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

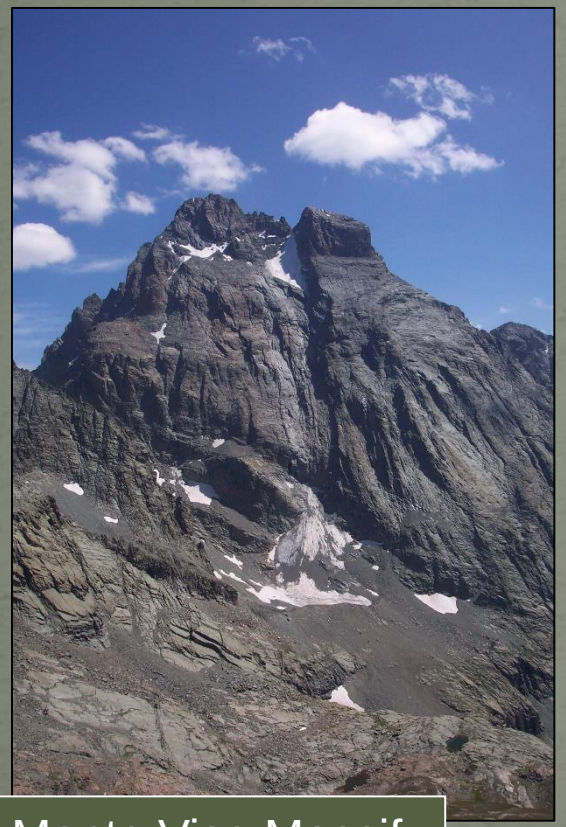
Crystal chemistry and nomenclature of pegmatitic iron-manganese phosphates

Prof. Frédéric Hatert

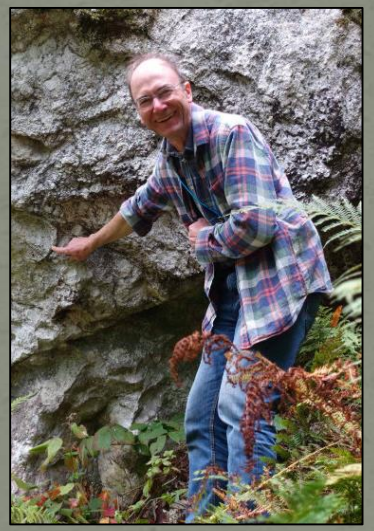
Paris, October 17th 2023

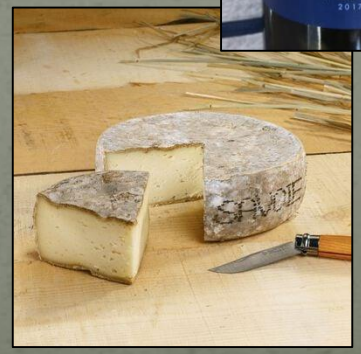
First meeting with Christian

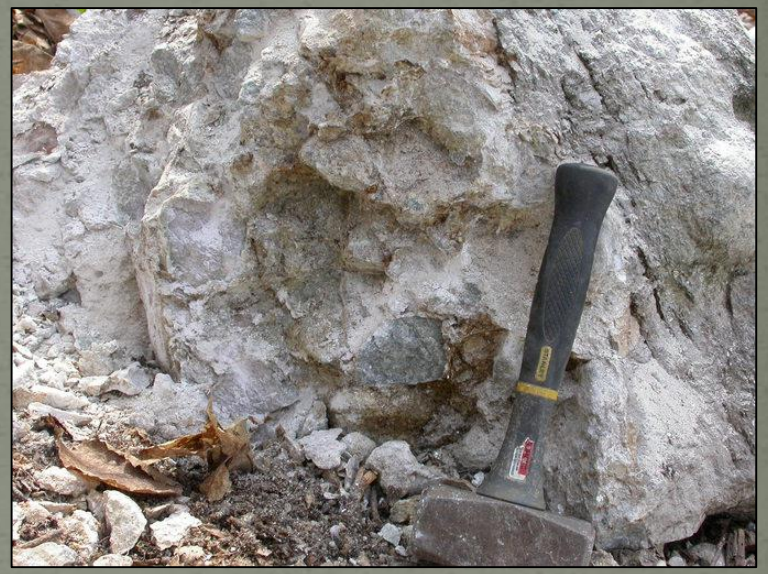
SFMC Field-trip - 1998
« Minéralogie du métamorphisme alpin »



Monte Viso Massif







Dora Maira Massif

Second meeting with Christian

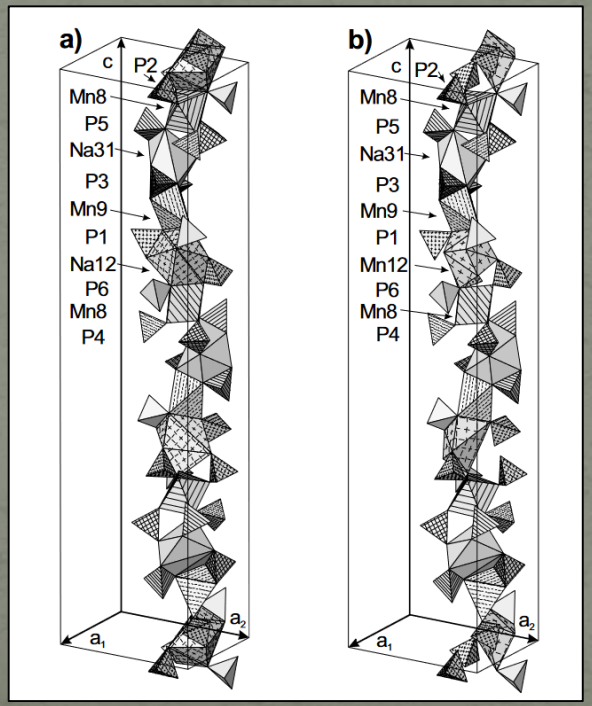
5 th International Conference
MINERALOGY AND MUSEUMS
Paris France 2004

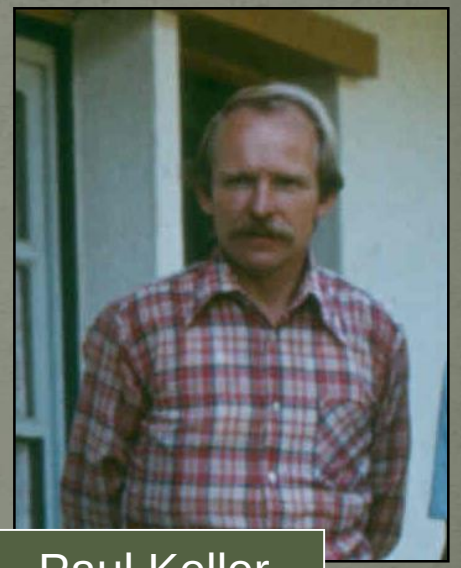
Hydrothermal synthesis and crystal structure of $Na(Na,Mn)_7Mn_{22}(PO_4)_{18}\cdot 0.5H_2O$, a new compound of fillowite structure type

