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The stability of iron-rich alluaudites in granitic pegmatites: an experimental investigation of the Na-Fe^{2+}-Fe^{3+} (+PO_4) system

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Alluaudite, Buranga pegmatite, Rwanda

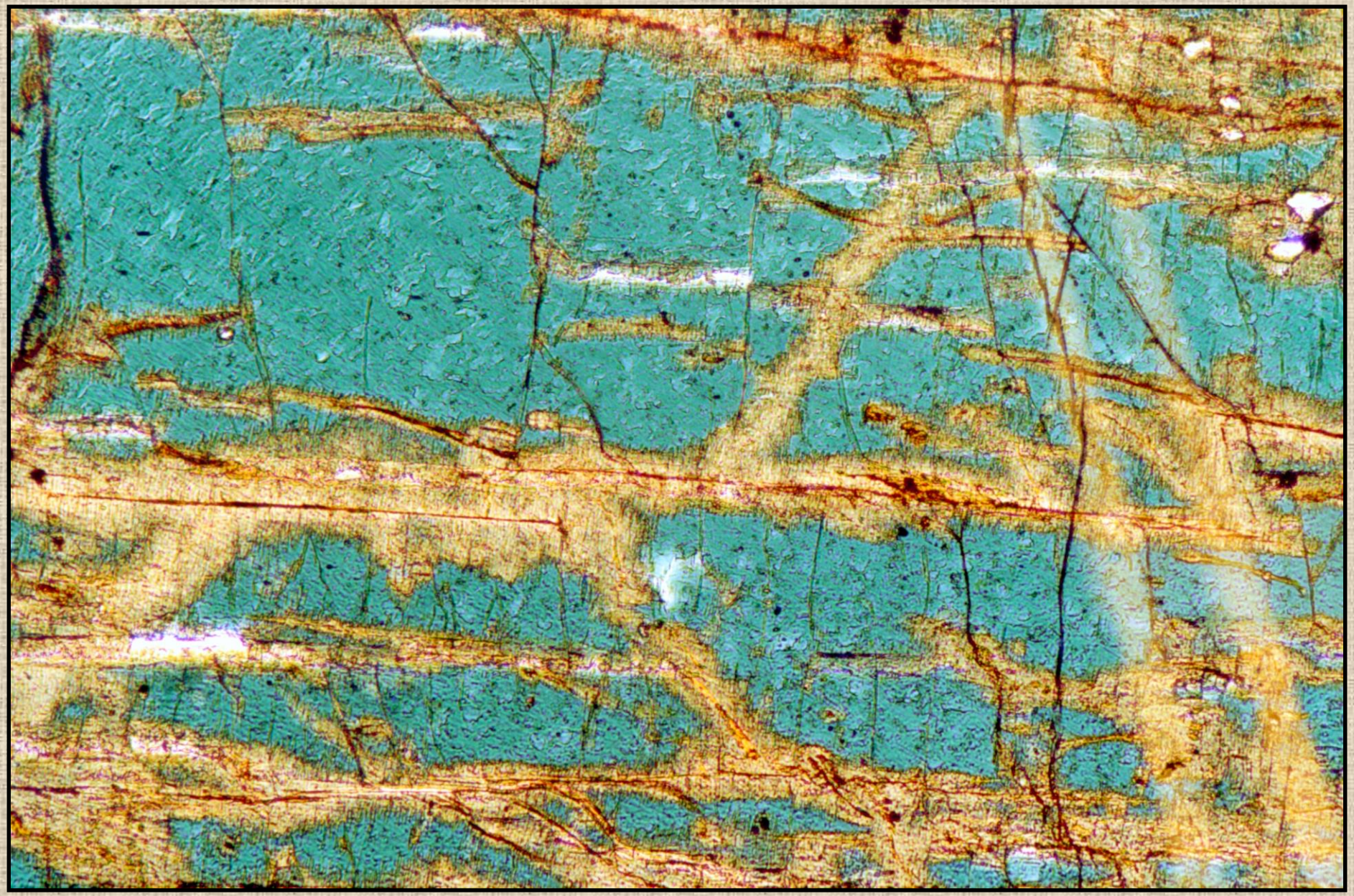
Oxidation mechanism of alluaudites

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

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

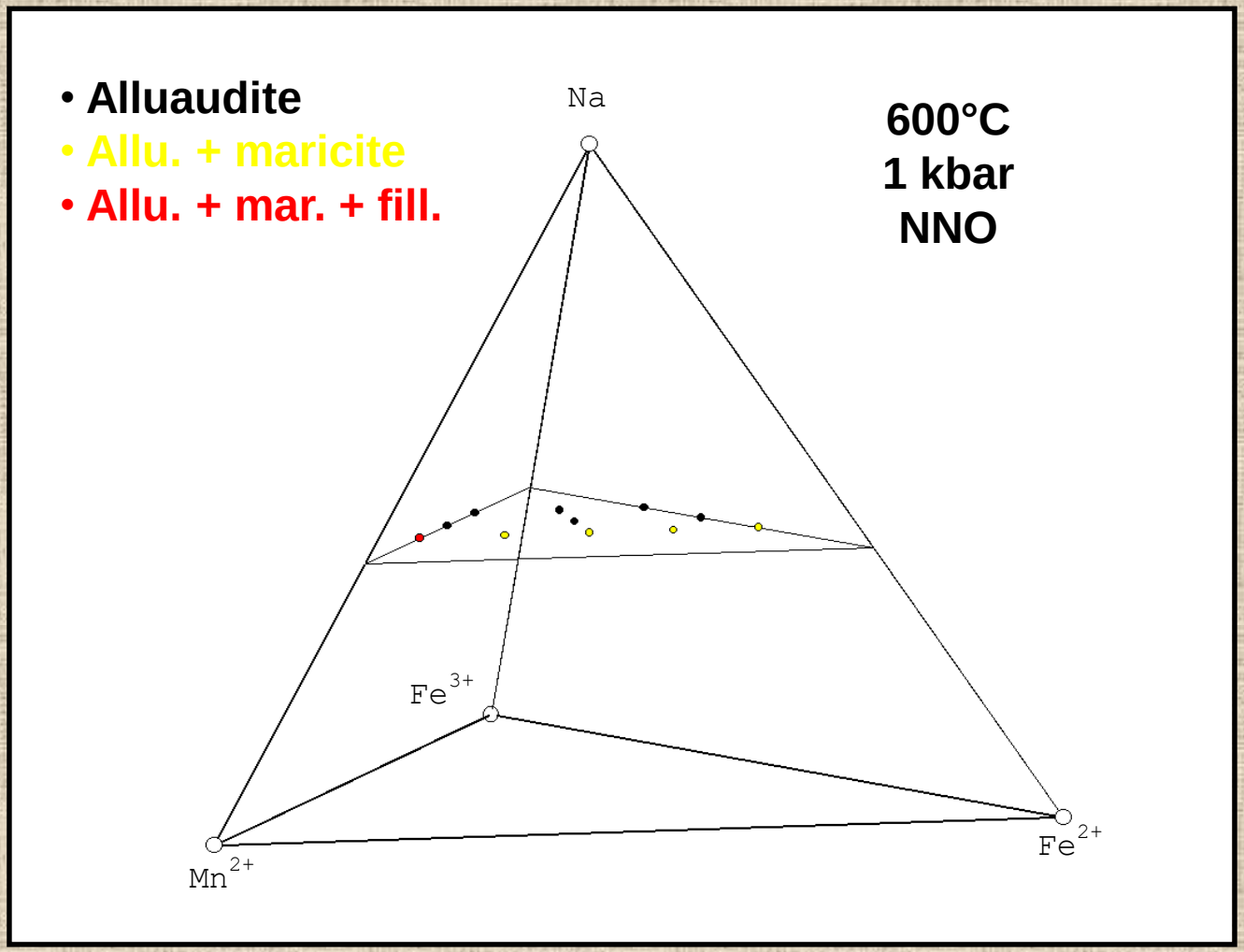
$$Na_2MnFe^{2+}Fe^{3+}(PO_4)_3 \Rightarrow \bullet NaMnFe^{3+}{}_2(PO_4)_3$$
$$Na_2Fe^{2+}{}_2Fe^{3+}(PO_4)_3 \Rightarrow \bullet NaFe^{2+}Fe^{3+}{}_2(PO_4)_3$$

Primary alluaudites belong to the $Na_2(Mn_{1-x}Fe^{2+}{}_x)_2Fe^{3+}(PO_4)_3$ solid solution

