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A new nomenclature scheme for the alluaudite supergroup

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Alluaudite-type phosphates

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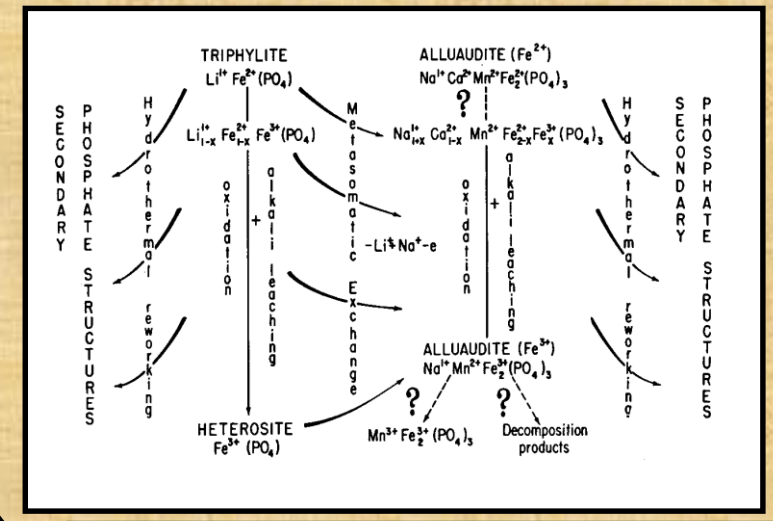
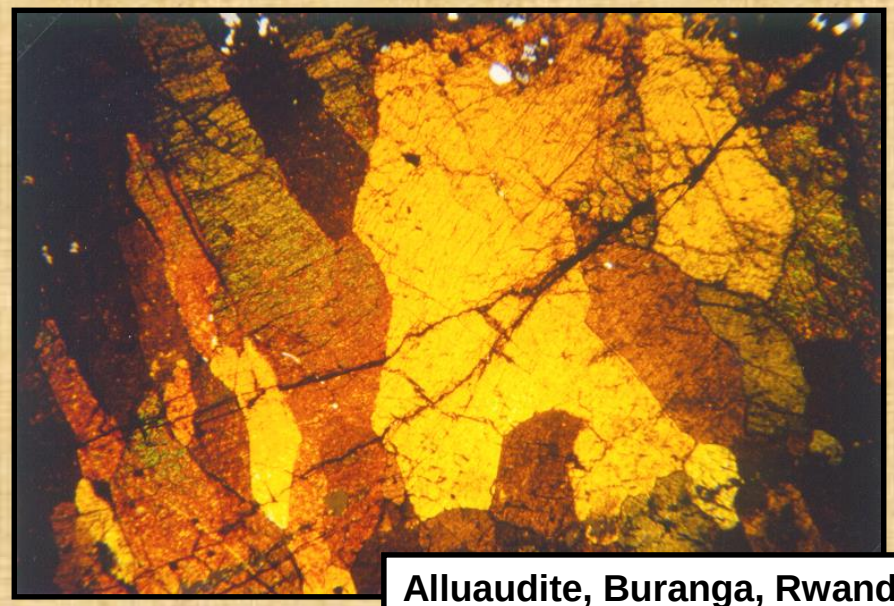
Na-Mn-Fe pegmatite phosphates

Primary origin

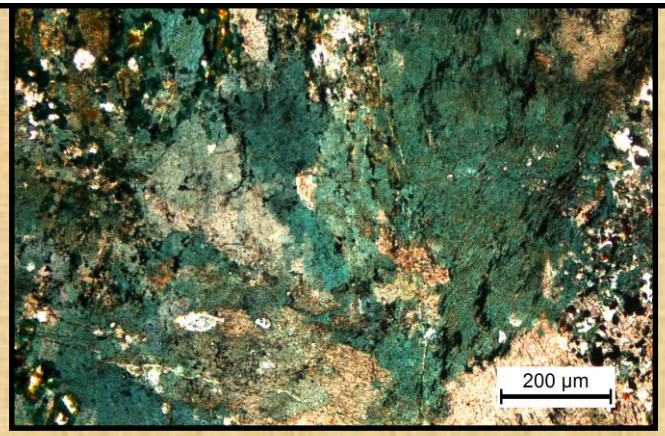
Secondary origin





Alluaudite, Buranga, Rwanda

Ferroalluaudite, Angarf-sud, Morocco



The alluaudite supergroup

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Alluaudite group (*C*2/*c*)