PAUL KELLER[1,*], FRÉDÉRIC HATERT[2,3], FALK LISSNER[4], THOMAS SCHLEID[4] and ANDRÉ-MATHIEU FRANSOLET[2]

- Synthetic fillowite-type phosphates
- 15 cationic sites and 6 PO_4 tetrahedra
- (a ~ 15 Å and c ~ 43 Å, space group R-3)
- Fe-Mn randomly distributed on several sites

- Impossible to apply the CNMMN « 50 % rule »
- Grouping of sites necessary





Paul Keller
1940-2022

The « Dominant constituent rule »

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THE IMA–CNMNC DOMINANT-CONSTITUENT RULE REVISITED AND EXTENDED

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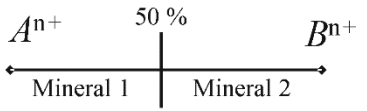
We thank Frank Hawthorne, Christian Chopin and Thomas Armbruster for starting the discussion on the application of the dominant-constituent rule, and for providing examples showing that it should be revised urgently. Several CNMNC members helped to improve

1. The « 50 % » rule

« 50 % mark »

$A^{n+}{}_M \rightarrow B^{n+}{}_M$



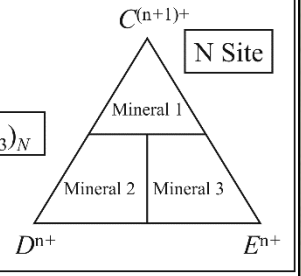
a

4. The « Dominant valency » rule

« Dominant valency rule »

$D^{n+}{}_N \rightarrow E^{n+}{}_N$

$(A_{0.4}B_{0.6})_M(C_{0.4}D_{0.3}E_{0.3})_N$

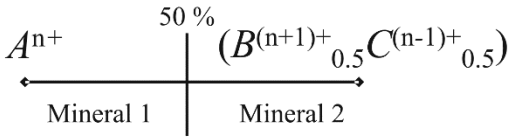


b

3. « Valency-imposed double-site occupancy »

« 50 % mark »

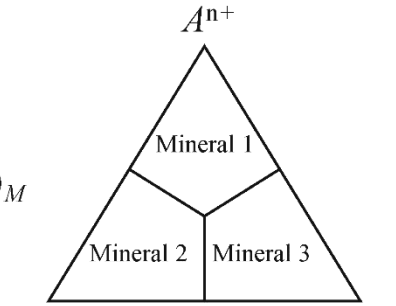
$A^{n+}{}_M \rightarrow (B^{(n+1)+}{}_{0.5}C^{(n-1)+}{}_{0.5})_M$



2. The « Dominant constituent » rule

« 33.3 % marks »

$A^{n+}{}_M \rightarrow (B^{n+},C^{n+})_M$

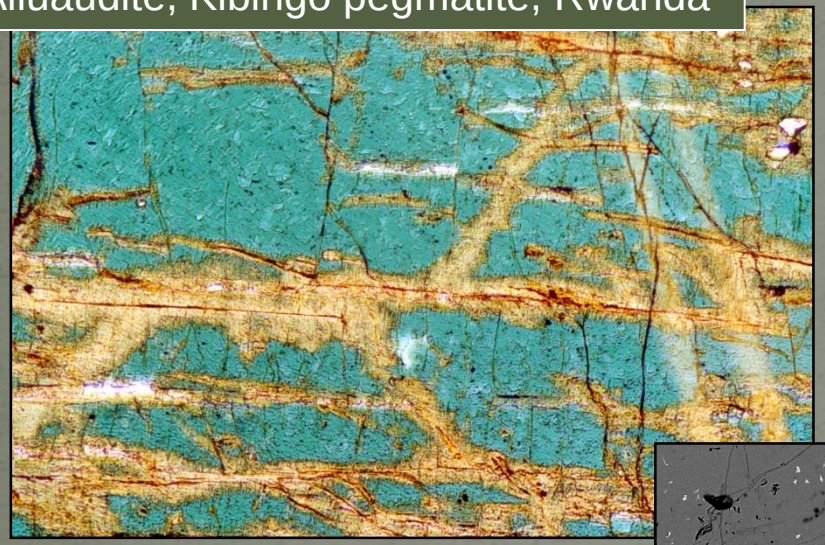


b

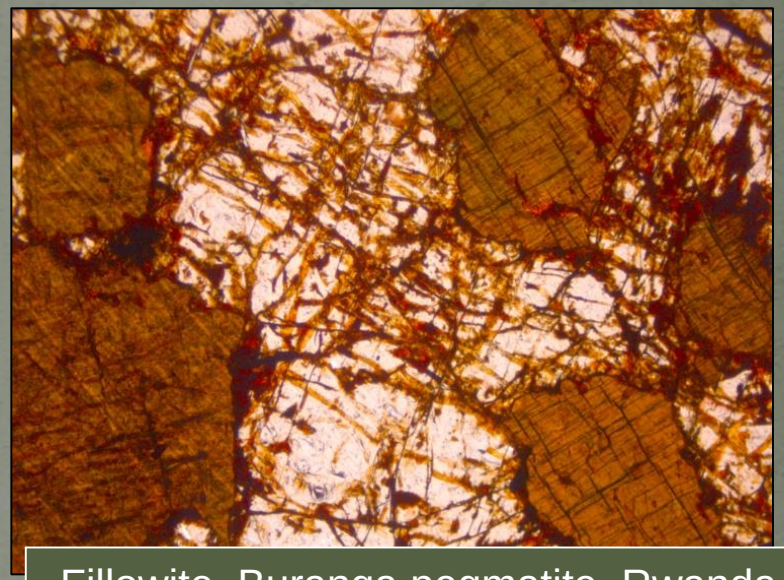
5. Grouping of sites with similar crystal-chemical affinities

Iron-manganese pegmatite phosphates

Alluaudite, Kibingo pegmatite, Rwanda



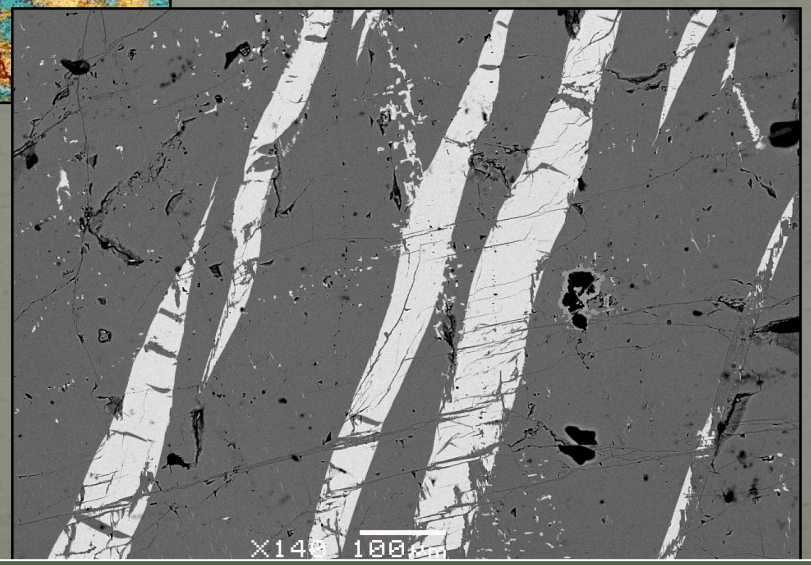
- $NaMnFe^{3+}_2(PO_4)_3$
- *a* ~ 12, *b* ~ 12.5, *c* ~ 6.5 Å, β ~ 115°
- Space group *C*2/*c*



