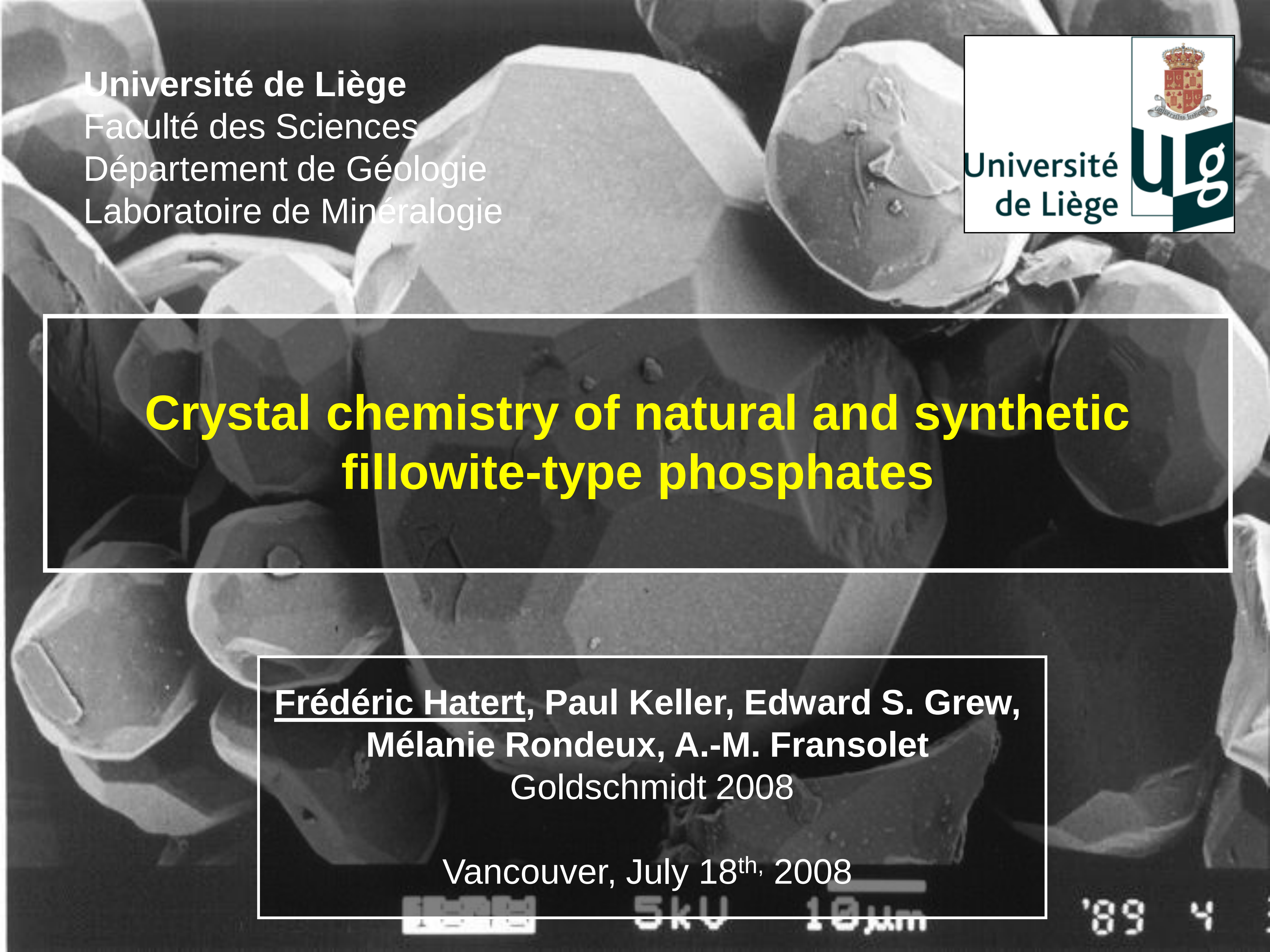

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Crystal chemistry of natural and synthetic fillowite-type phosphates

