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The structural complexity of phosphates in the $Na\text{-}Fe^{2+}\text{-}Fe^{3+}$ ($+PO_4$) system

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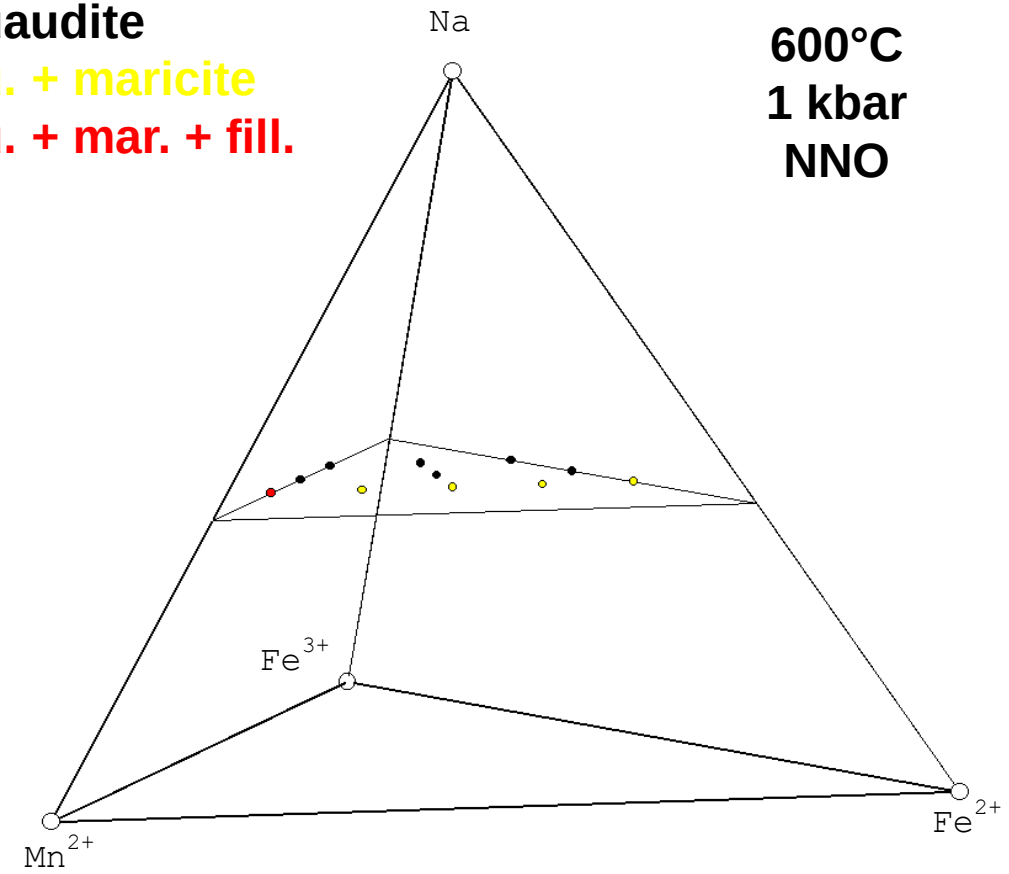
Alluaudite, Buranga pegmatite, Rwanda

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

- **Alluaudite**
- **Allu. + maricite**
- **Allu. + mar. + fill.**



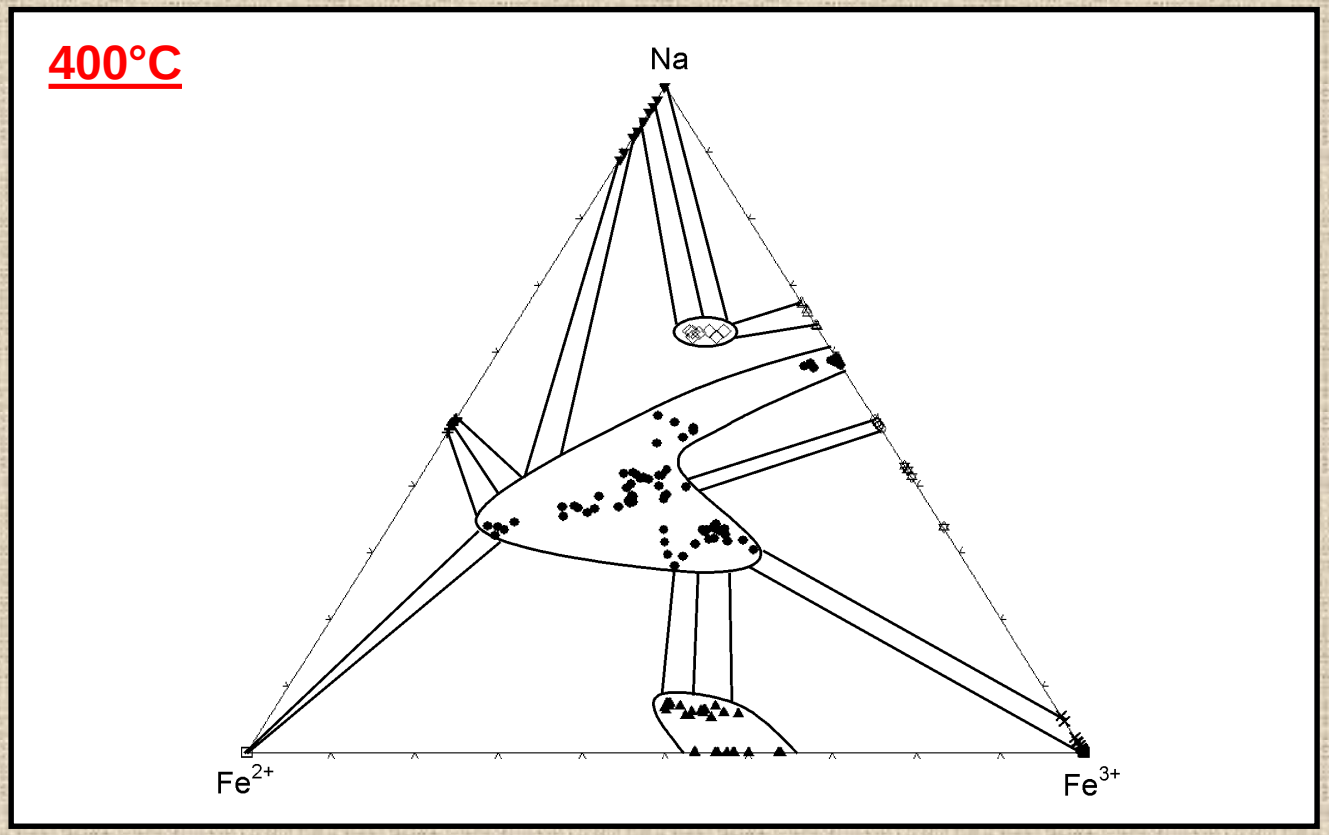
600°C
1 kbar
NNO

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)