Fillowite, Buranga pegmatite, Rwanda

- $Na_2Ca(Mn,Fe^{2+},Mg)_7(PO_4)_6$
- *a* ~ 15 Å and *c* ~ 43 Å
- Space group R-3

- $Li(Fe^{2+},Mn)(PO_4)$
- *a* ~ 4.7, *b* ~ 10.3, *c* ~ 6.0 Å
- Space group *Pbnm*



Triphylite + sarcopside, Cañada pegmatite, Spain (BSE)

The alluaudite group

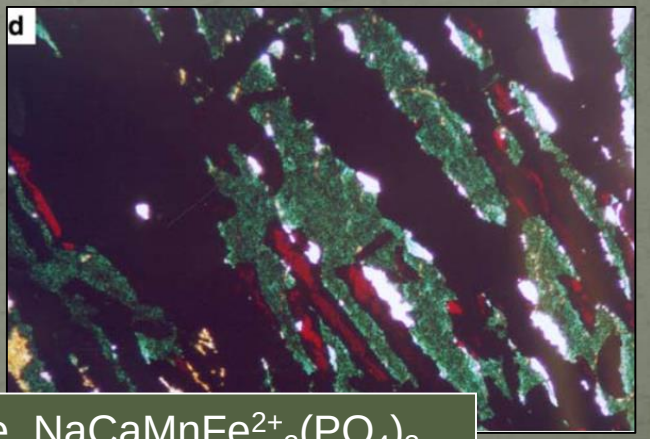
Alluaudite
Buranga pegmatite, Rwanda

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

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

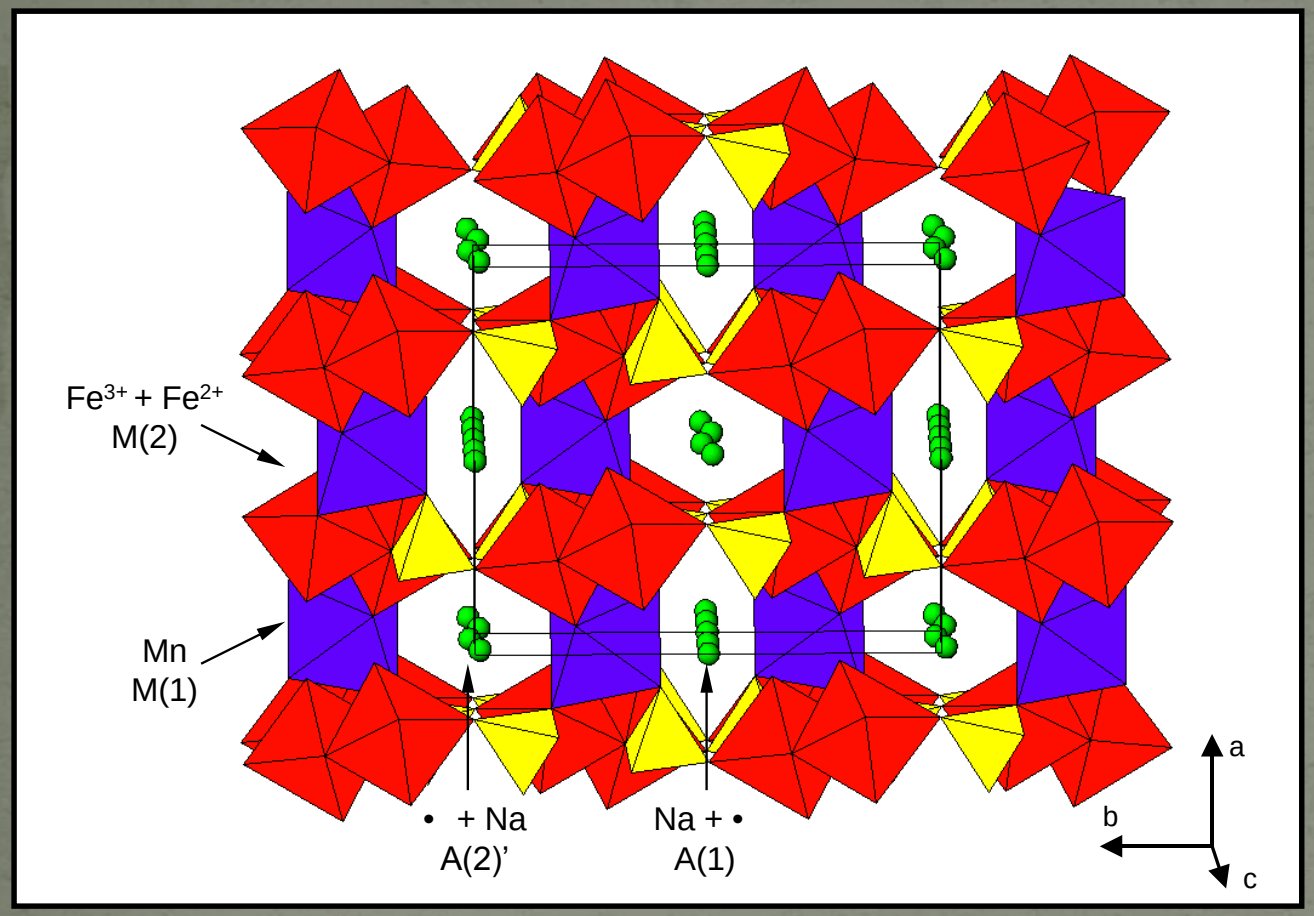
Augustin-Alexis Damour
(1808-1902)

Varulite, $NaCaMn^{2+}_3(PO_4)_3$
Varuträsk, Sweden



Hagendorfite, $NaCaMnFe^{2+}_2(PO_4)_3$
Hagendorf-Süd pegmatite, Germany

The alluaudite structure



A(2)': gable disphenoid
A(1): distorted cube
M(1): very distorted octahedron
M(2): distorted octahedron

C2/c, *Z* = 4

a ~ 12, *b* ~ 12.5, *c* ~ 6.5 Å, β ~ 115°

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

Crystal chemistry of natural and synthetic alluaudites

Crystal chemistry of the divalent cation in alluaudite-type phosphates: A structural and infrared spectral study of the $Na_{1.5}(Mn_{1-x}M^{2+}_x)_{1.5}Fe_{1.5}(PO_4)_3$ solid solutions ($x = 0$ to 1, $M^{2+} = Cd^{2+}, Zn^{2+}$)

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Moore & Ito (1979)

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

Nomenclature based on the M(2) content:

Alluaudite ⟹ $[]NaMn(Fe^{3+}Fe^{3+})(PO_4)_3$

Hagendorfite ⟹ $NaCaMn(Fe^{2+}Fe^{2+})(PO_4)_3$

Varulite ⟹ $NaCaMn(Mn^{2+}Mn^{2+})(PO_4)_3$

Valency-imposed double-site occupancy was not allowed in 1979!