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Goldschmidt 2008

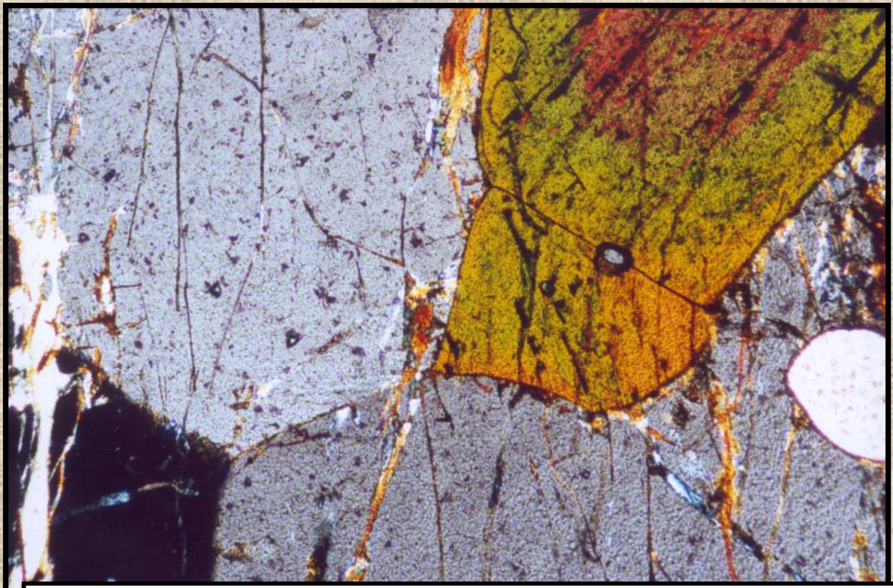
Vancouver, July 18th, 2008

The fillowite group

- Fillowite, $Na_2Ca(Mn,Fe^{2+})_7(PO_4)_6$ (Brush & Dana, 1879)
- Johnsomervilleite, $Na_2Ca(Fe^{2+},Mg,Mn)_7(PO_4)_6$ (Livingstone, 1980)
- Chladniite, $Na_2CaMg_7(PO_4)_6$ (McCoy *et al*., 1994)
- Galileiite, $Na_2Fe_8(PO_4)_6$ (Olsen & Steele, 1997)
- Stornesite-(Y), $Y\square_2Na_6(Ca_5Na_3)Mg_{43}(PO_4)_{36}$ (Grew *et al*., 2006)