PHOSPHATES (6):

Alluaudite: $[]NaMnFe^{3+}_2(PO_4)_3$
Ferroalluaudite: $[]NaFe^{2+}Fe^{3+}_2(PO_4)_3$
Hagendorfite: $Na_2MnFe^{2+}Fe^{3+}(PO_4)_3$
Ferrohagendorfite: $Na_2Fe^{2+}_2Fe^{3+}(PO_4)_3$
Varulite: $Na_2Mn_2Fe^{3+}(PO_4)_3$
Groatite: $[]NaCaMn_2(PO_4)(HPO_4)_2$

ARSENATES (10):

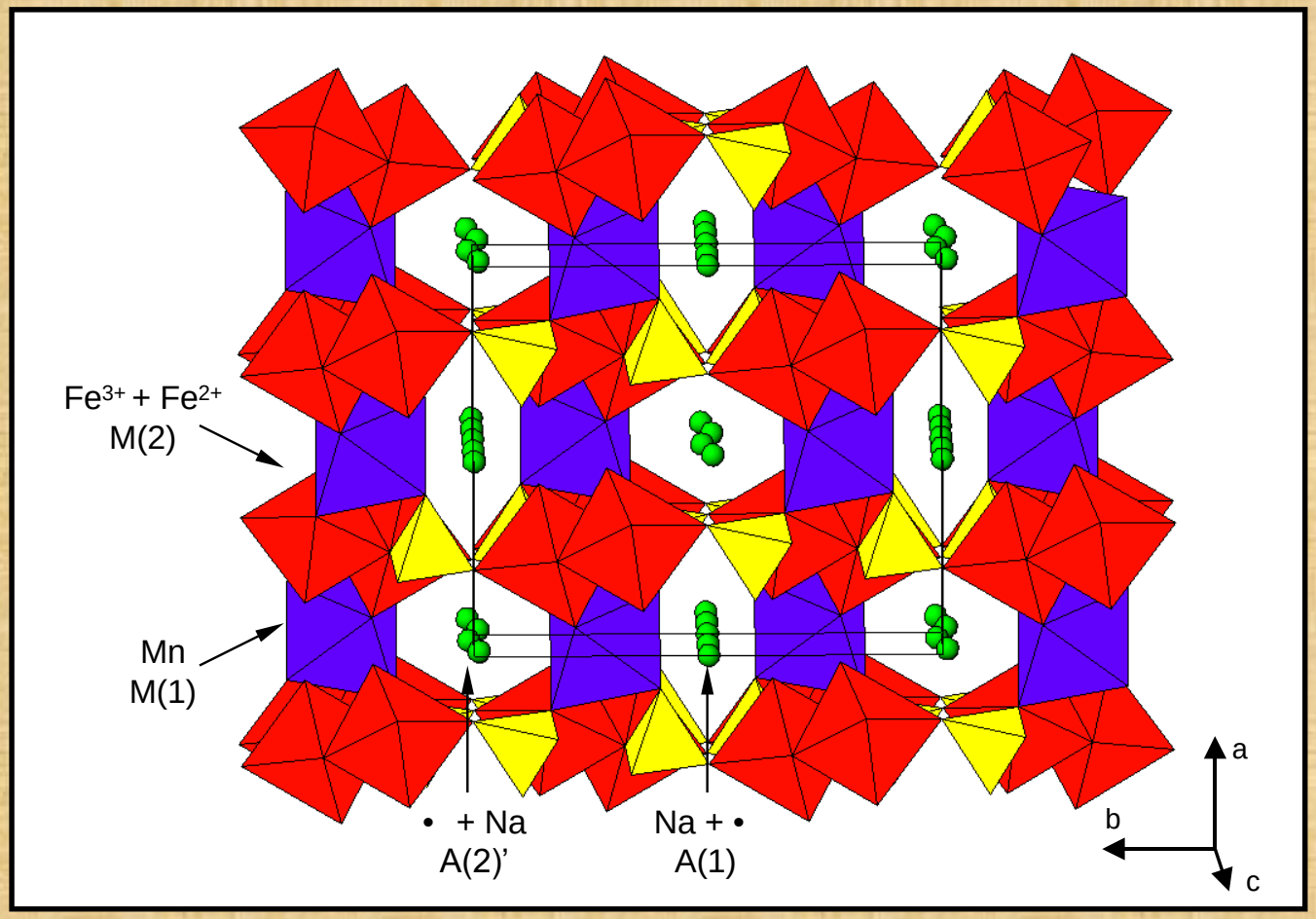
Arseniopleite: $NaCaMnMn_2(AsO_4)_3$
Bradaczekite: $NaCu^{2+}Cu^{2+}Cu^{2+}_2(AsO_4)_3$
Caryinite: $NaCaCaMn_2(AsO_4)_3$
Hatertite: $NaNaCa(Cu^{2+}Fe^{3+})(AsO_4)_3$
Johillerite: $NaCu^{2+}ZnMg_2(AsO_4)_3$
Nickenichite: $NaCaMgMg_2(AsO_4)_3$
O'Danielite: $[]NaZnZn_2(AsO_4)(HAsO_4)_2$
Yazganite: $[]NaMgFe^{3+}_2(AsO_4)_3 \bullet H_2O$
Canutite: $[]NaMnMn_2(AsO_4)(HAsO_4)_2$
Keyite: $Cu_{0.5}CuCdZn_2(AsO_4)_3$