Cation	Ionic radius (Å) [VI]	Ionic radius (Å) [VIII]	Site A(2)'	Site A(1)	Site M(1)	Site M(2)
Ag^+	1.15	1.28	X	X		
Na^+	1.02	1.18	X	X	X	
Cu^+	0.77	-	p	p		
Li^+	0.76	0.92	p	p		
Ca^{2+}	1.00	1.12	p	p	p	
Cd^{2+}	0.95	1.10		p	X	p
Mn^{2+}	0.830	0.96	p	p	X	X
Fe^{2+}	0.780	0.92			X	X
Co^{2+}	0.745	0.90			X	X
Zn^{2+}	0.740	0.90			X	P
Cu^{2+}	0.73	-		p		
Mg^{2+}	0.720	0.89			X	X
In^{3+}	0.800	0.92			p	X
Fe^{3+}	0.645	0.78		p		X
Ga^{3+}	0.620	-				p
Cr^{3+}	0.615	-				p
Al^{3+}	0.535	-				p

X : Complete occupancy of the site
p : Partial occupancy of the site

A new nomenclature scheme for alluaudites

Eur. J. Mineral.
2019, **31**, 807–822
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To Christian Chopin, for 30 years of dedicated service to EJM

A new nomenclature scheme for the alluaudite supergroup

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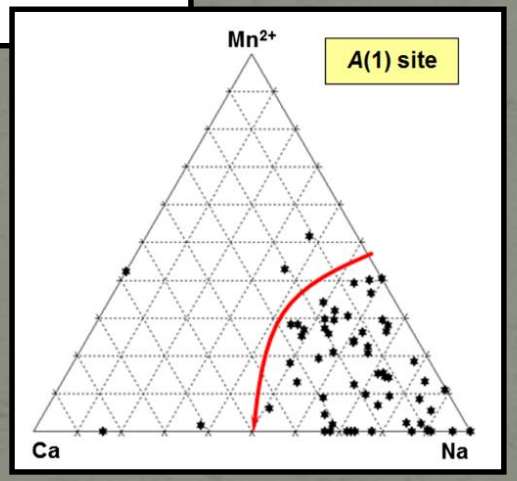
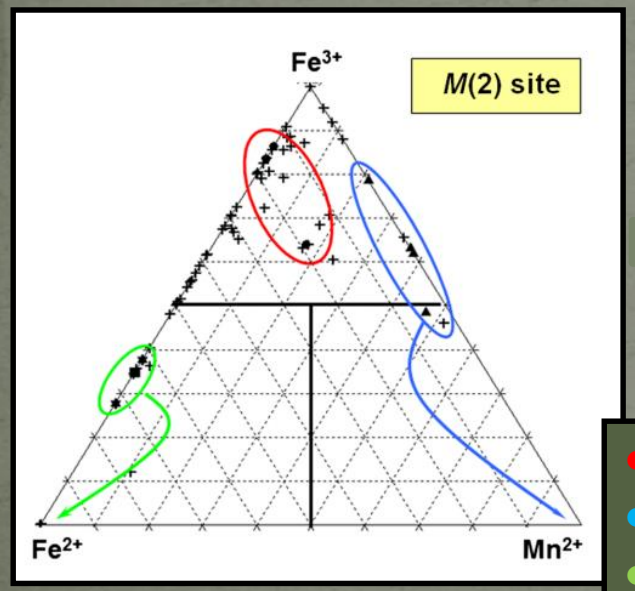
Most alluaudites do not contain Ca on the *A*(1) site, but mainly Na





- Alluaudites: Fe^{3+}-dominant
- Varulites: 50 % Mn^{2+} and 50 % Fe^{3+}
- Hagendorfites: 50 % Fe^{2+} and 50 % Fe^{3+}

New nomenclature scheme based on a double occupancy on *M*(2)

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

□$NaM^{2+}Fe^{3+}_2(PO_4)_3$: ALLUAUDITES
□$NaM^{2+}Mn^{3+}_2(PO_4)_3$: ROOT1

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

$Na_2M^{2+}Fe^{2+}Fe^{3+}(PO_4)_3$: HAGENDORFITES
$Na_2M^{2+}Mn^{2+}Fe^{3+}(PO_4)_3$: VARULITES
$Na_2M^{2+}MgFe^{3+}(PO_4)_3$: ROOT2

New end-member formulae

Mineral name	Old CNMNC formula	New ideal formula
Alluaudite	$(Na,Ca)(Mn,Mg,Fe^{2+})(Fe^{3+},Mn^{2+})_2(PO_4)_3$	$\square NaMnFe^{3+}_2(PO_4)_3$
Ferroalluaudite	$NaFe^{2+}Fe^{3+}_2(PO_4)_3$	$\square NaFe^{2+}Fe^{3+}_2(PO_4)_3$
Hagendorfite	$NaCaMn^{2+}Fe^{2+}_2(PO_4)_3$	$Na_2MnFe^{2+}Fe^{3+}(PO_4)_3$
Maghagendorfite	$(Na,\square)MgMn^{2+}(Fe^{2+},Fe^{3+})_2(PO_4)_3$	$Na_2MgFe^{2+}Fe^{3+}(PO_4)_3$
Varulite	$NaCaMn^{2+}_3(PO_4)_3$	$Na_2Mn_2Fe^{3+}(PO_4)_3$

+ Wyllieite-type phosphates: topologically similar structure, but significant Al and $P2_1/n$ space group

+ Alluaudite-type arsenates: 6 formulae redefined

Fillowite-type phosphates

- Accessory Na-Ca-(Mn-Fe-Mg)-bearing anhydrous phosphates
- Occurring in granitic pegmatites, in metamorphic rocks and in iron meteorites
- Very complex crystal structure (*a* ~ 15 Å and *c* ~ 43 Å, space group *R*-3)
- The fillowite group contains 5 species, according to the CNMNC mineral list:

- Fillowite: $Na_2CaMn^{2+}_7(PO_4)_6$ (Brush & Dana, 1879)
- Johnsomervilleite: $Na_{10}Ca_6Fe^{2+}_{25}Mg_{18}(PO_4)_{36}$ (Livingstone, 1980)
- Chladniite: $Na_2CaMg_7(PO_4)_6$ (McCoy *et al*., 1994)
- Galileiite: $NaFe^{2+}_4(PO_4)_3$ (Olsen & Steele, 1997)
- Stornesite-(Y), $Na_6(Ca_5Na_3)YMg_{43}(PO_4)_{36}$ (Grew *et al*., 2006)