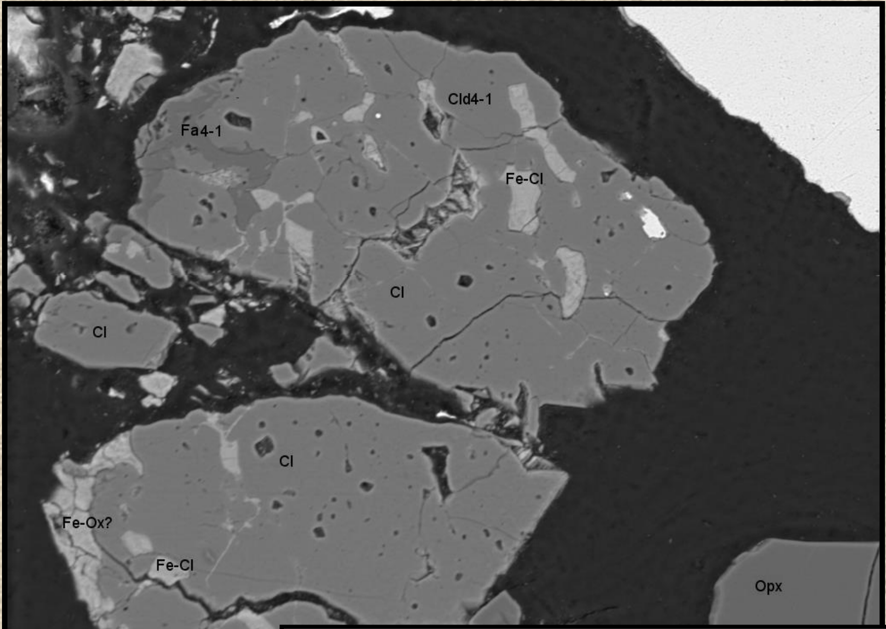
Occurrence

-Granitic pegmatites
-High grade metamorphic rocks
-Meteorites



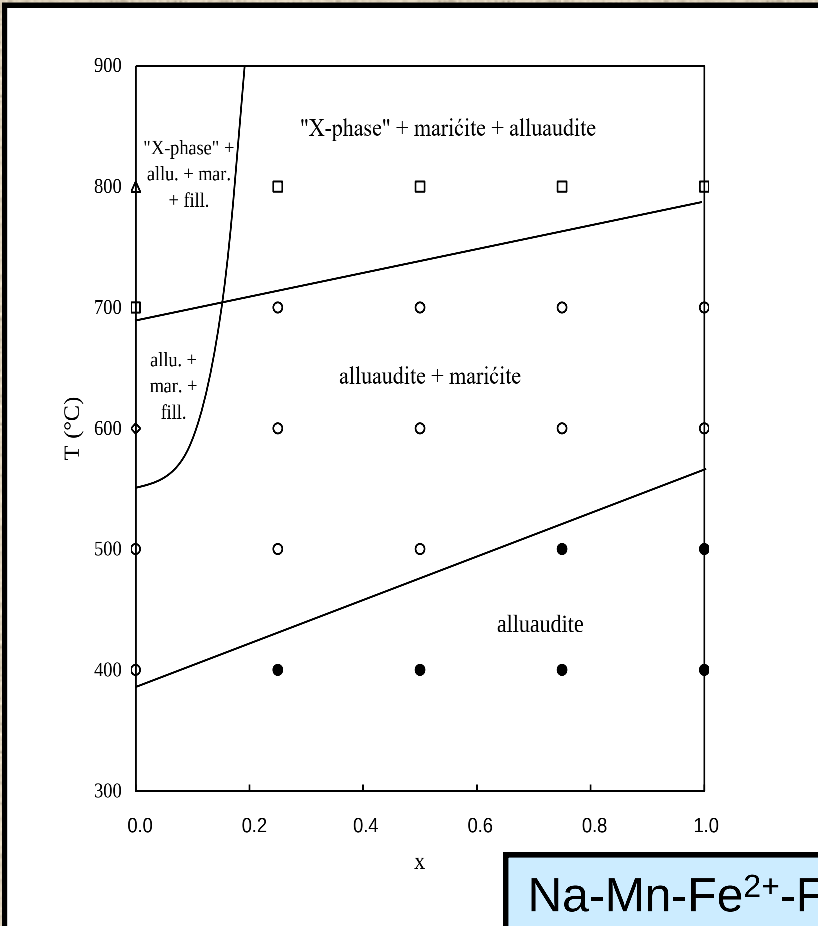
Fillowite + alluaudite, Kabira pegmatite, Uganda

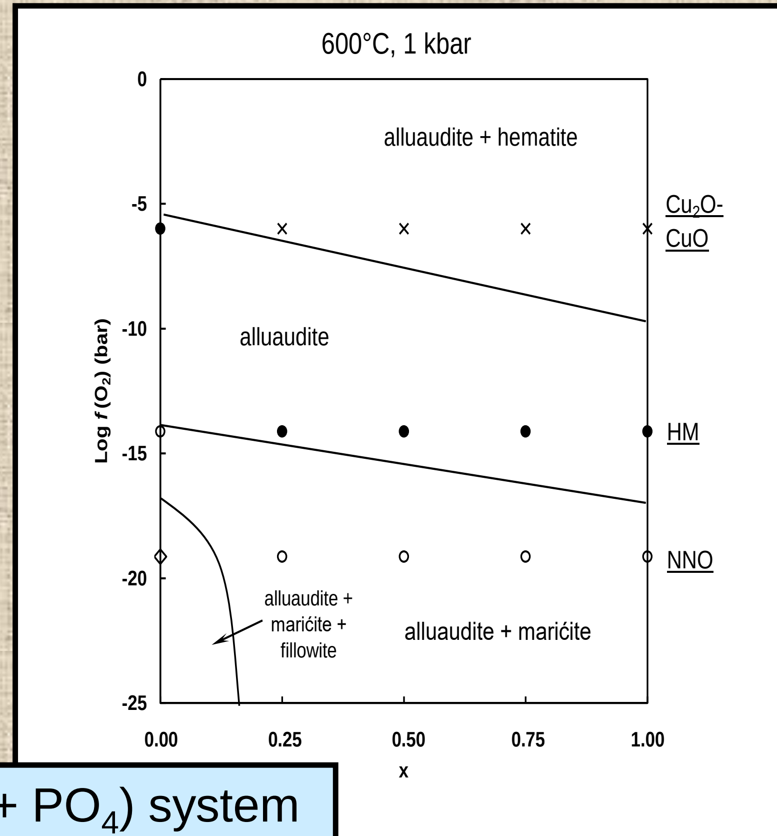
Johnsomervilleite, Loch Quoich, Scotland