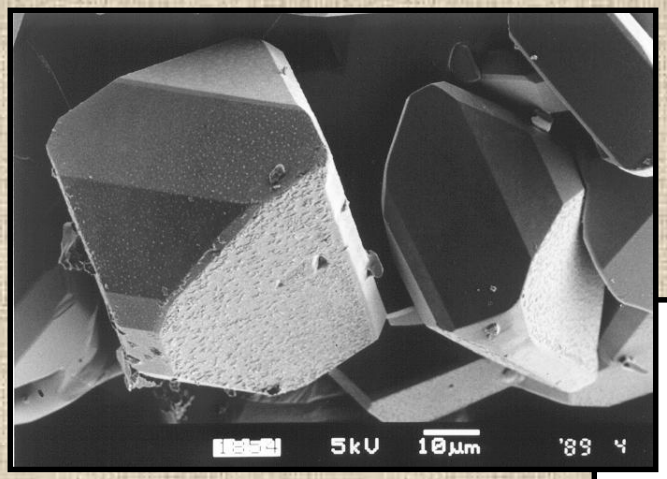
Phase diagram at 400°C / 1 kbar



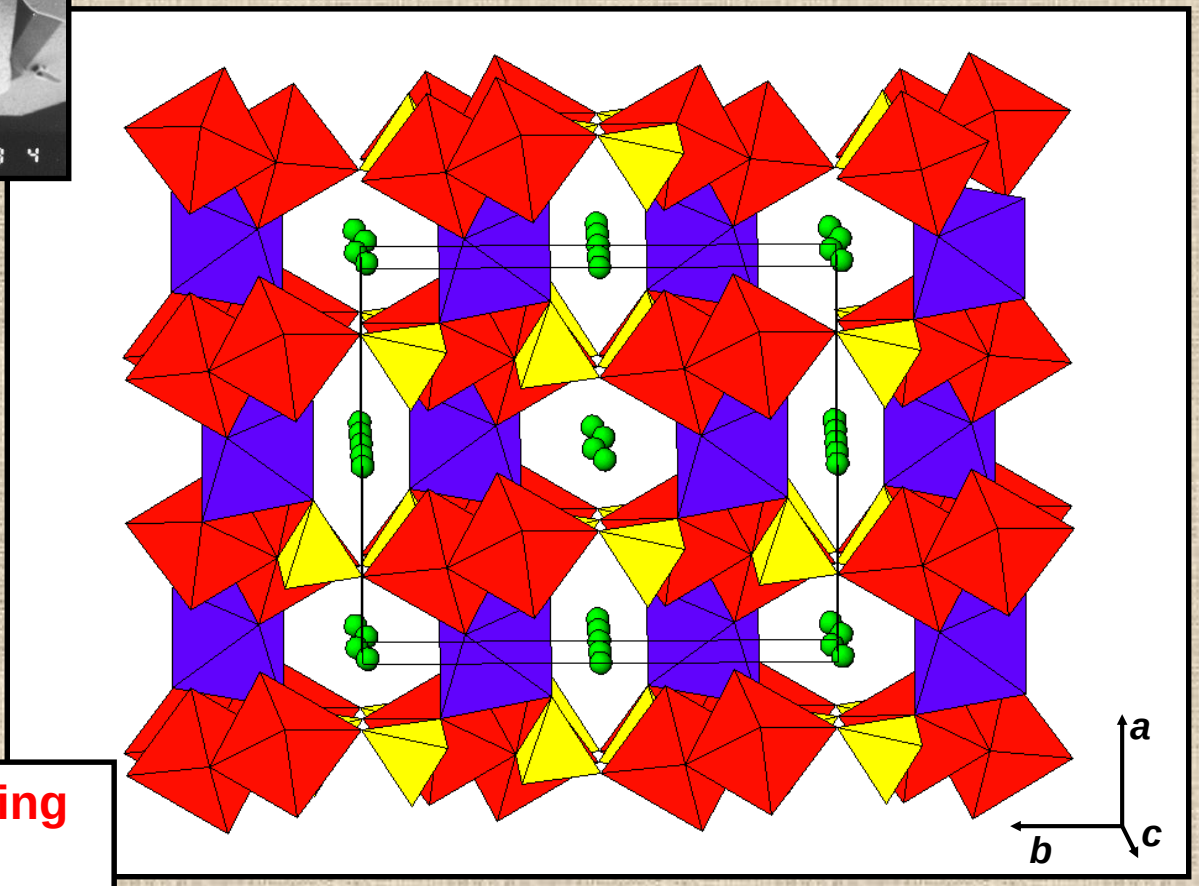
- Center ⇒ alluaudite
- Fe^{3+} part ⇒ $Fe^{3+}_4(PO_4)_3(OH)_3$
- Fe^{2+} part ⇒ $Fe^{2+}_3(PO_4)_2$ (sarcopside)
- Na-rich part ⇒ $Na_2HPO_4.nH_2O$

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

Alluaudite-type phosphates



$Na_2 Fe^{2+}_2 Fe^{3+}(PO_4)_3$
(Na/Fe = 0.67)