Wyllieite group ($P2_1/n$)

Wyllieite: $Na_2MnFe^{2+}Al(PO_4)_3$
Rosemaryite: $[]NaMnFe^{3+}Al(PO_4)_3$
Ferrowyllieite: $Na_2Fe^{2+}_2Al(PO_4)_3$
Ferrorosemaryite: $[]NaFe^{2+}Fe^{3+}Al(PO_4)_3$
Qingheiite: $Na_2MnMgAl(PO_4)_3$
Qingheiite-(Fe^{2+}): $Na_2Fe^{2+}MgAl(PO_4)_3$

Ferrorosemaryite, Rubindi, Rwanda

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

$[A(2)A(2)'A(2)''_2][A(1)A(1)'A(1)''_2]M(1)M(2)_2[(P,As)O_4]_3$

The nomenclature of alluaudites

- **Moore & Ito (1979)**

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

- ***M*(2) site:**

$Fe^{3+} \Rightarrow$ Alluaudites
$Fe^{2+} \Rightarrow$ Hagendorfites
$Mn \Rightarrow$ Varulite

- ***M*(1) site:**

Normally occupied by Mn, but the prefixes « - ferro » or « - mag » are added when these elements dominate

- **Valid IMA-CNMNC species:**

Alluaudite, ferroalluaudite, hagendorfite, ferrohagendorfite, varulite

Cation distribution in alluaudite-type phosphates

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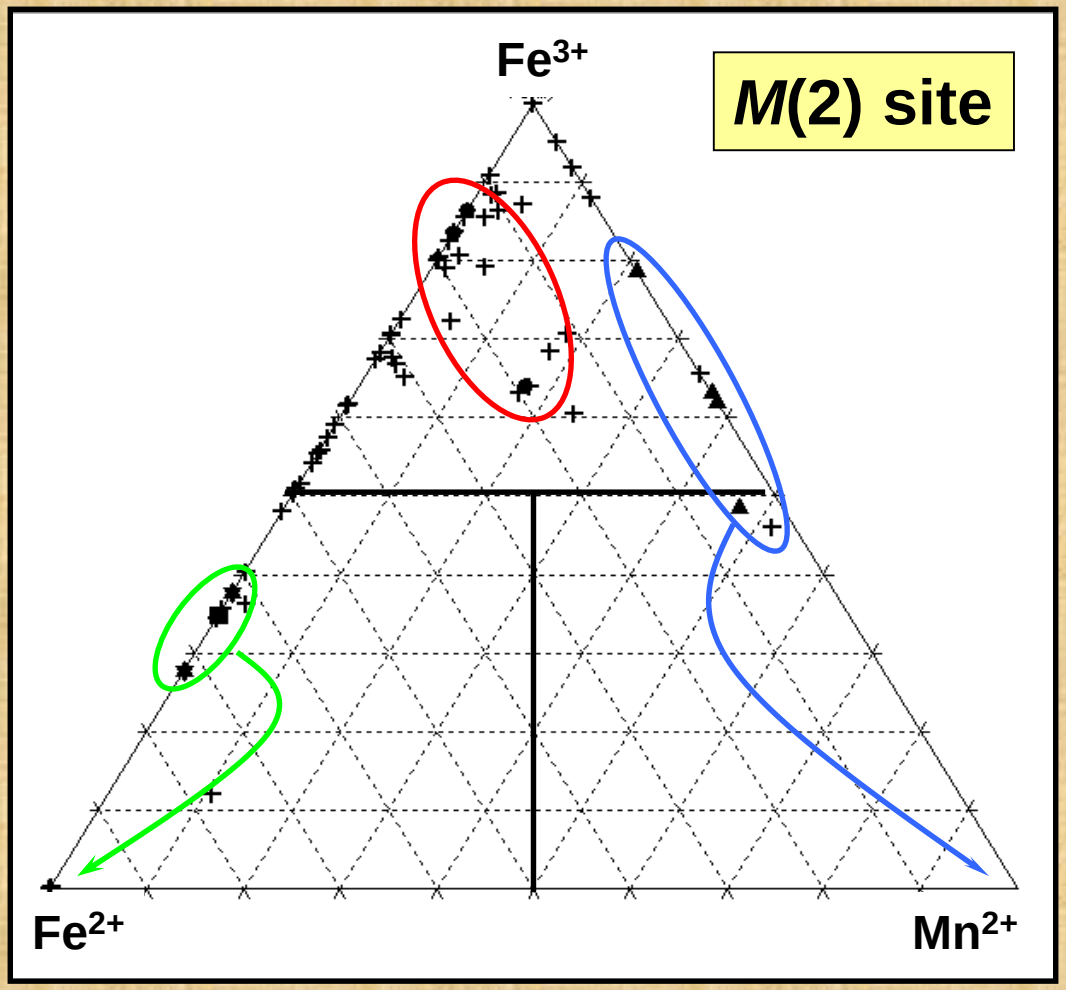