Chladniite, GRA 95209 meteorite

Stability of fillowite-type phosphates

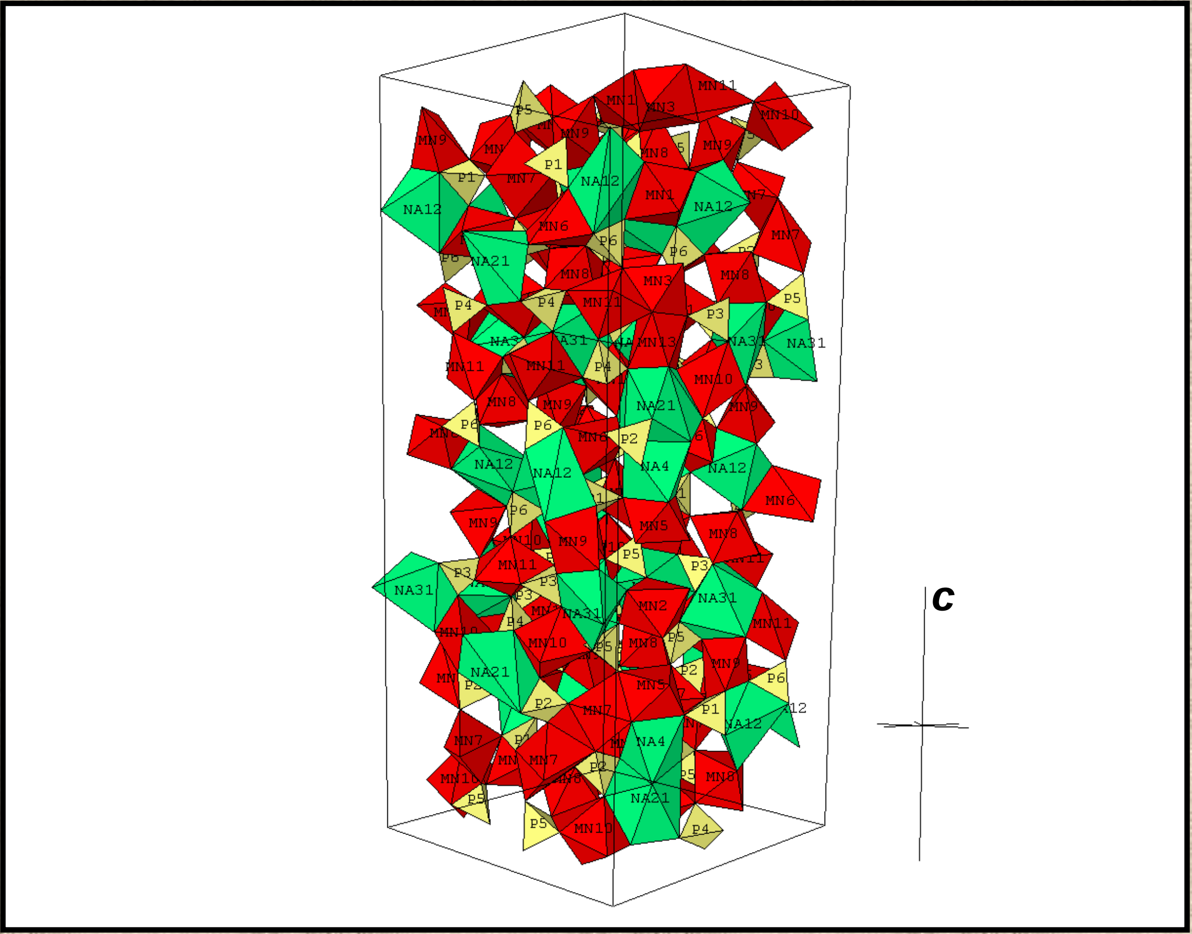




Na-Mn-Fe^{2+}-Fe^{3+} (+ PO_4) system
1 kbar

Petrologically significant accessory minerals!