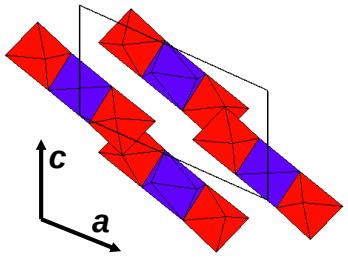


C2/c
a = 12.001(2) Å
b = 12.538(2) Å
c = 6.405(1) Å
β = 114.45(1)°

Chains of edge-sharing
M octahedra

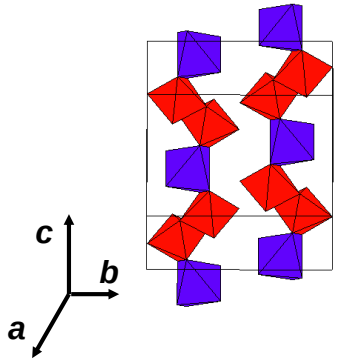
Alluaudite-type phosphates

M(1)-M(2) chains

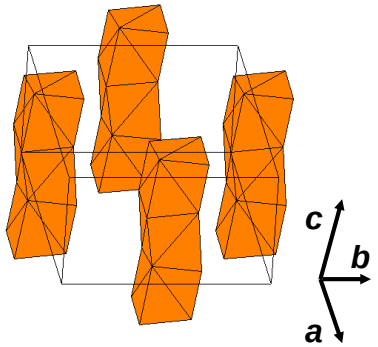


M(1): Fe^{2+}
M(2): Fe^{2+}, Fe^{3+}

M(1)-M(2) chains

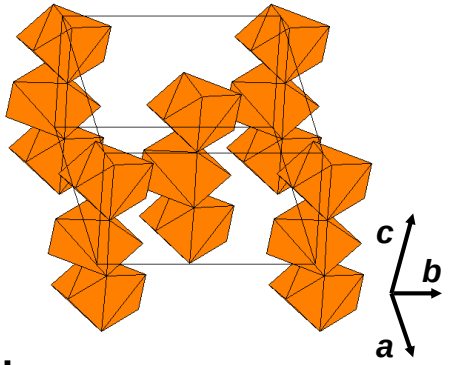


A(1) chains



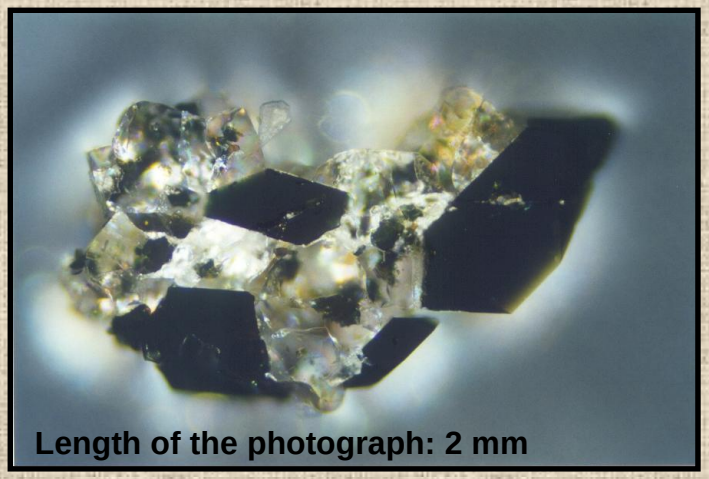
A(1): Na

A(2)' chains



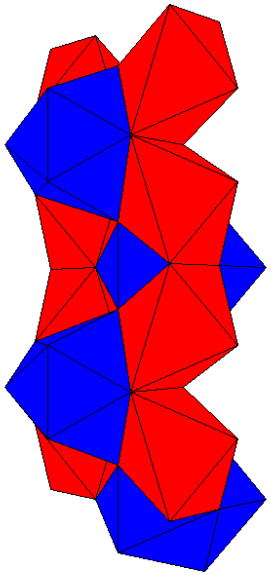
A(2)': Na

Maricite-type phosphates



Chains of edge-sharing M(1) octahedra

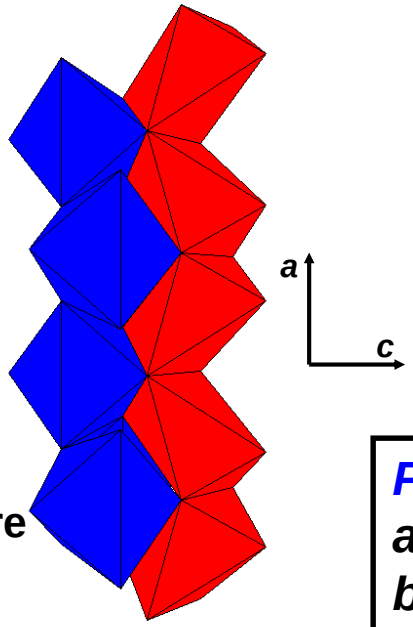
Maricite
$NaFe^{2+}(PO_4)$
(Na/Fe = 1)