Alluaudites

Fe^{3+} dominant

Hagendorfites

Close to $Fe^{3+}_{0.5}Fe^{2+}_{0.5}$

Varulites

Close to $Fe^{3+}_{0.5}Mn^{2+}_{0.5}$

Observed compositions of type material are far away from the end-member compositions defined by Moore & Ito (1979)!

Re-examination of chemical data from the literature

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- Re-calculation of 67 chemical analyses from the literature
- Calculation basis: 3 P atoms, Fe^{2+}/Fe^{3+} to maintain charge balance.
- Distribution of cations on the different crystallographic sites, according to their ionic radii.

Impossible to establish a coherent nomenclature scheme, since **44 % of the end-member formulae** obtained by considering a single cation on *M*(2) **are not charge-balanced!**

Most common examples:

$NaNa(Fe,Mn)^{2+}Fe^{3+}_2(PO_4)_3$ ⇒ Excess of 1 positive charge

$NaNa(Fe,Mn)^{2+}Fe^{2+}_2(PO_4)_3$ ⇒ Deficit of 1 positive charge

Necessity to consider valency-imposed double site occupancy on *M*(2), for the nomenclature of the alluaudite supergroup.

$NaNa(Fe,Mn)^{2+}(Fe^{2+}Fe^{3+})(PO_4)_3$

Cation distributions assuming a double site occupancy on *M*(2)

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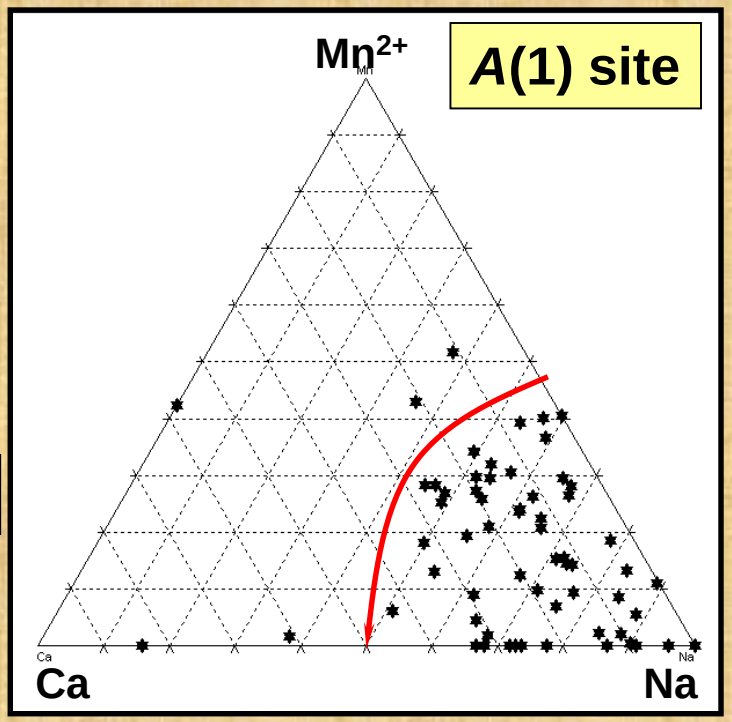
Old formulae