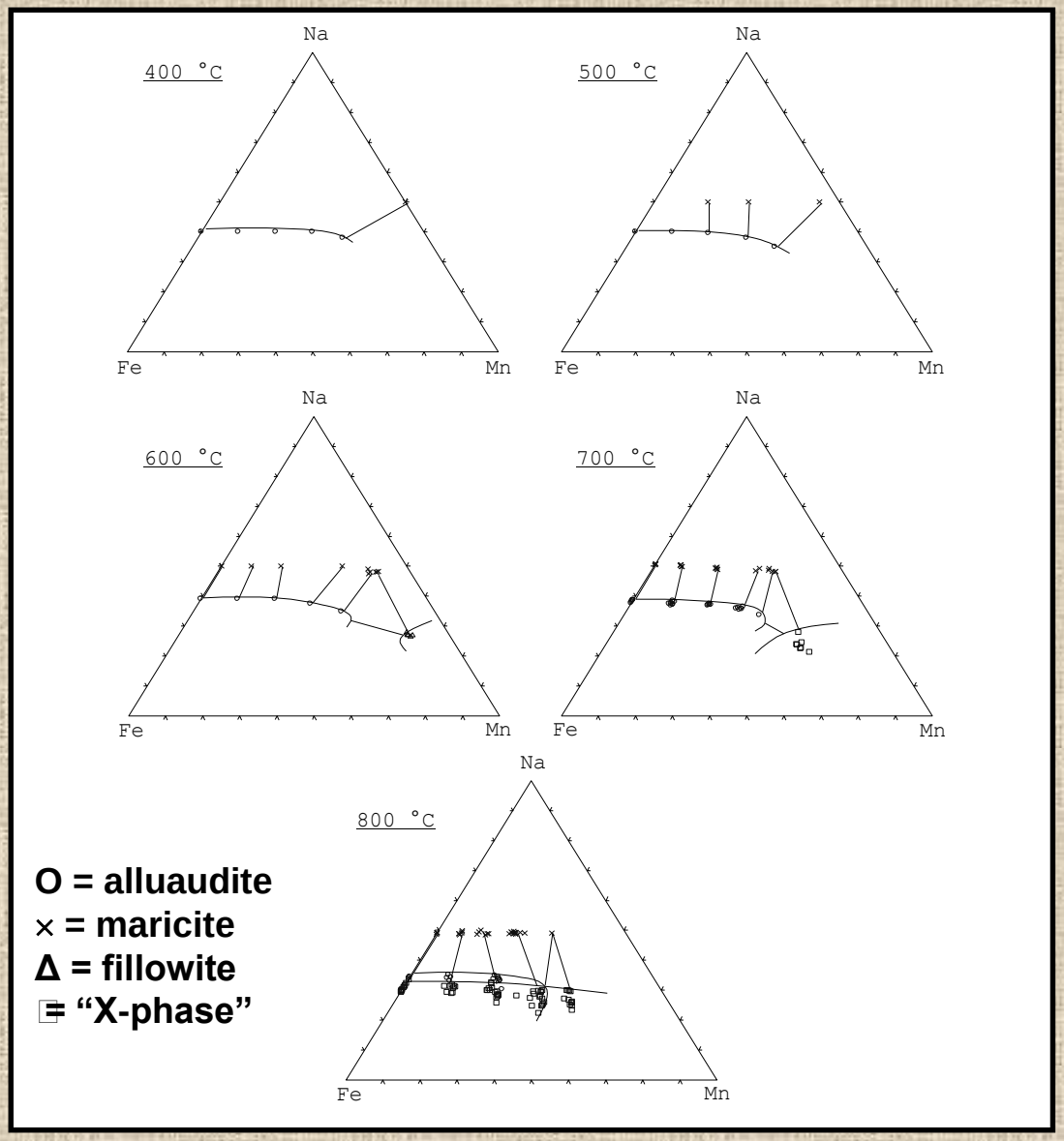


Alluaudite, Kibingo pegmatite, Rwanda

The Na-Mn-Fe^{2+}-Fe^{3+}-P-O system



Na-Mn-Fe$_{total}$ phase diagrams (NNO)



O = alluaudite
× = maricite
Δ = fillowite
▣ = "X-phase"

Superposition of alluaudite and "X-phase" fields

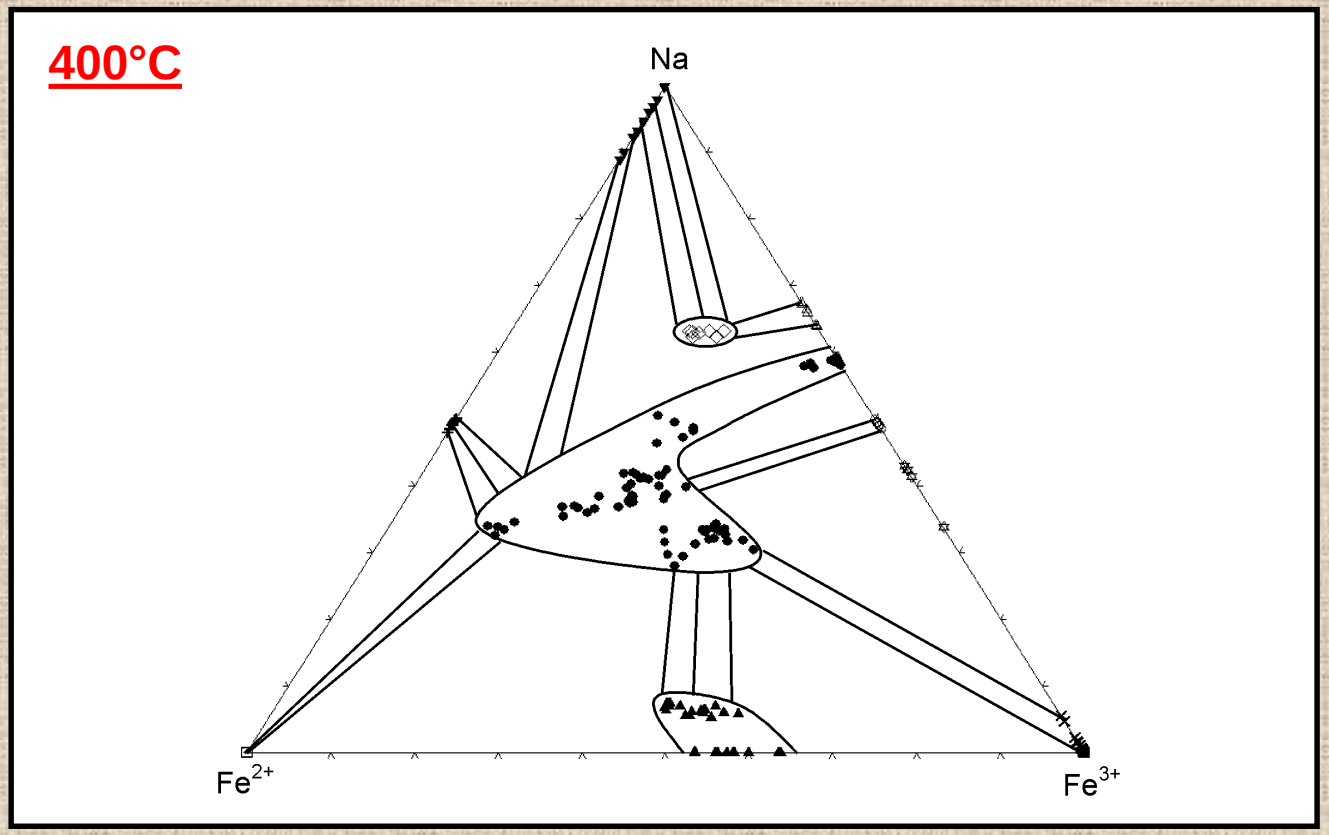
Investigation of the Na-Fe^{2+}-Fe^{3+} system