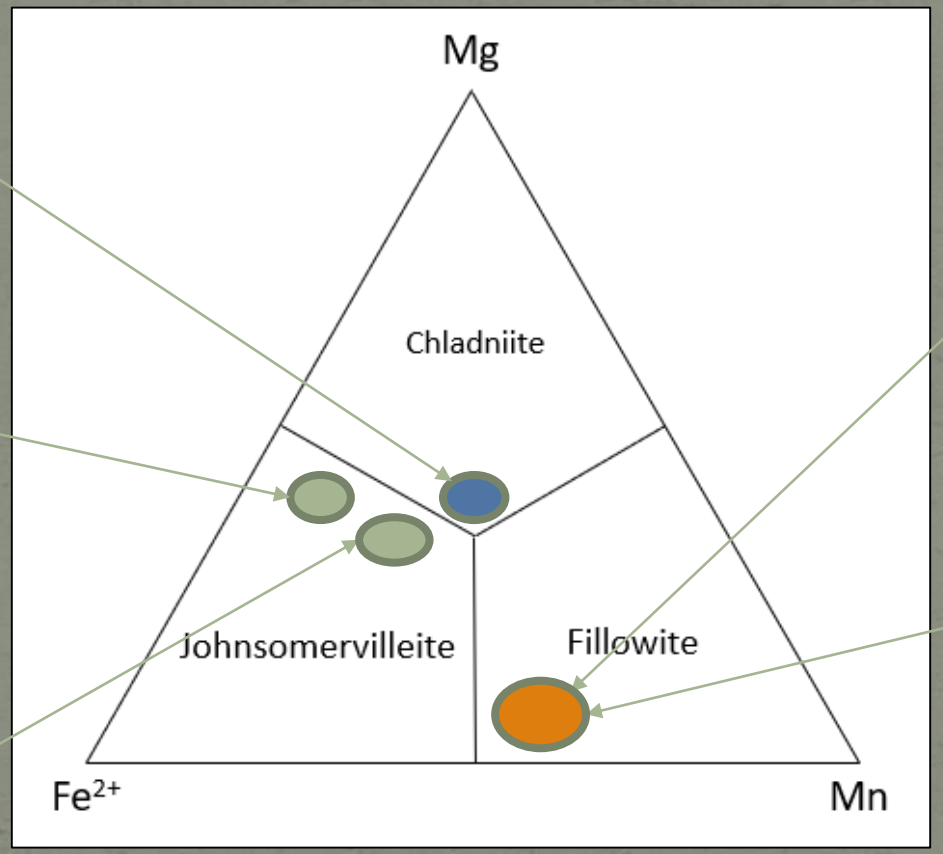
Extremely heterogeneous nomenclature!

Chemical analyses and structural data

Chladniite, Sapucaia
a = 15.1416(6) Å
c = 43.123(2) Å
R_1 = 5.59 %

Johnsomervilleite, Loch Quoich
a = 15.036(2) Å
c = 42.972(9) Å
R_1 = 4.14 %

Johnsomervilleite, Maplensata
a = 15.090(2) Å
c = 43.050(9) Å
R_1 = 4.04 %

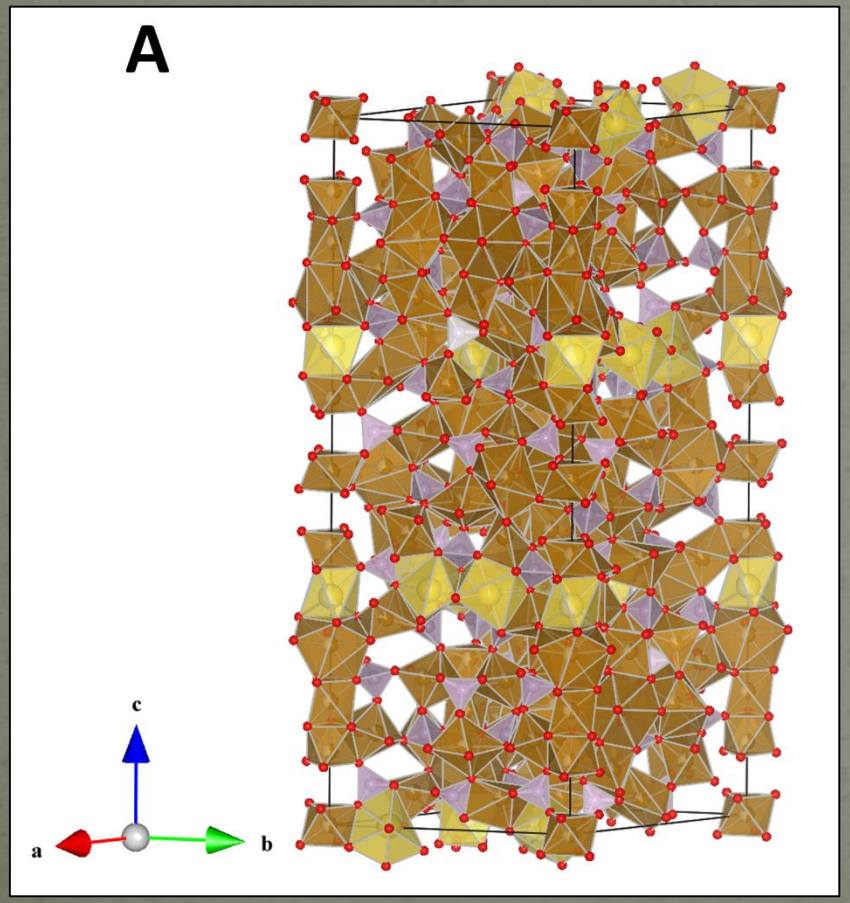


Fillowite, Buranga
a = 15.122(1) Å
c = 43.258(4) Å
R_1 = 3.79 %

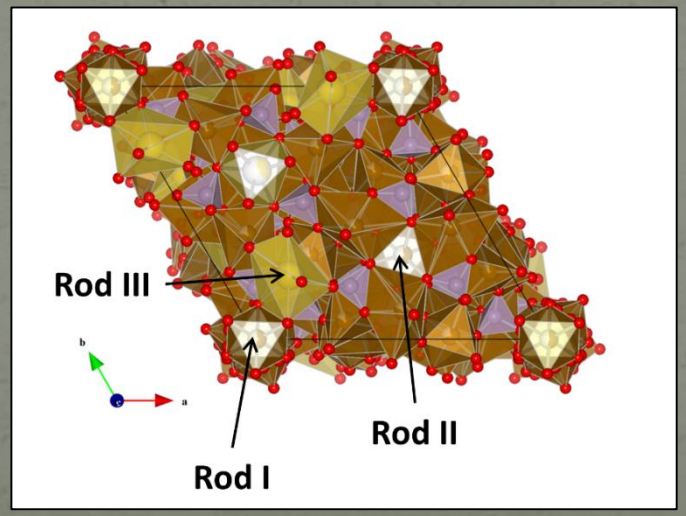
Fillowite, Kabira
a = 15.125(1) Å
c = 43.198(3) Å
R_1 = 3.52 %

