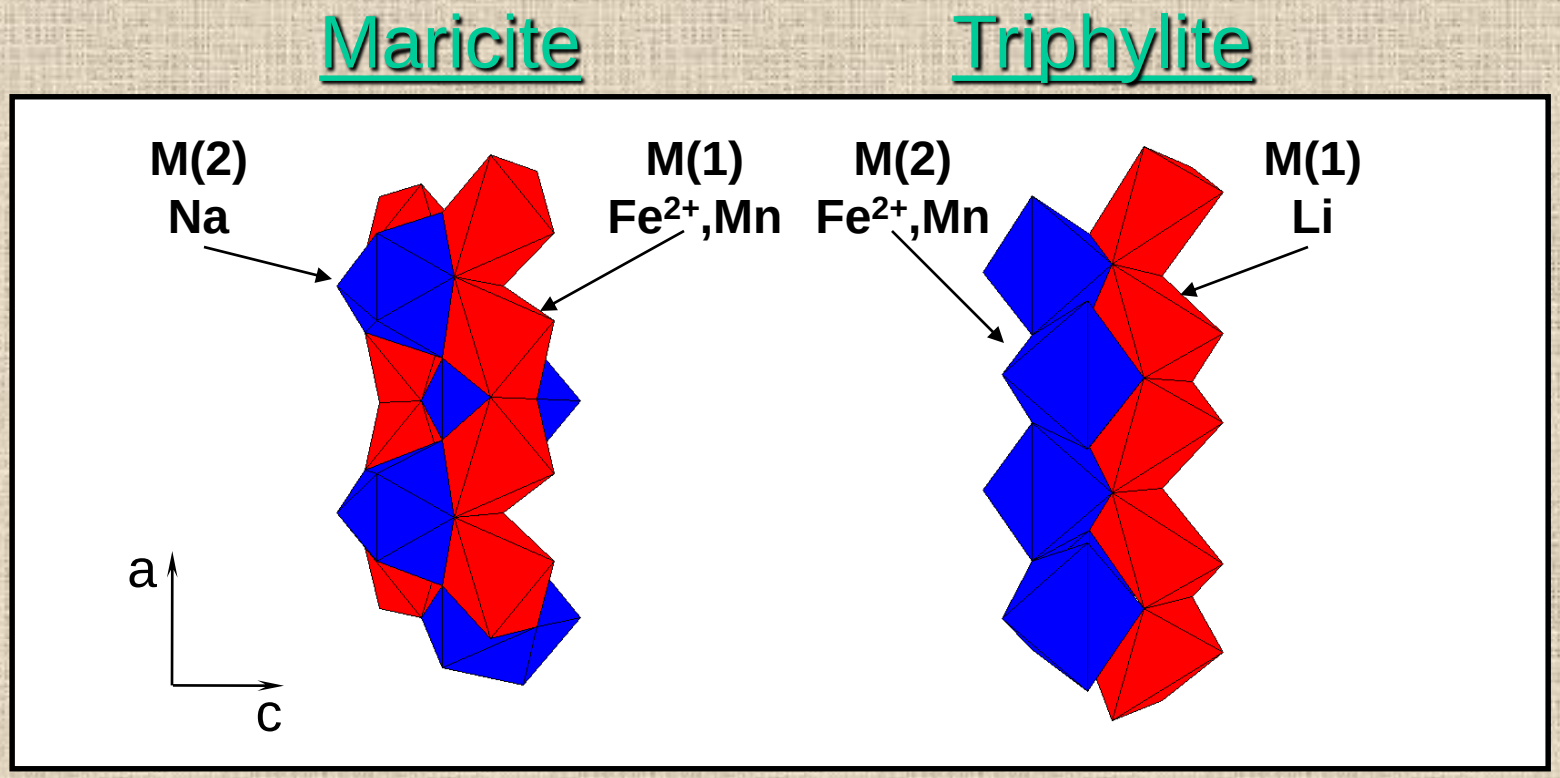
Triphylite-II

0.72 wt. % Na_2O

0.04 *a.p.f.u.* Na

T ~ 600°C

Crystal structures of maricite and triphylite



- Similar crystal structures
- Existence of natrophilite, $NaMn(PO_4)$, with the olivine structure-type

Chemical analyses of natural triphylites

Na-content of triphylites generally low, below ca. 0.20 wt % Na_2O

Temperature of crystallization below 600-550°C

!! Necessary to obtain good microprobe data, because alluaudite frequently occurs as impurity

Higher Na-content in the wet chemical analyses

Angarf-Sud, Morocco: 0.23 % Na_2O (Wet chemical analysis)
: 0.01 % Na_2O (Microprobe analysis)

Conclusions

- The alluaudite + triphylite primary paragenesis has been reproduced experimentally below 500-600°C. At higher temperatures appear maricite and X-phase.
- A partitioning of Na and Li exists between triphylite and maricite above ca. 550°C, and the Na-content of triphylite can reach 1.5 wt. % Na_2O at 800°C.
- SIMS analyses must be performed in order to measure the Li-content of synthesized alluaudites, maricites, and X-phase, and to estimate the Na-Li partitioning among these phosphates.
- It is necessary to obtain good electron microprobe data on natural triphylites, in order to measure their Na-content and to estimate their temperatures of crystallization.