Experimental

$Na\text{-}Fe^{2+}\text{-}Fe^{3+}$ (+ PO_4) system

- Hydrothermal synthesis
- Tuttle-type cold-seal bombs
- T = 400-700 °C
- P = 1 kbar
- Oxygen fugacity: close to Ni/NiO (NNO)

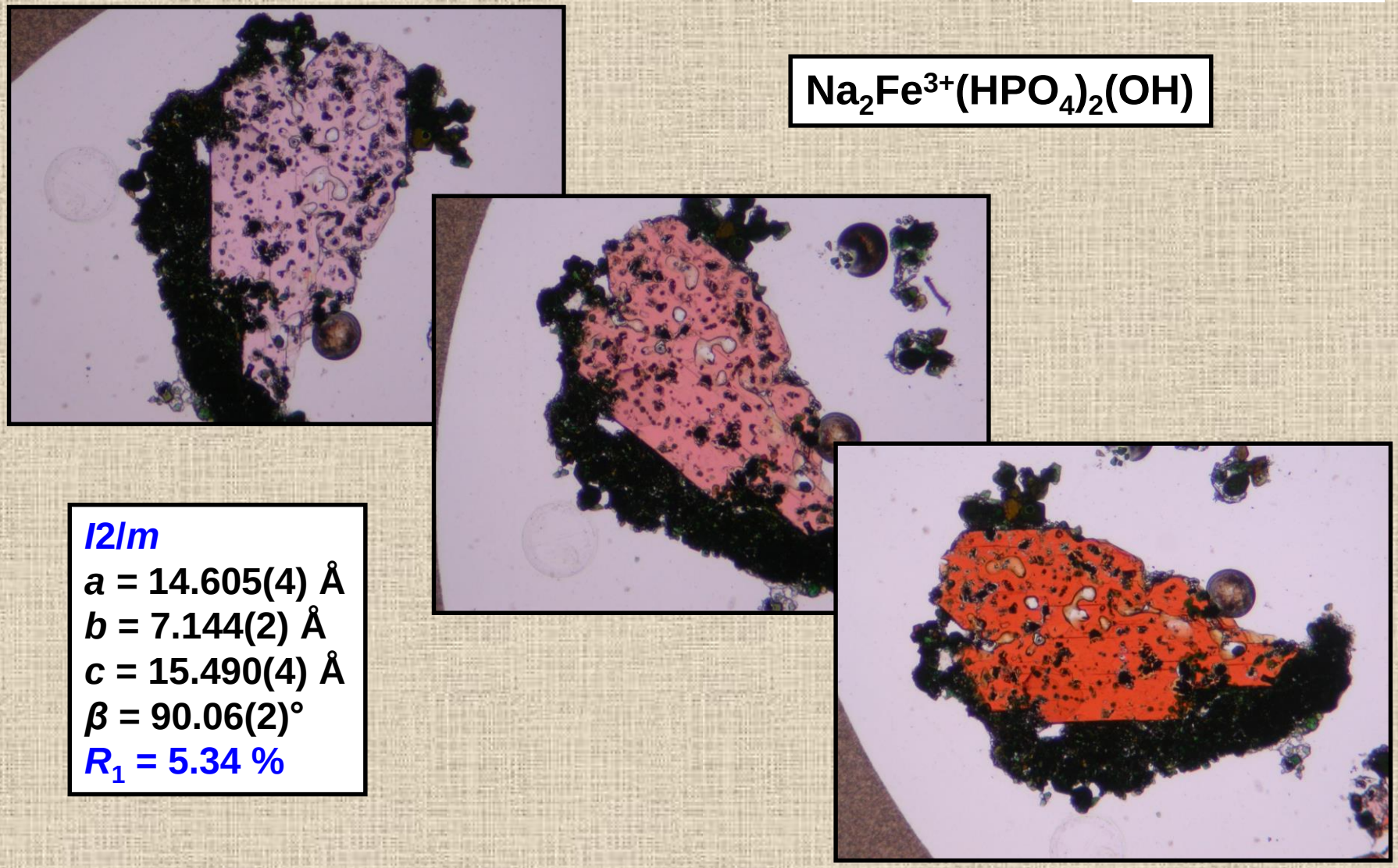
Phase diagram at 400°C / 1 kbar



- Center ⇒ alluaudite
- Fe^{3+} part ⇒ $Fe^{3+}_4(PO_4)_3(OH)_3$
- Fe^{2+} part ⇒ $Fe^{2+}_3(PO_4)_2$ (sarcopside)
- Na-rich part ⇒ $Na_2HPO_4.nH_2O$

- ▲ ⇒ $Fe^{3+}_4Fe^{2+}_3(PO_4)_6$
- Δ ⇒ $Na_2Fe^{3+}(HPO_4)_2(OH)$ (Phase A)
- ◊ ⇒ $Na_7Fe^{3+}_3Fe^{2+}(PO_4)_6$