M(1): $^{[6]}Fe^{2+}$
M(2): $^{[10]}Na$

Pmnb
a = 6.864(4) Å
b = 8.986(6) Å
c = 5.040(2) Å

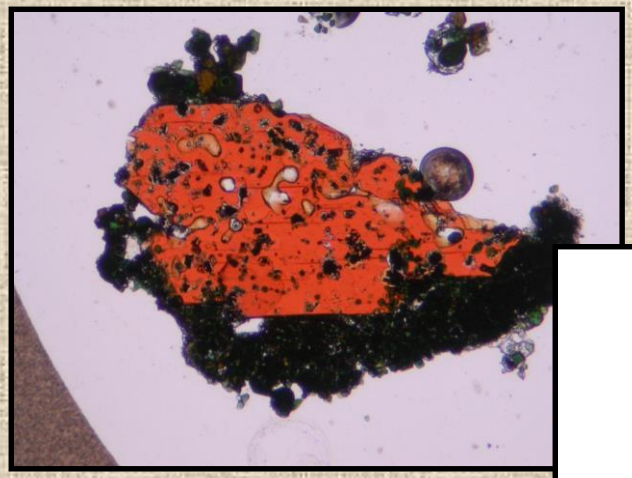
Natrophilite
$NaMn(PO_4)$



Olivine structure
M(1): $^{[6]}Fe^{2+}$
M(2): $^{[6]}Na$

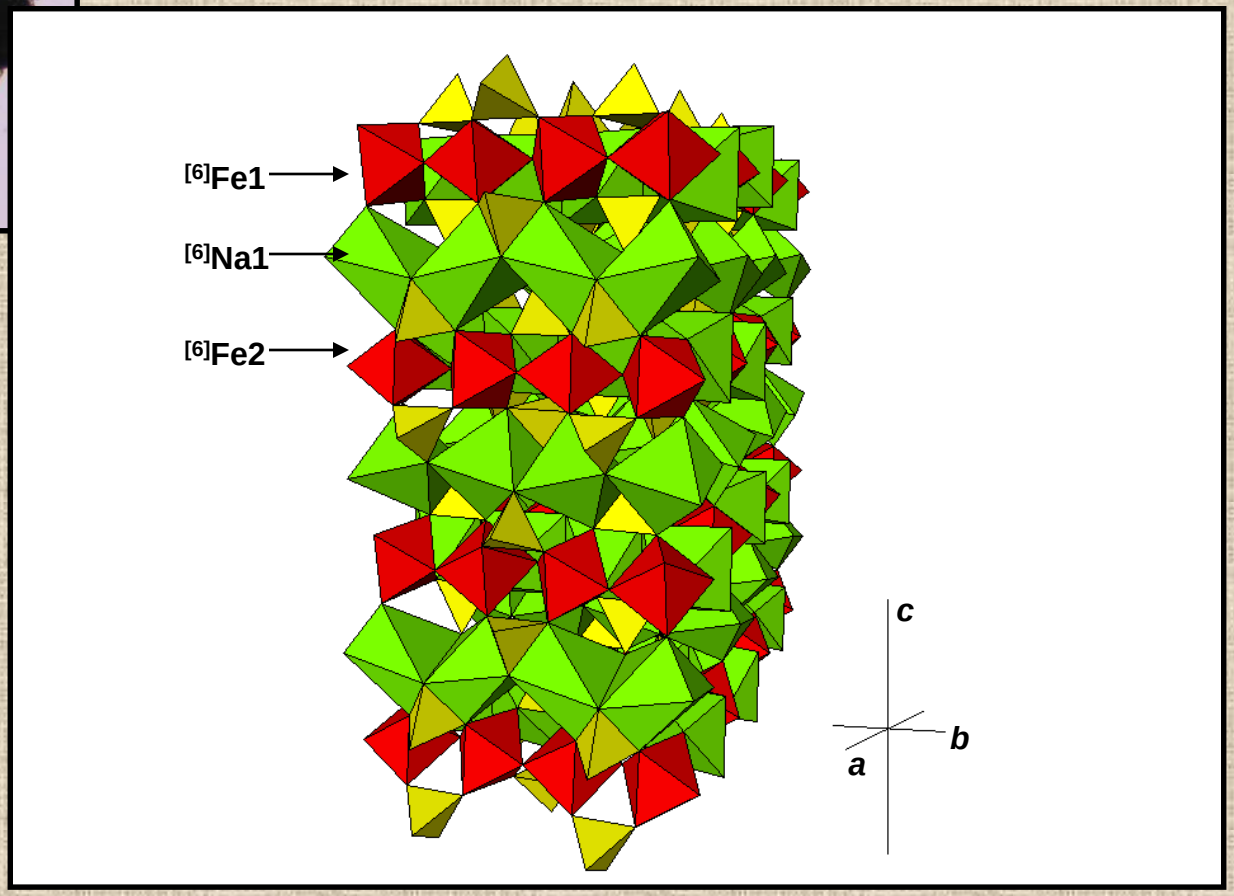
Pmnb
a = 6.312(3) Å
b = 10.523(5) Å
c = 4.987(2) Å

Phase A



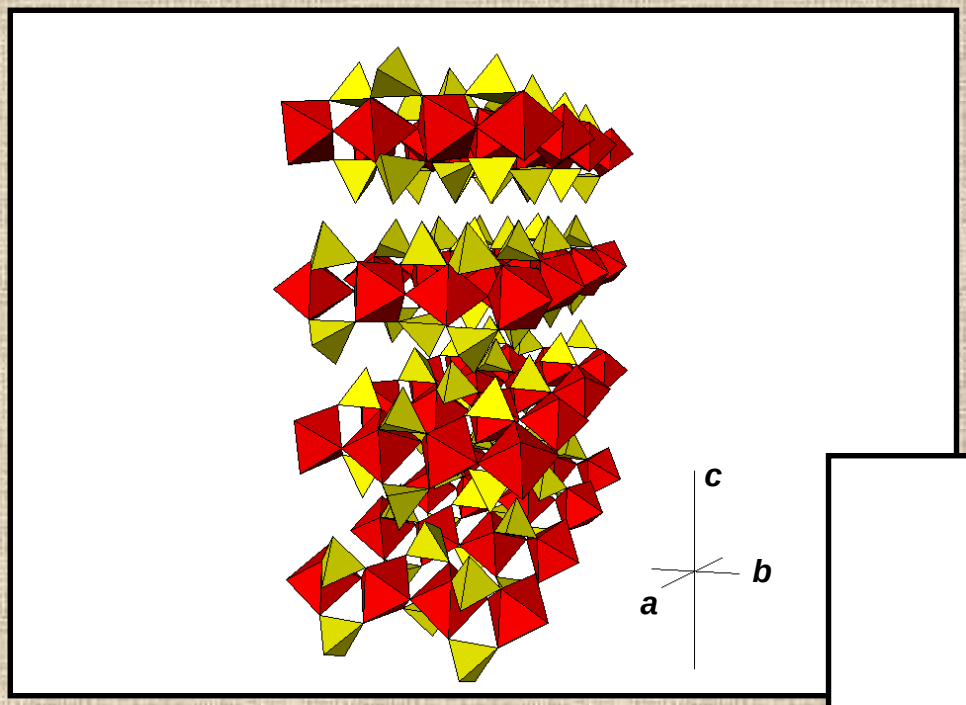
Length of the photograph: 3 mm

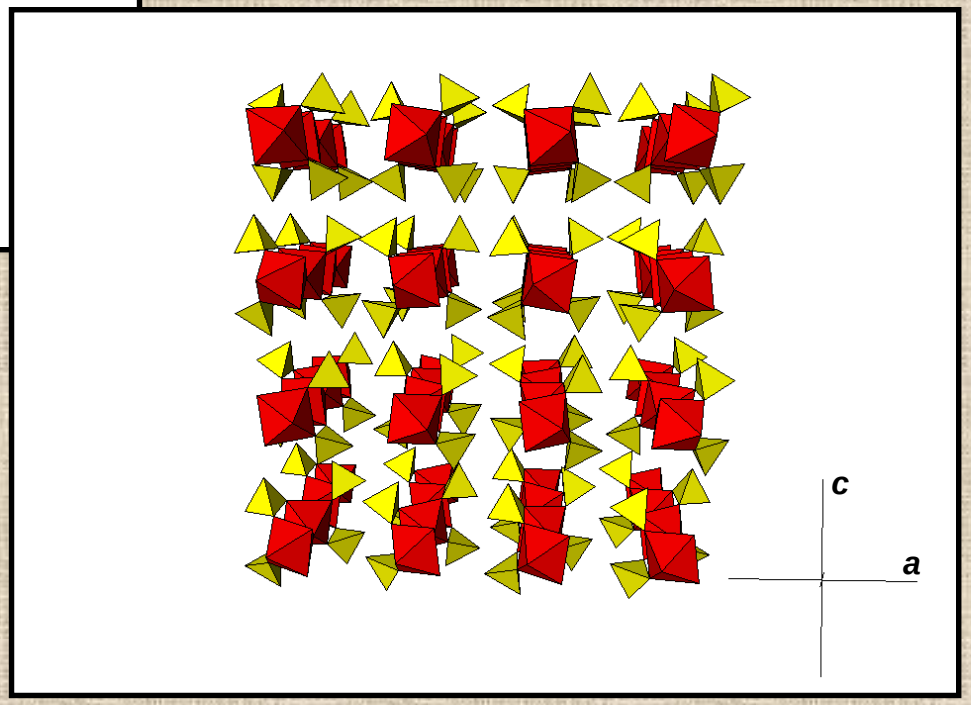
$Na_2Fe^{3+}(HPO_4)_2(OH)$
(Na/Fe = 2)