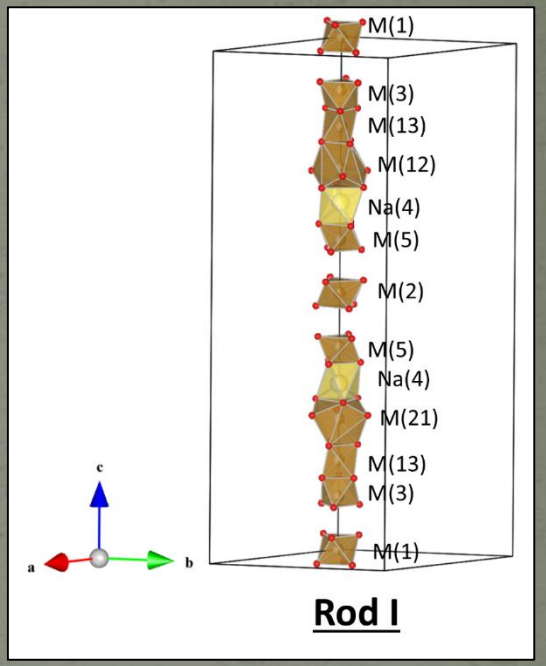
The fillowite structure

- Extremely complex and compact crystal structure
- Alternation of polyhedra, forming rods aligned along the *c* axis



- 6 PO_4 tetrahedra
- 11 (Fe^{2+},Mn^{2+},Mg)-sites [V] to [VII]
- 3 Na sites [VII] to [IX]
- 1 Ca site [VII] to [VIII]





- Rod I at (0, 0)
- Rod II at (2/3, 1/3)
- Rod III at (1/9, 2/9)

Examples of cationic distributions

	Fillowite, Buranga, Rwanda (A)					Fillowite, Kabira, Uganda (B)				
Site	ASP	RSS	CSS	TV	BVS	ASP	RSS	CSS	TV	BVS
M(1)	1.00 Mn	23.15	25.00	2.00	2.02	0.60 Mn + 0.40 Ca	22.70	23.00	2.00	2.06
M(2)	0.50 Mn + 0.50 Ca	21.65	22.50	2.00	2.07	1.00 Mn	23.38	25.00	2.00	2.03
M(3)	0.65 Mn + 0.25 Fe^{3+} + 0.10 □	22.24	22.75	2.05	1.99	1.00 Fe^{2+}	25.38	26.00	2.00	2.09
M(4)	1.00 Na	10.79	11.00	1.00	1.08	0.40 Mn + 0.50 Fe^{3+} + 0.1 □	22.70	23.00	2.30	2.27
M(5)	0.50 Mn + 0.50 Fe^{3+}	25.45	25.50	2.50	2.33	1.00 Fe^{2+}	24.13	26.00	2.00	1.98
M(6)	1.00 Mn	25.00	25.00	2.00	1.99	0.40 Mn + 0.60 Fe^{2+}	25.06	25.60	2.00	2.03
M(7)	0.35 Mn + 0.65 Fe^{2+}	25.21	25.65	2.00	1.92	0.40 Mn + 0.60 Fe^{2+}	25.44	25.60	2.00	2.00
M(8)	0.55 Mn + 0.45 Fe^{2+}	25.08	25.45	2.00	1.96	0.55 Mn + 0.45 Fe^{2+}	25.12	25.45	2.00	1.99
M(9)	0.55 Mn + 0.45 Fe^{2+}	24.94	25.45	2.00	1.97	0.70 Mn + 0.30 Fe^{2+}	25.00	25.30	2.00	2.01
M(10)	0.48 Mn + 0.52 Fe^{2+}	25.29	25.52	2.00	2.04	1.00 Mn	25.00	25.00	2.00	2.02
M(11)	0.66 Mn + 0.34 Fe^{2+}	25.33	25.26	2.00	2.02	0.60 Mn + 0.40 Fe^{2+}	25.39	25.40	2.00	2.00
M(12)	1.00 Na	10.91	11.00	1.00	1.01	0.65 Ca + 0.35 Na	17.03	16.85	1.65	1.36
M(13)	0.60 Fe^{2+} + 0.40 Fe^{3+}	24.28	26.00	2.40	2.31	1.00 Na	11.03	11.00	1.00	1.11
M(21)	1.00 Na	11.31	11.00	1.00	0.88	0.10 Ca + 0.90 Na	12.08	11.90	1.10	0.94
M(31)	0.70 Ca + 0.30 Na	17.17	17.30	1.70	1.45	1.00 Na	11.00	11.00	1.00	1.01
EMP	$Na_{1.795}Ca_{0.822}Mn_{4.077}Fe^{2+}_{2.486}Fe^{3+}_{0.359}(PO_4)_6$					$Na_{1.905}Ca_{0.908}Mn_{3.903}Fe^{2+}_{2.823}Fe^{3+}_{0.259}(PO_4)_6$				
STR	$Na_{1.967}Ca_{0.783}Mn_{4.230}Fe^{2+}_{2.600}Fe^{3+}_{0.383}(PO_4)_6$					$Na_{1.983}Ca_{0.750}Mn_{4.050}Fe^{2+}_{3.017}Fe^{3+}_{0.167}(PO_4)_6$				

- M(1) to M(11): M^{2+}
- M(12) to M(31): Na and Ca

Exchange of Na and (Fe,Mn)

Exchange of Na and Ca

Extremely disordered cationic distribution!

Definition of a new general formula

Sites	Occupancy	Total multiplicity (basis = 36 P)	Number of atoms in the formula (basis = 36 P)
M(1), M(2)	Fe^{2+}, Mn, Mg (+ minor Ca, REE)	1 x 2 sites = 2	2 M^{2+}
M(3), M(5)	Fe^{2+}, Mn, Mg	2 x 2 sites = 4	4 M^{2+}
M(6), M(7), M(8), M(9), M(10), M(11)	Fe^{2+}, Mn, Mg	6 x 6 sites = 36	36 M^{2+}
M(4), M(13), M(21)	Two of these three sites are dominantly occupied by Na, while the other site is dominantly occupied by M^{2+}.	2 x 3 sites = 6	4 Na 2 M^{2+}
M(12), M(31)	One of these two sites is dominantly occupied by Na, while the other site is dominantly occupied by (Ca, Na) with a Ca/Na ratio close to 2.	6 x 2 sites = 12	6 Na (4 Ca + 2 Na)
TOTAL			44 M^{2+} (= C sites) 12 Na (= A sites) 4 Ca (= B sites)

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CRYSTAL CHEMISTRY AND NOMENCLATURE OF FILLOWITE-TYPE PHOSPHATES

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New formulae!