Phase A

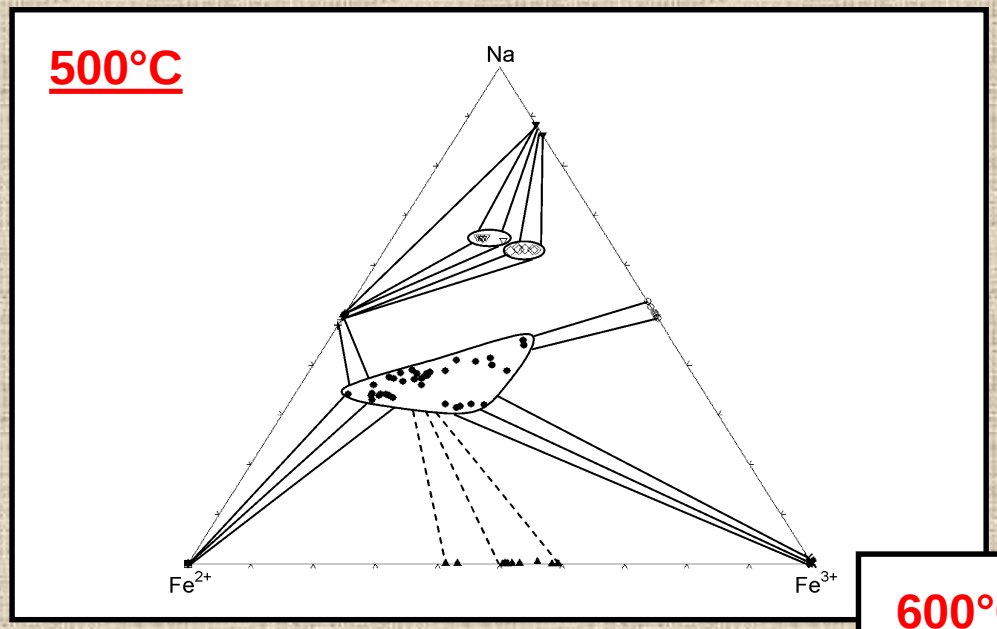


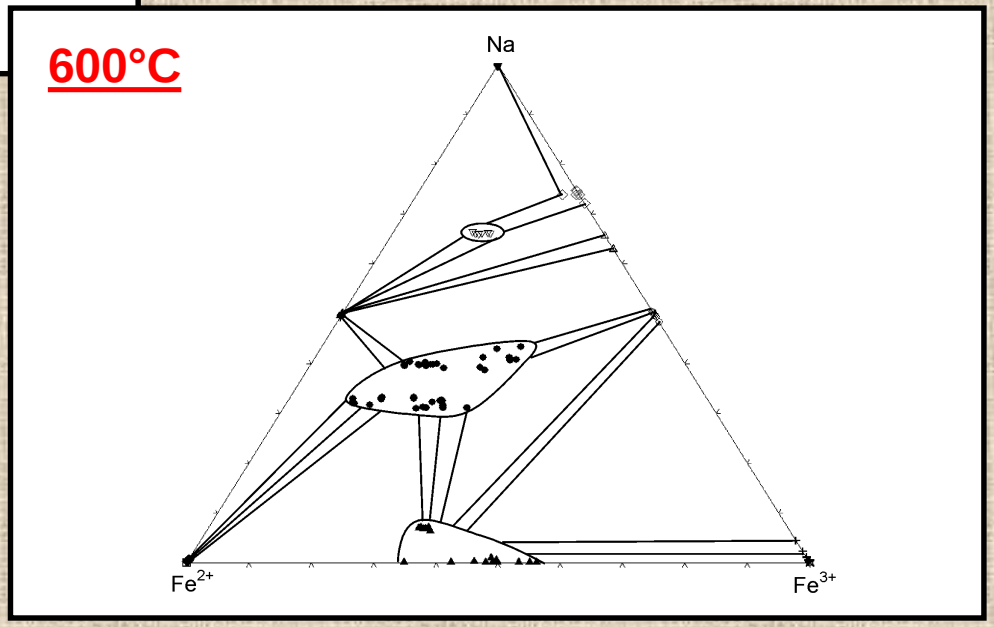
$Na_2Fe^{3+}(HPO_4)_2(OH)$

I2/m
a = 14.605(4) Å
b = 7.144(2) Å
c = 15.490(4) Å
β = 90.06(2)°
R_1 = 5.34 %

Length of the photographs: 3 mm