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

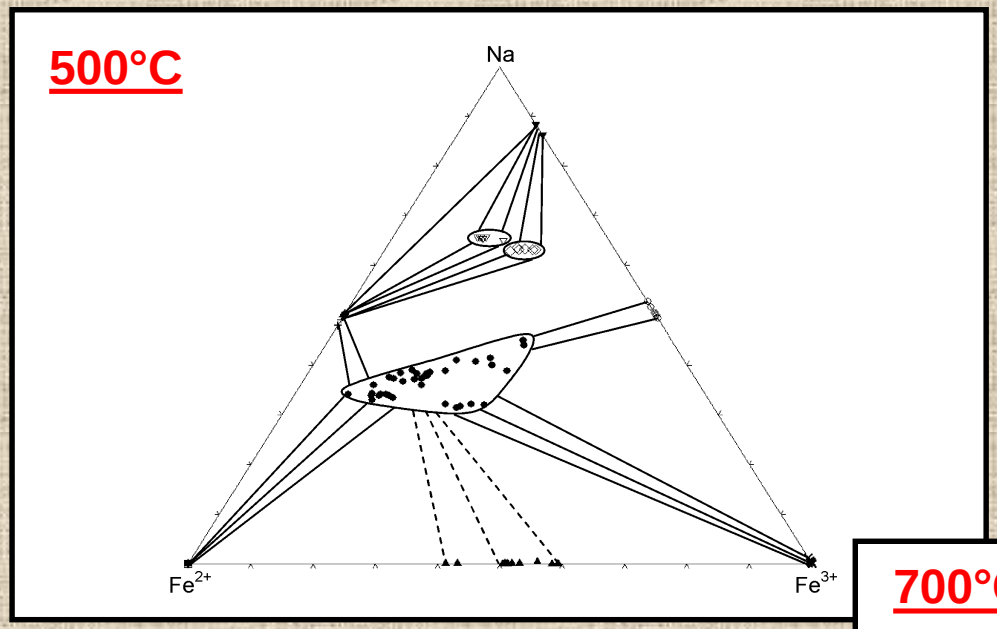
Phase A

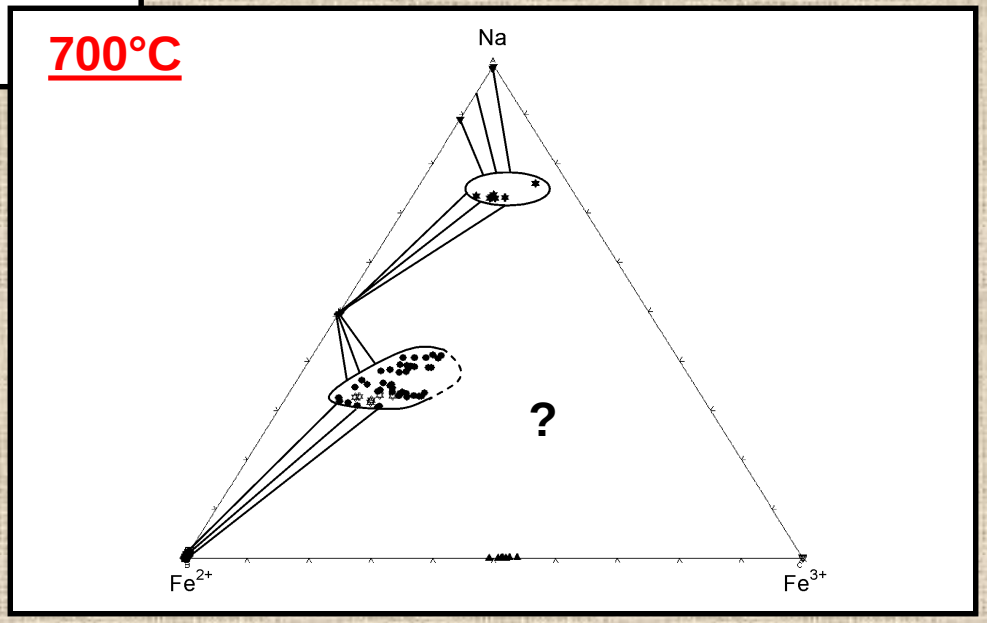




Chains of corner-sharing octahedra

Phase diagrams at 500-700°C / 1 kbar

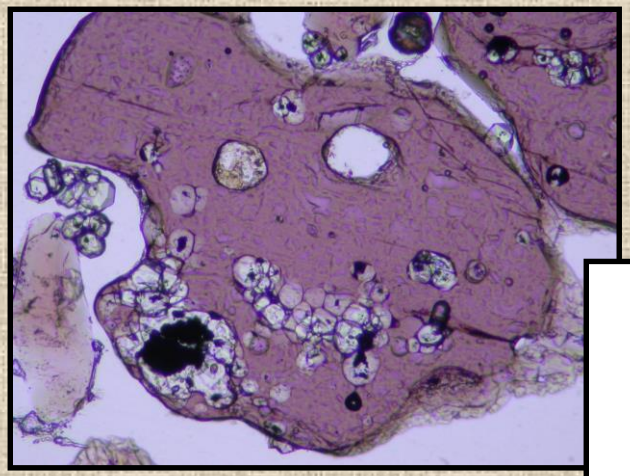




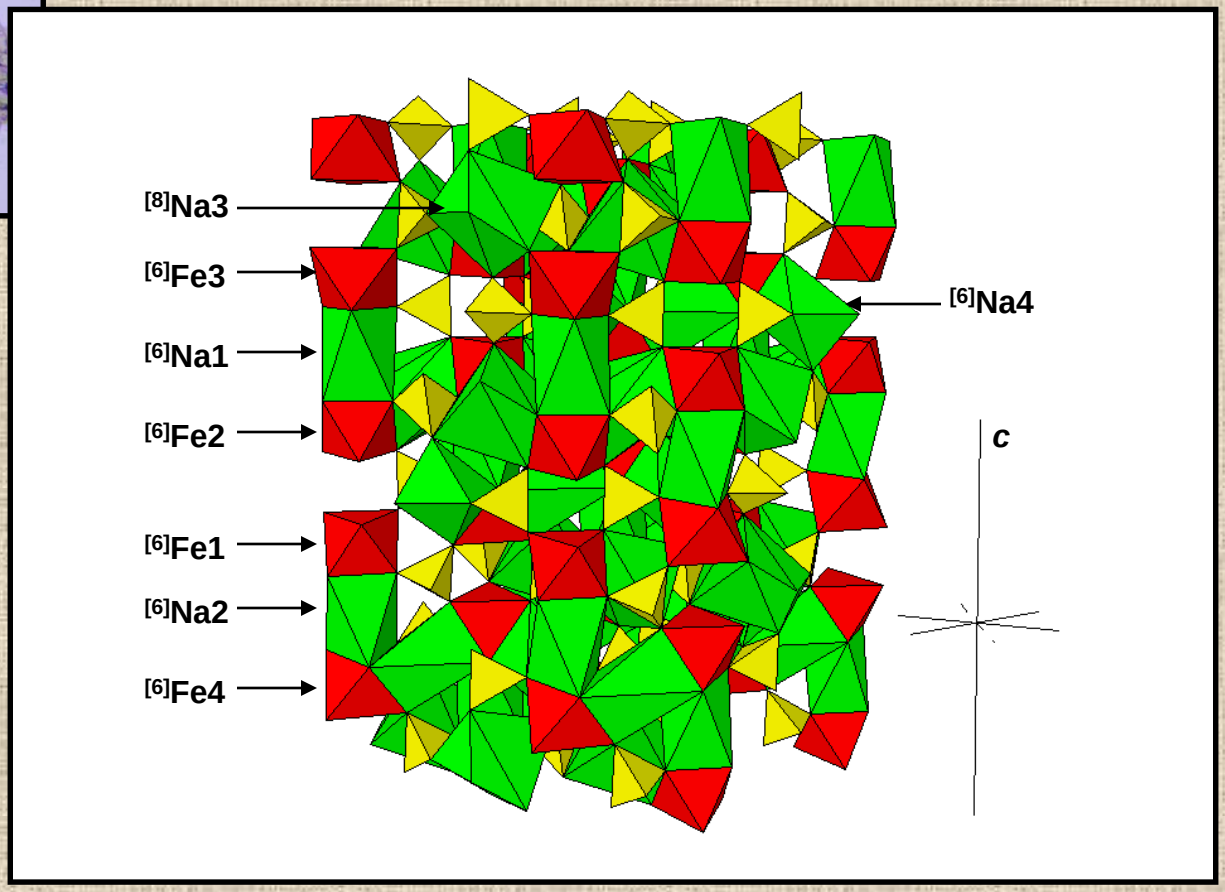
- ▽ ⇒ $Na_4Fe^{3+}Fe^{2+}(PO_4)_3$ (Phase B)
- ◊ ⇒ $Na_7Fe^{3+}{}_3Fe^{2+}(PO_4)_6$
- ★ ⇒ $Na_3Fe^{3+}(PO_4)_2$ (Phase C)