Alluaudite: $[]NaMnFe^{3+}_2(PO_4)_3$
Hagendorfite: $NaCaMnFe^{2+}_2(PO_4)_3$
Varulite: $NaCaMnMn_2(PO_4)_3$

- Na dominant on *A*(1)
- Double site occupancy on *M*(2)

New formulae

Alluaudite: $[]NaMnFe^{3+}_2(PO_4)_3$
Hagendorfite: $NaNaMn(Fe^{2+}Fe^{3+})(PO_4)_3$
Varulite: $NaNaMn(Mn^{2+}Fe^{3+})(PO_4)_3$



- **Only 30 % of the formulae are not charge-balanced**
  → **Significant improvement!**
- **Coherent with the nomenclature of the wyllieite group, where the *M*(2) site is splitted in two *M*(2a) and *M*(2b) crystallographically distinct positions!**

Oxydation mechanism of alluaudites

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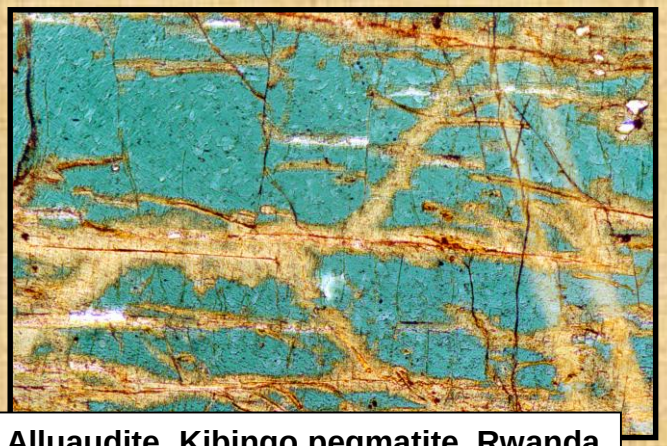
Fransolet *et al*. (1985, 1986, 2004)

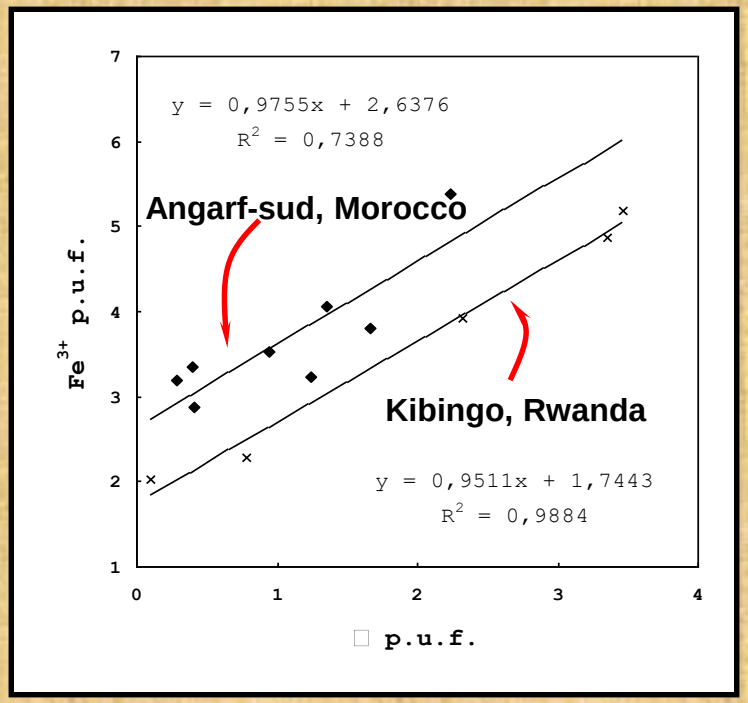
$$Na^{+} + Fe^{2+} \Rightarrow \bullet + Fe^{3+}$$