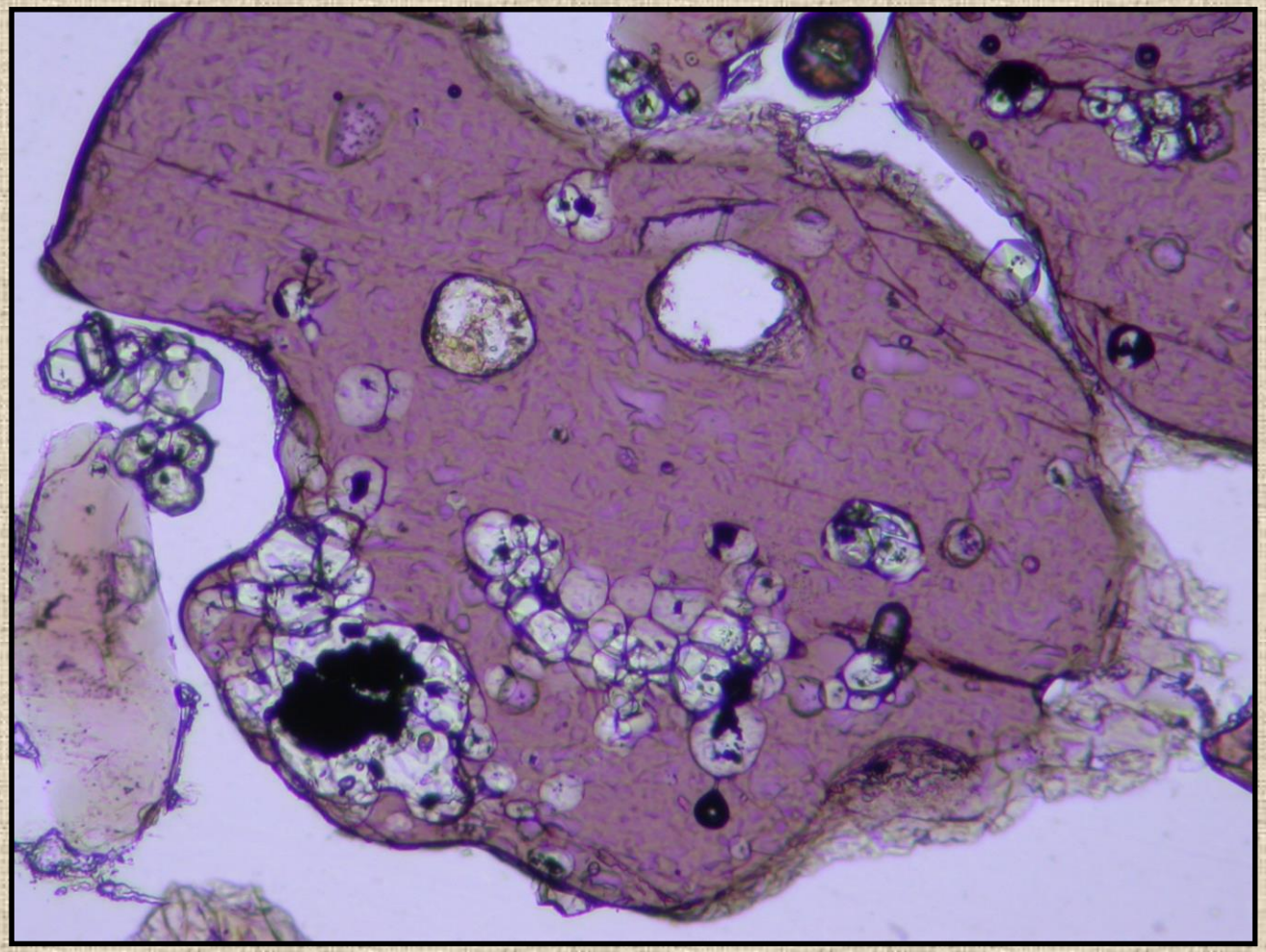
Phase diagrams at 500-600°C / 1 kbar





- $\nabla \Rightarrow Na_4Fe^{3+}Fe^{2+}(PO_4)_3$ (Phase B)
- $\Diamond \Rightarrow Na_7Fe^{3+}{}_3Fe^{2+}(PO_4)_6$
- Surface of the alluaudite field decreases