Phase B

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

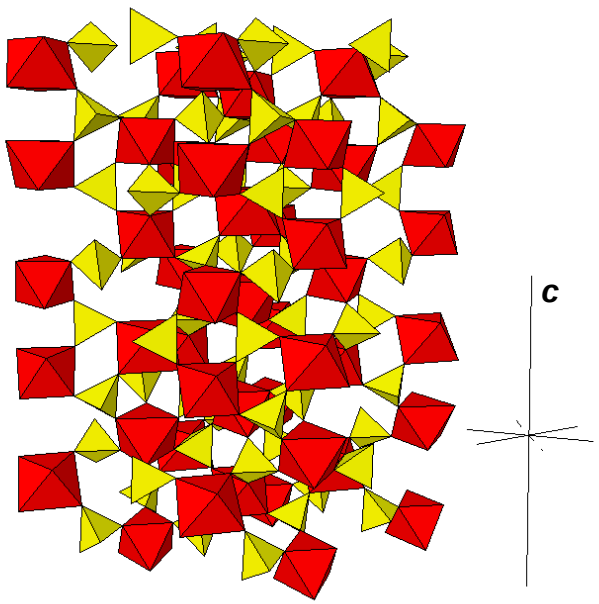


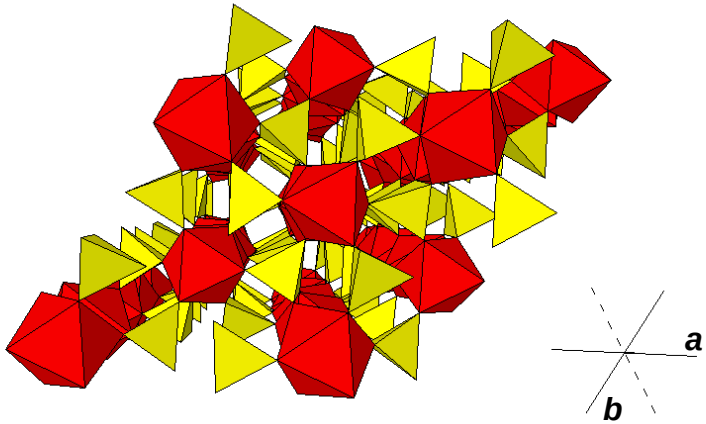
Length of the photograph: 2 mm



*R*3
a = 8.954(1) Å
c = 21.280(4) Å
R_1 = 3.28 %

Phase B

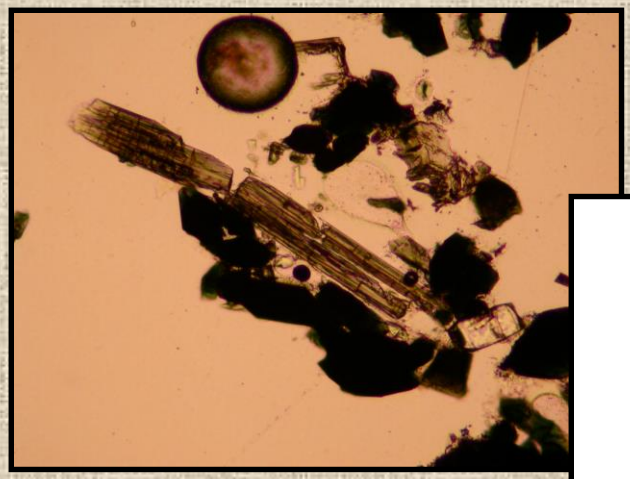




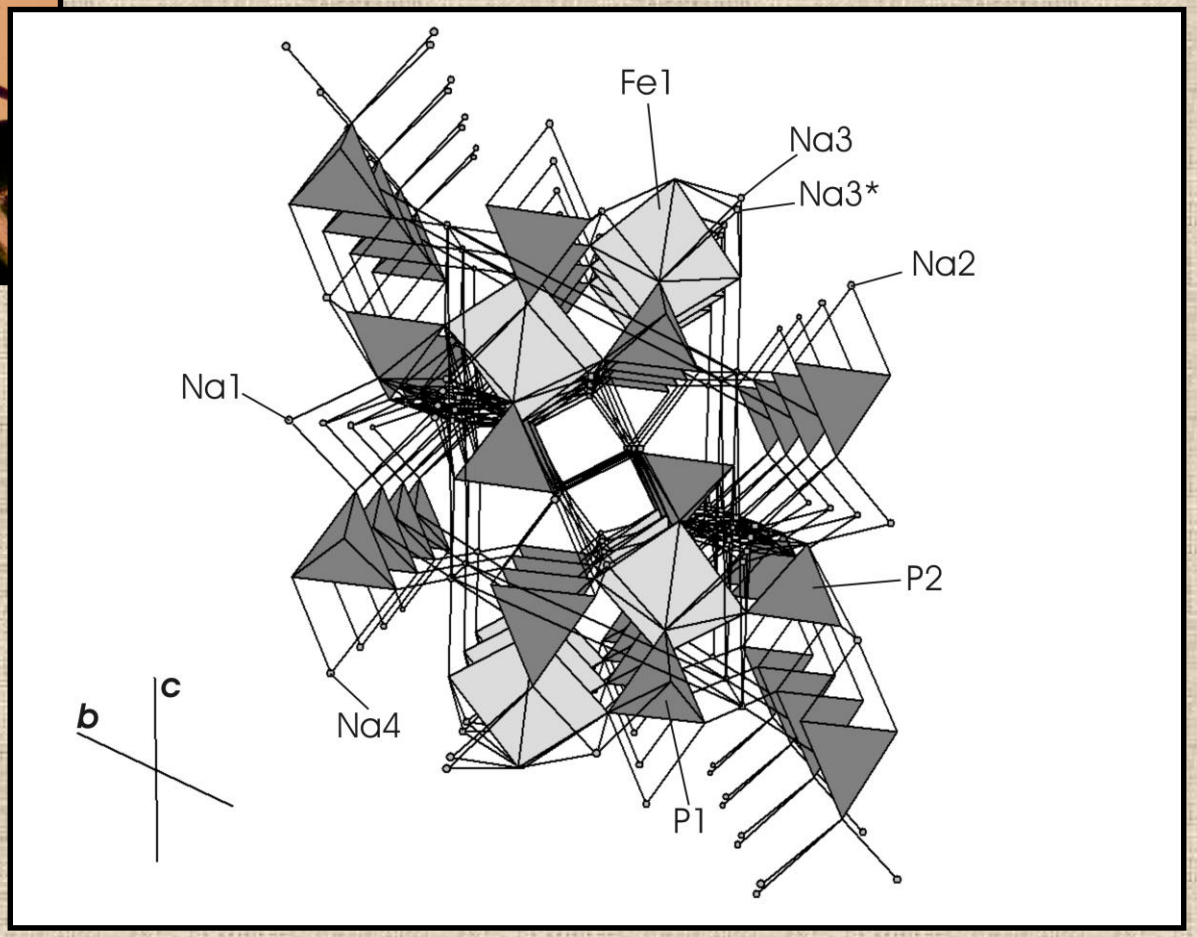