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

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

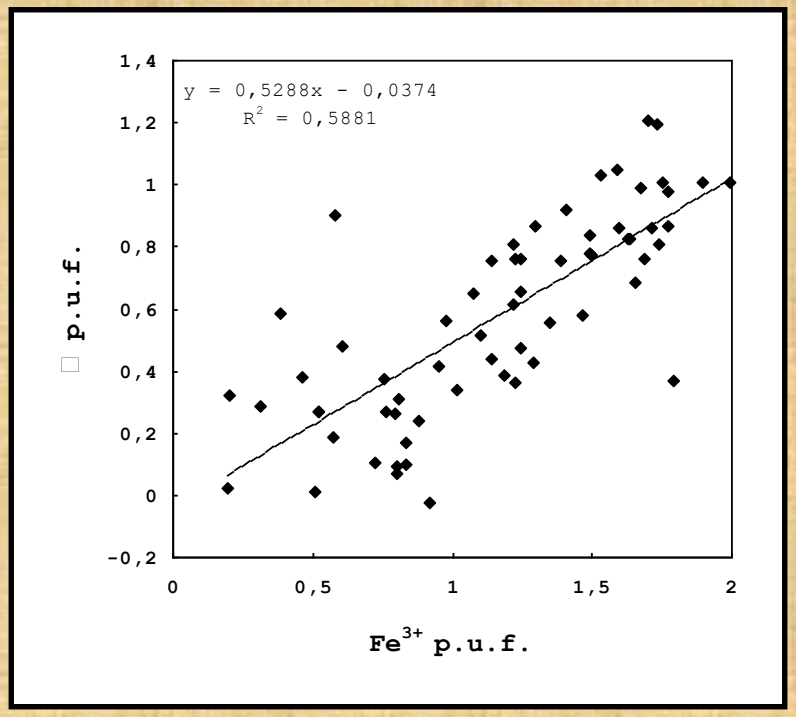


Alluaudite, Kibingo pegmatite, Rwanda

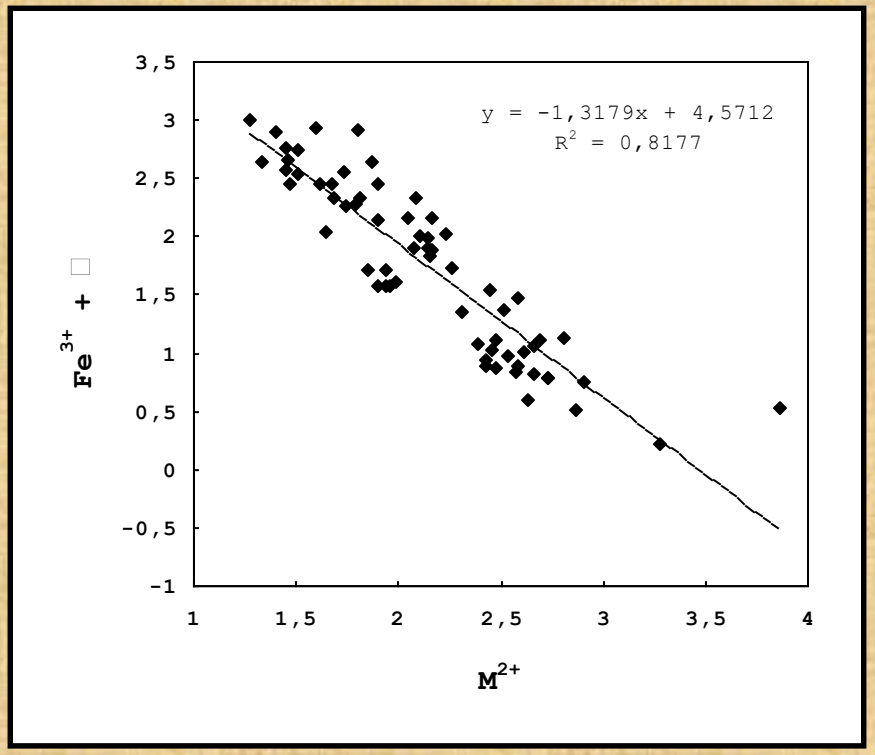


Starting from the end-member formula of alluaudite, the oxidation mechanism produces a mineral with ca. 50 % Fe^{2+} and 50 % Fe^{3+} on *M*(2): Primary hagendorfite.