Phase B

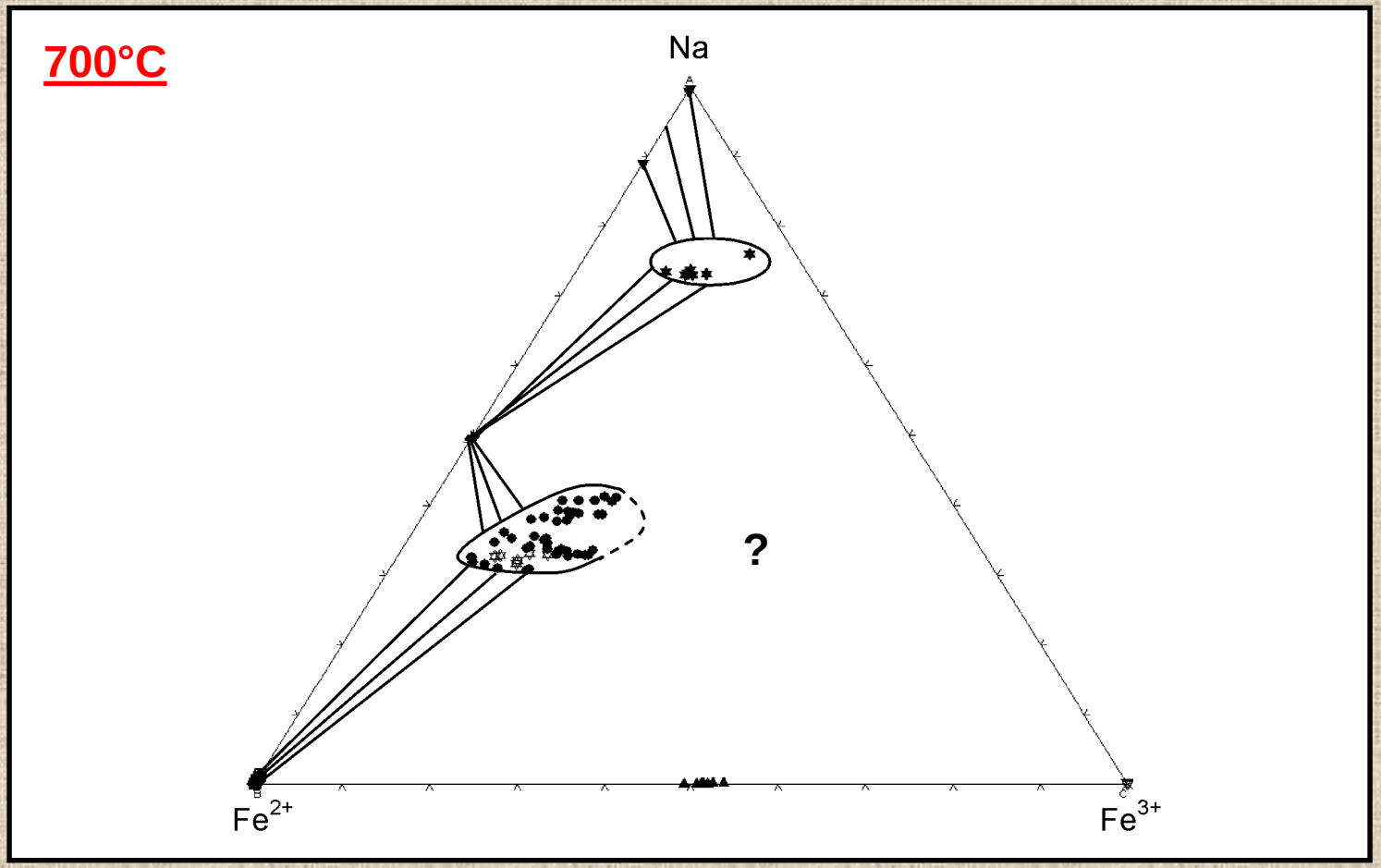


Length of the photograph: 2 mm

$Na_4Fe^{3+}Fe^{2+}(PO_4)_3$

R-3
a = 8.946(1) Å
c = 21.272(2) Å
R_1 = 6.79 %

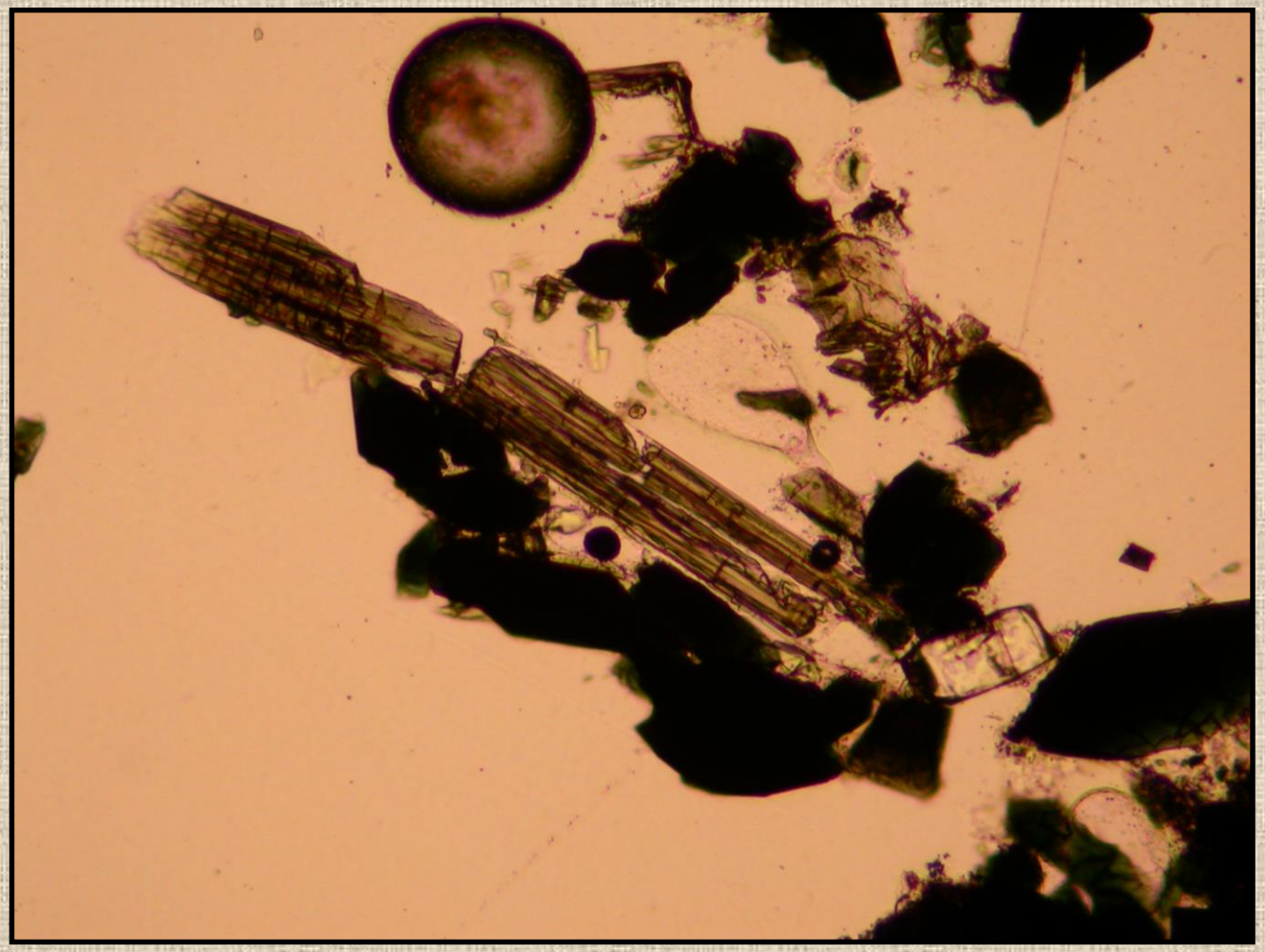
Phase diagram at 700°C / 1 kbar



- ★ ⇒ $Na_4Fe^{3+}Fe^{2+}(PO_4)_3$ (Phase C)
- Very small alluaudite field

Phase C

$Na_6Fe^{3+}Fe^{2+}(PO_4)_3(HPO_4)$



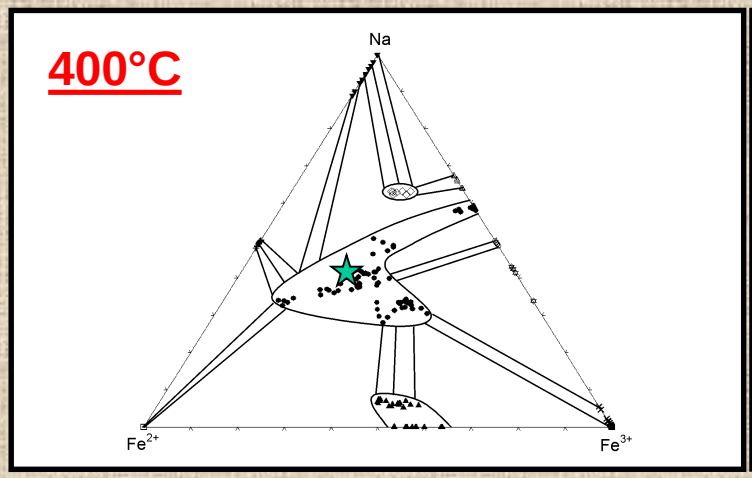
Length of the photograph: 2 mm