Heteropolyhedral framework

Phase C

$Na_3Fe^{3+}(PO_4)_2$
(Na/Fe = 3)



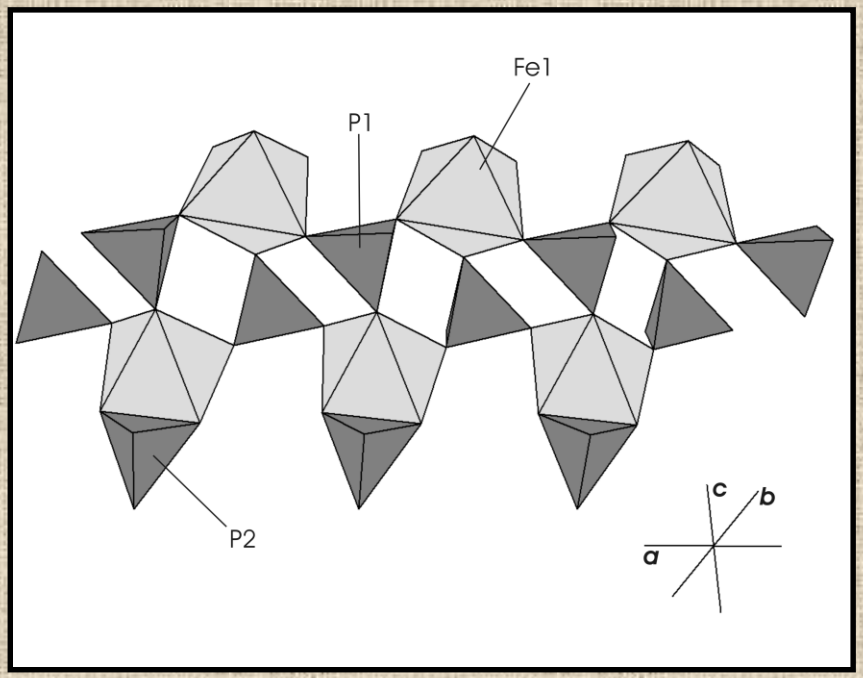
Length of the photograph: 2 mm



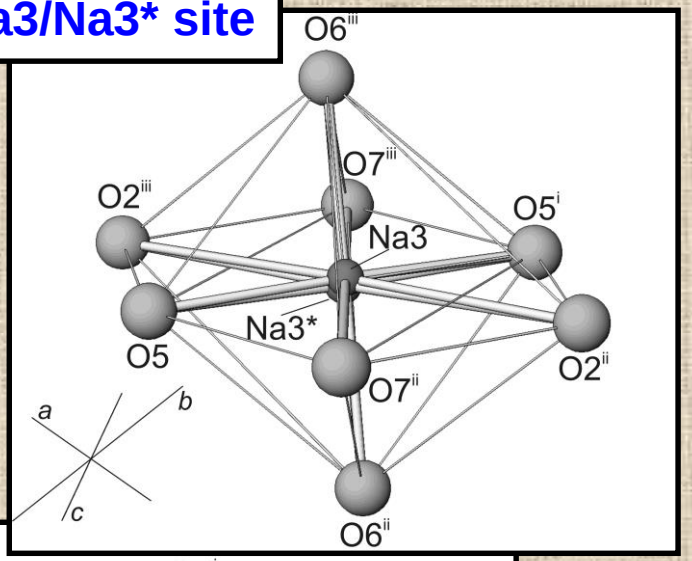
***P*-1**
a **= 5.3141(6) Å**
b **= 8.5853(9) Å**
c **= 8.7859(8) Å**
α **= 114.429(9)°**
β **= 92.327(9)°**
γ **= 106.08(1)°**
R_1 **= 2.77 %**