Substitution mechanisms in alluaudites



$[] + 2\ Fe^{3+} = 3\ M^{2+}$ (Na constant)



$Na^{+} + M^{2+} = [] + Fe^{3+}$ (oxidation)

$Na^{+} + Fe^{3+} = 2\ M^{2+}$ (without [])

Hypothetical end-members

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$[]NaM^{2+}Fe^{3+}_2(PO_4)_3$
(Type 1)

$[] + 2\ Fe^{3+} = 3\ M^{2+}$

$[] + Fe^{3+} = Na^{+} + M^{2+}$

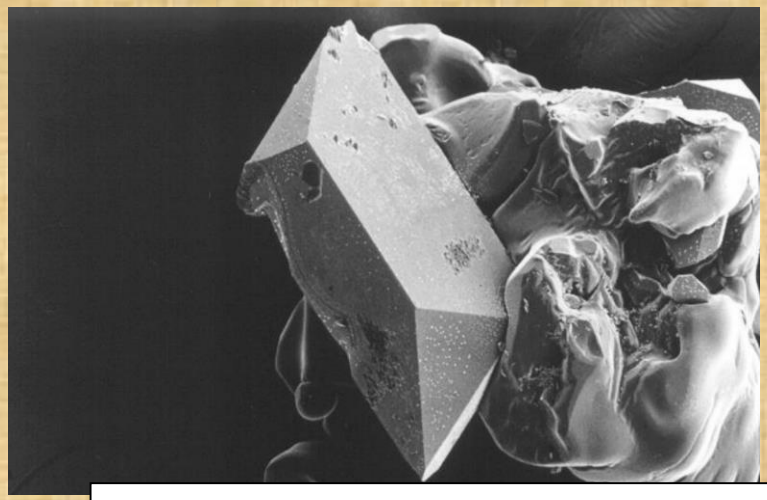
$NaM^{2+}_4(PO_4)_3$
(Type 3)

$Na^{+} + Fe^{3+} = 2\ M^{2+}$

$Na_2M^{2+}_2Fe^{3+}(PO_4)_3$
(Type 2)

$Na^{+} + M^{2+} = [] + Fe^{3+}$

$[]M^{2+}_3Fe^{3+}(PO_4)_3$
(Type 4)



Synthetic alluaudite crystal (600°C / 1 kbar)

New observed end-members

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Type 1

$[]NaM^{2+}Fe^{3+}_2(PO_4)_3$: ALLUAUDITES

Type 2

$Na_2M^{2+}Fe^{2+}Fe^{3+}(PO_4)_3$: HAGENDORFITES
$Na_2M^{2+}Mn^{2+}Fe^{3+}(PO_4)_3$: VARULITES
$Na_2M^{2+}MgFe^{3+}(PO_4)_3$: ROOT 1

Type 3

$NaCaM^{2+}Fe^{2+}_2(PO_4)_3$: ROOT 2
$NaCaM^{2+}Fe^{2+}Mg(PO_4)_3$: ROOT 3
$NaCaM^{2+}MnFe^{2+}(PO_4)_3$: ROOT 4

$NaCaMnFe^{2+}_2(PO_4)_3$ (ROOT 2)

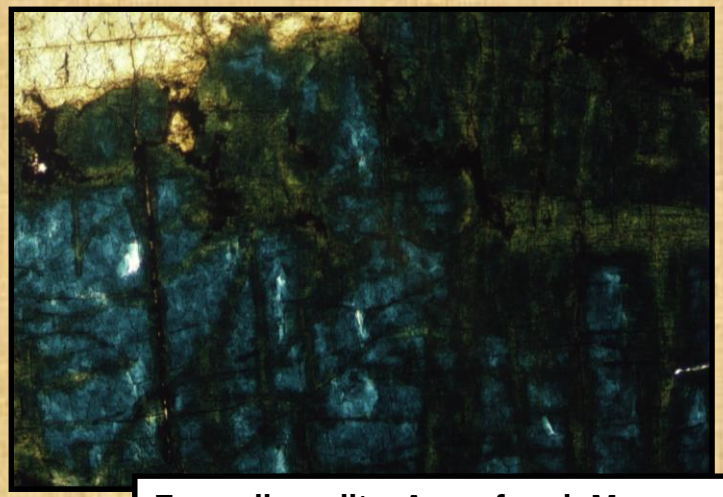
↓

Ideal composition of hühnerkobelite (to revalidate; Mason 1942)

Chemical analyses

↓

New species hagendorfite-Ca, ROOT1, ferroROOT1, ferroROOT3 (under study).