$Na_{12}Ca_4M^{2+}_{44}(PO_4)_{36}$ (Z = 3)

$Na_3CaM^{2+}_{11}(PO_4)_9$ (Z = 12)

$A_3BC_{11}(PO_4)_9$ (Z = 12)

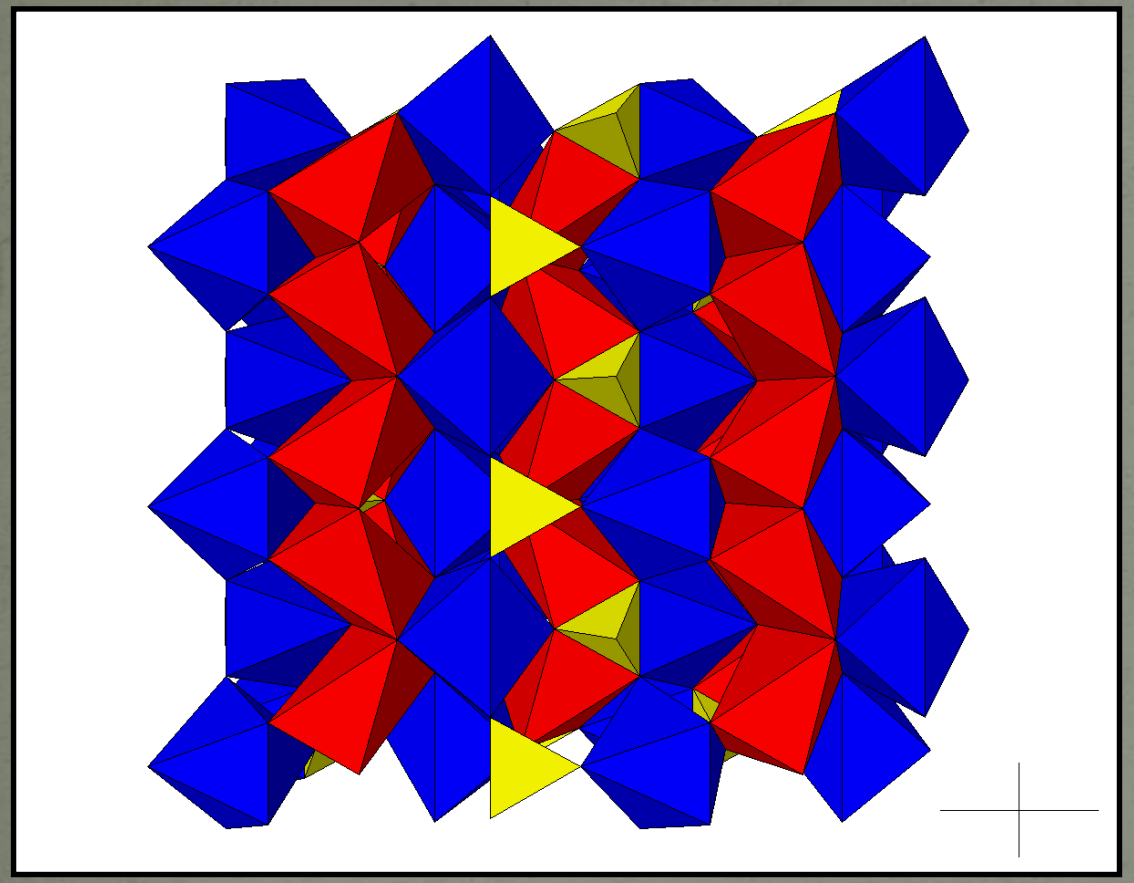
Nomenclature modifications

$A_3BC_{11}(PO_4)_9$

Grouping of crystallographic sites with the same affinities

Mineral name	Old CNMNC formula	New ideal formula	
Fillowite	$Na_2CaMn^{2+}_7(PO_4)_6$	$Na_3CaMn^{2+}_{11}(PO_4)_9$	$C = Mn^{2+}$
Johnsomervilleite	$Na_{10}Ca_6Mg_{18}Fe^{2+}_{25}(PO_4)_{36}$	$Na_3CaFe^{2+}_{11}(PO_4)_9$	$C = Fe^{2+}$
Chladniite	$Na_2CaMg_7(PO_4)_6$	$Na_3CaMg_{11}(PO_4)_9$	$C = Mg$
Galileiite	$NaFe^{2+}_4(PO_4)_3$	$Na_3Fe^{2+}Fe^{2+}_{11}(PO_4)_9$	$C = Fe^{2+}$, $B = Fe^{2+}$
« Stornesite-(Y) »	$Na_6(Ca_5Na_3)YMg_{43}(PO_4)_{36}$	DISCREDITED	

The triphylite group



Red octahedra: M1 (Li, Na)
Blue octahedra: M2 (Fe, Mn)

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Karenwebberite, $Na(Fe^{2+},Mn^{2+})PO_4$, a new member of the triphylite group from the Malpensata pegmatite, Lecco Province, Italy

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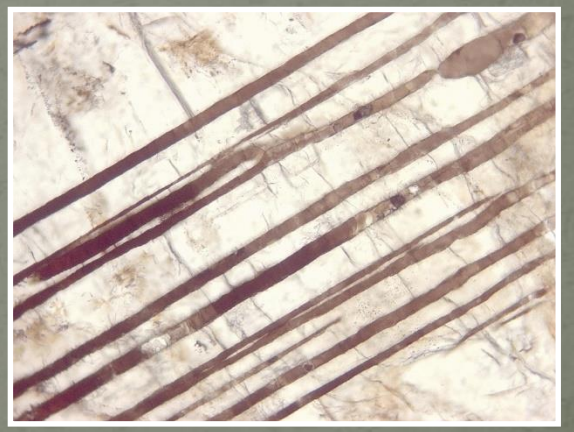
- Triphylite, $LiFe^{2+}(PO_4)$
- Lithiophilite, $LiMn(PO_4)$
- Natrophilite, $NaMn(PO_4)$
- Karenwebberite, $NaFe^{2+}(PO_4)$