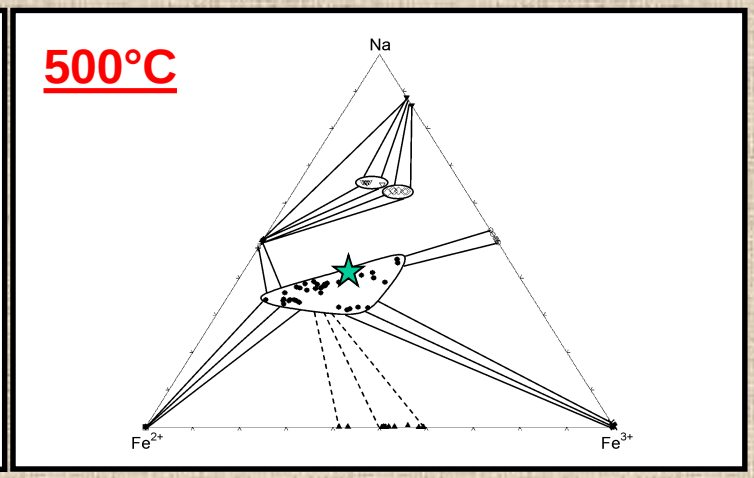
***P*-1**
a = 5.3141(6) Å
b = 8.5853(9) Å
c = 8.7859(8) Å
α = 114.429(9)°
β = 92.327(9)°
γ = 106.08(1)°
R_1 = 2.77 %

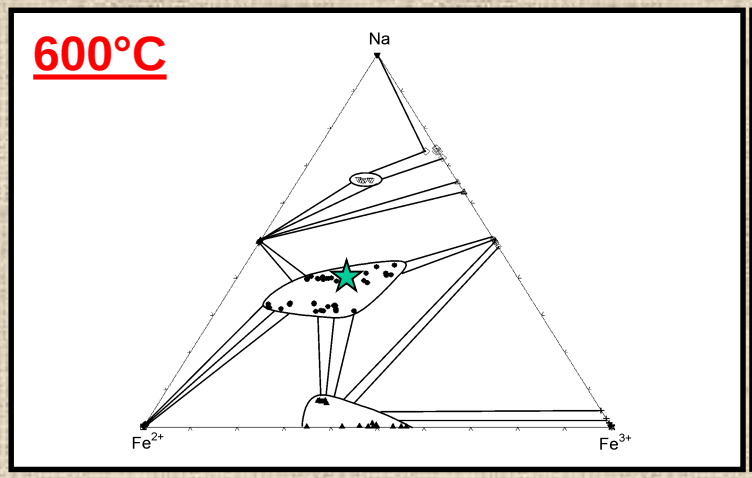
Ferroalluaudite from Angarf-Sud (Morocco)

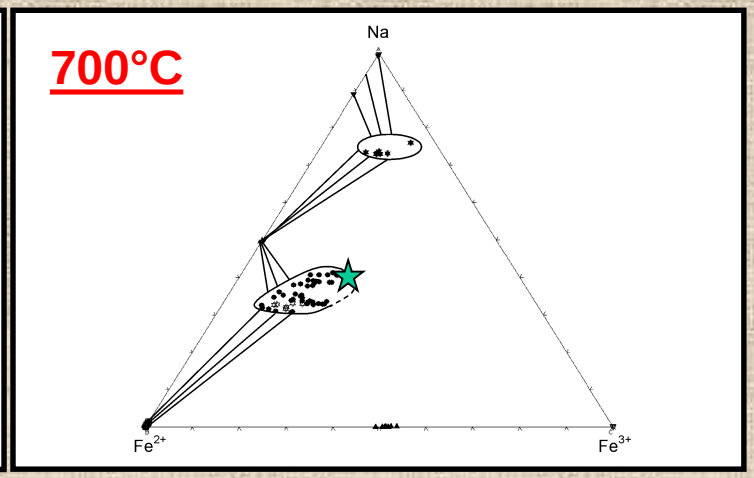
(Fransolet *et al.*, 1985)

$$Na_{1.025}Ca_{0.428}Mn_{0.345}Fe^{2+}_{0.943}Fe^{3+}_{1.368}Mg_{0.393}(PO_4)_3$$









Cristallisation between 400 and 600°C → primary origin

Conclusions

- Alluaudite covers a wide compositional field in the Na-Fe^{2+}-Fe^{3+} (+PO_4) system, and is stable from 400 to 700°C
- The surface of this field decreases significantly when the temperature increases
- Ferroalluaudite from Angarf-Sud crystallized between 400 and 600°C, thus confirming its primary origin
- Three new phosphates were synthesized in the Na-rich part of the diagram, and their structural study is still in progress.