Ferroalluaudite, Angarf-sud, Morocco

New nomenclature scheme for the alluaudite-type phosphates

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Alluaudite group – Phosphates

Alluaudite: $[]NaMnFe^{3+}_2(PO_4)_3$
Ferroalluaudite: $[]NaFe^{2+}Fe^{3+}_2(PO_4)_3$
Hagendorfite: $Na_2Mn(Fe^{2+}Fe^{3+})(PO_4)_3$
Ferrohagendorfite: $Na_2Fe^{2+}(Fe^{2+}Fe^{3+})(PO_4)_3$
Varulite: $Na_2Mn(MnFe^{3+})(PO_4)_3$

« ROOT1 »: $Na_2Mn(MgFe^{3+})(PO_4)_3$
« FerroROOT1 »: $Na_2Fe^{2+}(MgFe^{3+})(PO_4)_3$
« Hühnerkobelite »: $NaCaMnFe^{2+}_2(PO_4)_3$
« Ferrohühnerkobelite »: $NaCaFe^{2+}Fe^{2+}_2(PO_4)_3$
« ROOT3 »: $NaCaMn(Fe^{2+}Mg)(PO_4)_3$
« FerroROOT3 »: $NaCaFe^{2+}(Fe^{2+}Mg)(PO_4)_3$
« ROOT4 »: $NaCaMn(MnFe^{2+})(PO_4)_3$

Groatite: $[]NaCaMn_2(PO_4)(HPO_4)_2$
« Manganogroatite »: $[]NaMnMn_2(PO_4)(HPO_4)_2$

« Maghagendorfite »
« Ferrovarulite »
« FerroROOT4 »

Unstable cationic arrangments

New nomenclature scheme for wyllieite-type phosphates

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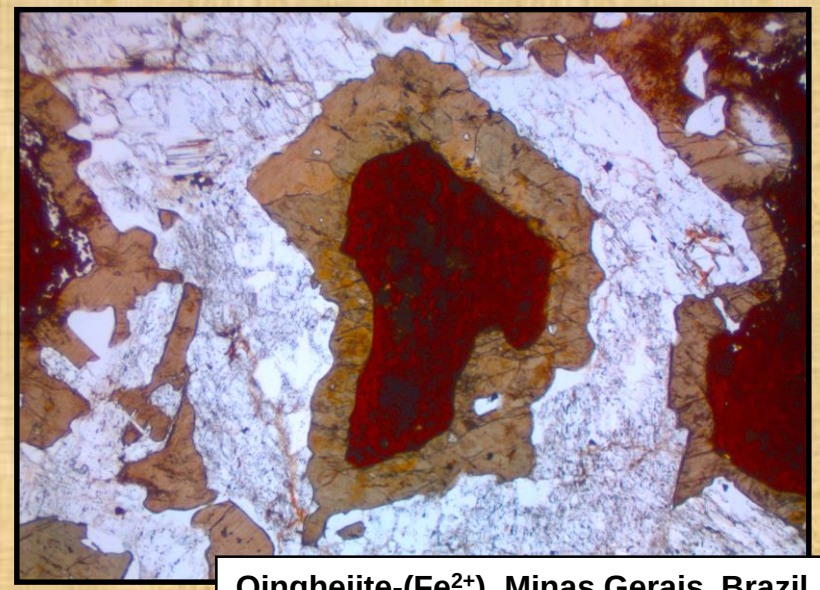
Wyllieite group

Wyllieite: $Na_2MnFe^{2+}Al(PO_4)_3$
Ferrowyllieite: $Na_2Fe^{2+}Fe^{2+}Al(PO_4)_3$

Rosemaryite: $[]NaMnFe^{3+}Al(PO_4)_3$
Ferrorosemaryite: $[]NaFe^{2+}Fe^{3+}Al(PO_4)_3$

Qingheiite: $Na_2MnMgAl(PO_4)_3$
Qingheiite-(Fe^{2+}): $Na_2Fe^{2+}MgAl(PO_4)_3$



Qingheiite-(Fe^{2+}), Minas Gerais, Brazil

Qingheiite-(Fe^{2+}) ⟹ Te be renamed « Ferroqingheiite »

Conclusions

- The nomenclature of the alluaudite supergroup, established by Moore & Ito (1979), does not work for 44% of the compositions reported in the literature.
- A new nomenclature scheme is proposed, in which valency-imposed double site occupancy is allowed on the *M*(2) site.
- The end-member formulae of hagendorfites and varulites are significantly modified, and 3 new root-names are suggested
- Hühnerkobelite will be revalidated, and qingheiite-(Fe^{2+}) will be renamed « ferroqingheiite ».