S.G. *Pmnb*

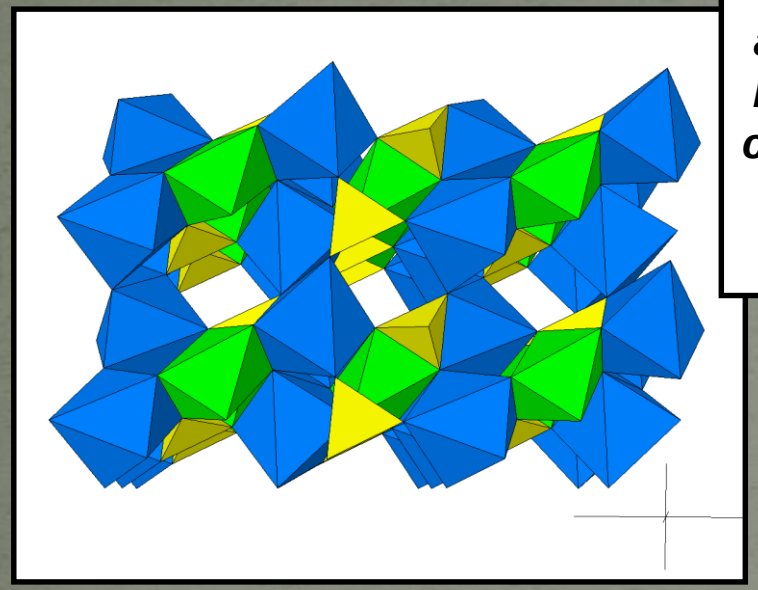
a = 6.092 Å
b = 10.429 Å
c = 4.738 Å

Karen Louise Webber



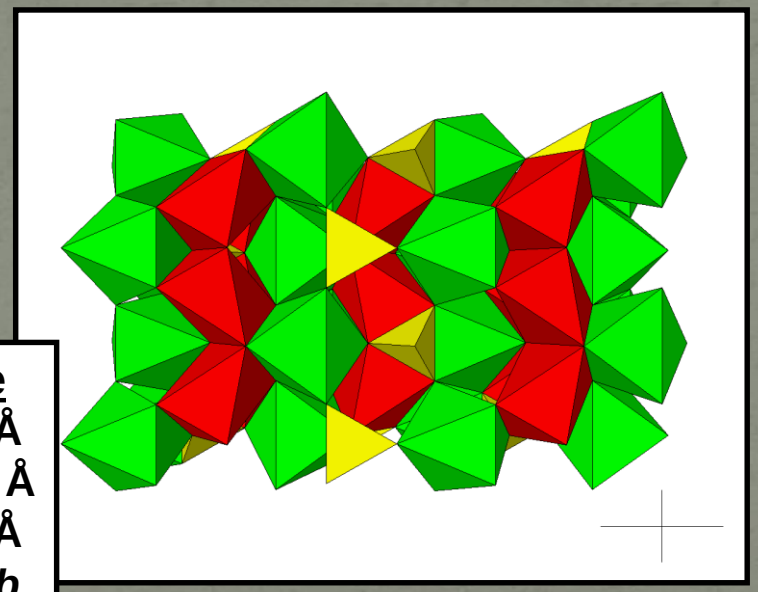
Malpensata pegmatite, Italy

The triphylite and sarcopside structures



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***

- **Sarcopside: $Fe_3(PO_4)_2$**
- **Zavalíaite: $Mn_3(PO_4)_2$**
- **Chopinite: $Mg_3(PO_4)_2$**



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**

Christian Chopin

Florencia Márquez Zavalía

The Quensel-Mason oxidation sequence

Percy Quensel (1881-1966)

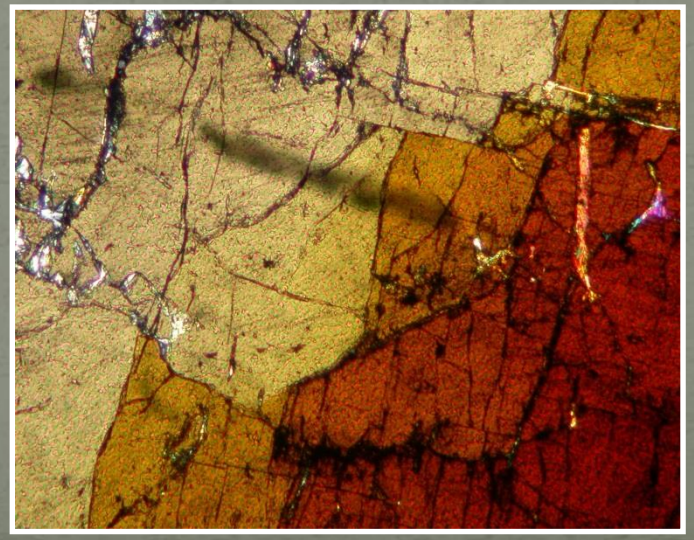
Brian Mason (1917-2009)

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

(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)



Nomenclature modifications

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Nomenclature of the triphylite group of minerals

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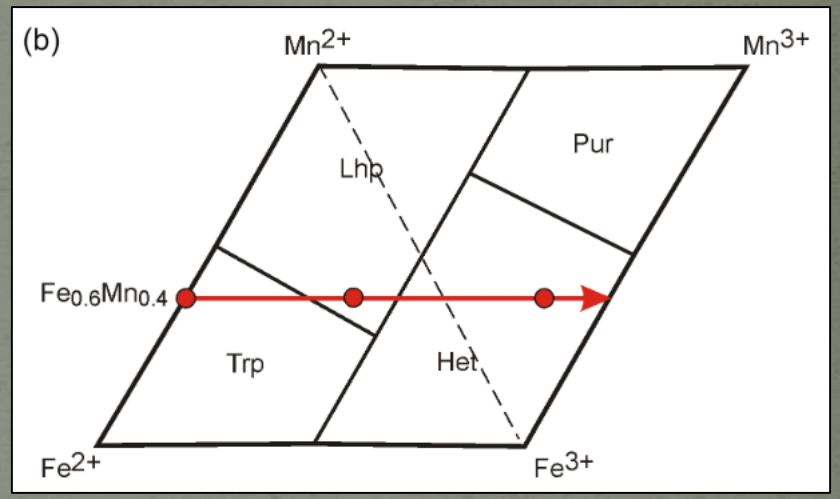
Mineral	IMA List of Minerals, December 2022	New end-member formulae
Triphylite	$LiFe^{2+}(PO_4)$	$LiFe^{2+}(PO_4)$
Lithiophilite	$LiMn^{2+}(PO_4)$	$LiMn^{2+}(PO_4)$
Heterosite	$Fe^{3+}(PO_4)$	$Fe^{3+}(PO_4)$
Purpurite	$Mn^{3+}(PO_4)$	$Mn^{3+}(PO_4)$
Sicklerite	$LiMn^{2+}(PO_4)$	Discredited
Ferrisicklerite	$Li_{1-x}(Fe^{3+},Mn^{2+})(PO_4)$	Discredited
Simferite	$Li(Mg,Fe^{3+},Mn^{3+})_2(PO_4)_2$	$LiMg(PO_4)$
Karenwebberite	$NaFe^{2+}(PO_4)$	$NaFe^{2+}(PO_4)$
Natrophilite	$NaMn^{2+}(PO_4)$	$NaMn^{2+}(PO_4)$



Conclusions

• The CNMNC « Dominant constituent rule » now allows the grouping of crystallographic sites and a valency-imposed double-site occupancy.

• Nomenclature schemes of three Fe-Mn-phosphate groups were revisited according to these new guidelines.

• In alluaudites, a double occupancy is allowed on the *M*(2) sites of varulites and hagendorfites, for example.

• In fillowites, a grouping of several cationic sites is necessary to reduce the number of potential new species.

• In the triphylite group, ferrisicklerite and sicklerite were discredited since they correspond to intermediate members of solid solutions.