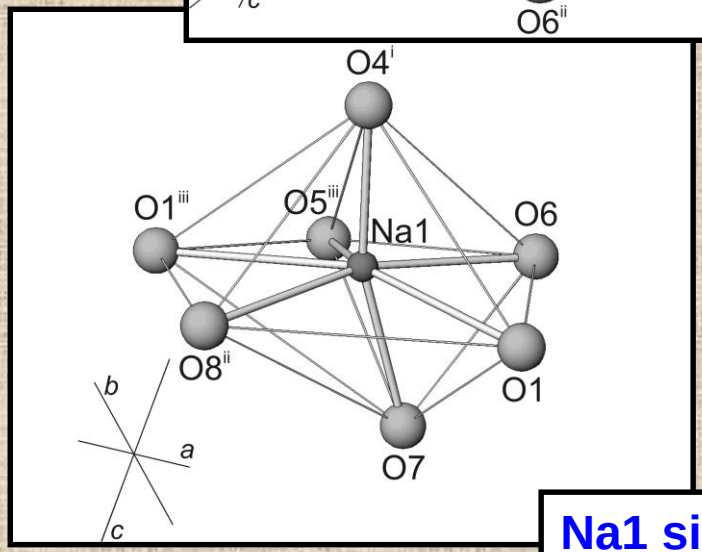
Phase C

Hannayite-type heteropolyhedral chains



Na3/Na3* site

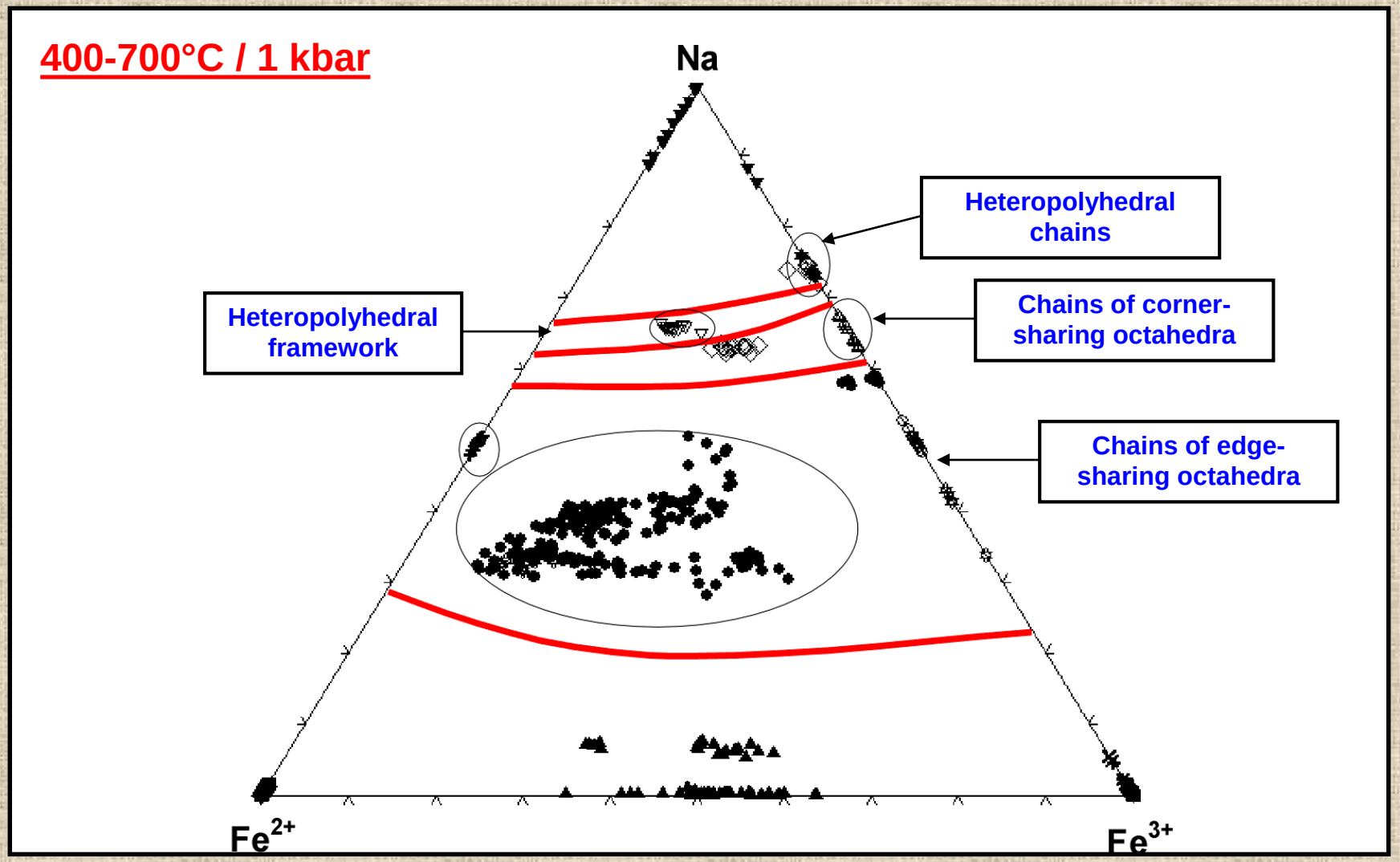




Na1 site

Hatert, F. (2007), Z. Kristallogr. NCS, 222, 6-8

Structural domains



Conclusions

- Alluaudite-type phosphates cover a wide compositional field in the centre Na-Fe^{2+}-Fe^{3+} (+PO_4) diagram
- In the Na-rich portion of the diagram, three phosphates with new crystal structures were synthesized
- With increasing Na content, the FeO_6 octahedra become progressively diluted in the framework
- Progressive transition from crystal structures based on octahedral chains, to structures based on heteropolyhedral units.

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