The fillowite structure



Trigonal, *R*-3

***a* ~ 14.9-15.3 Å**
***b* ~ 41.7-43.5 Å**

Hexagonal rod packing based on the glaserite arrangement

- **M1-M11: Fe,Mn,Mg [5], [6]**
- **Na1-Na3: Na [6], [7]**
- **Ca: Ca [8]**

The fillowite structure

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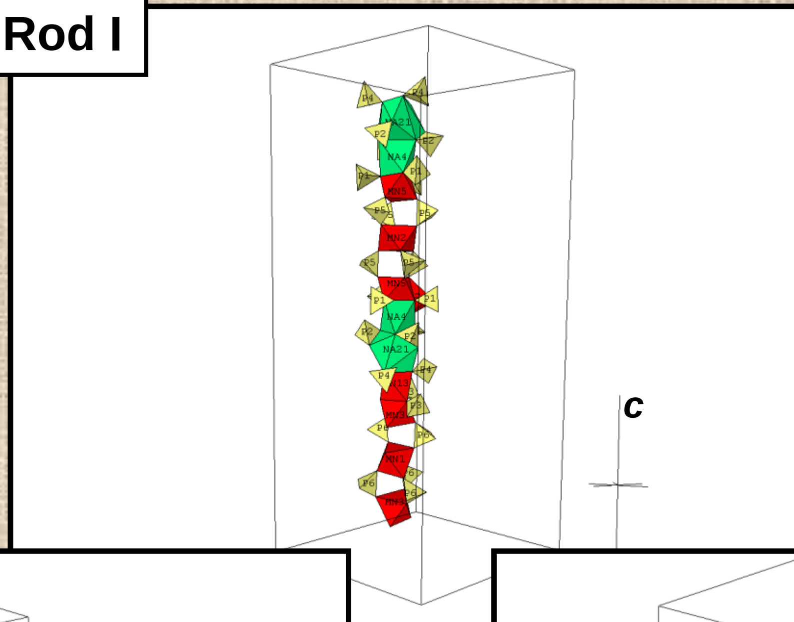
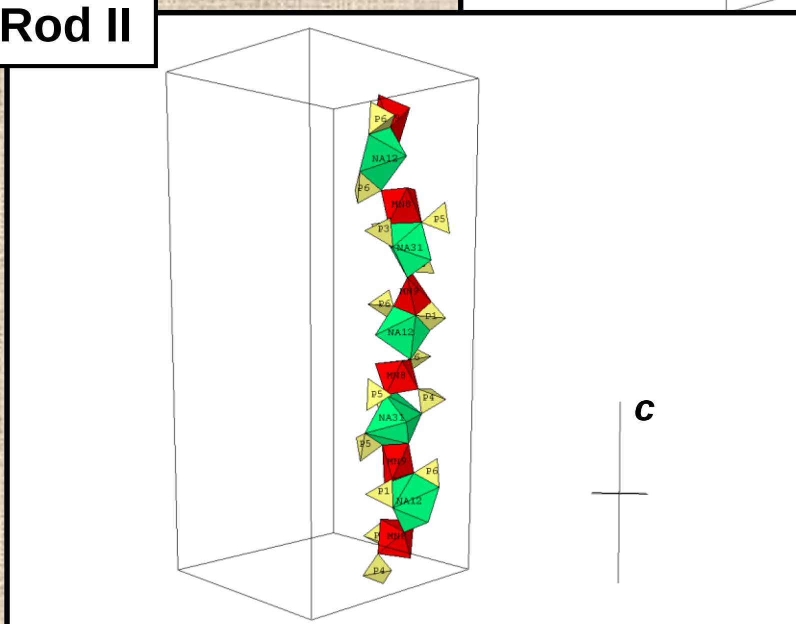
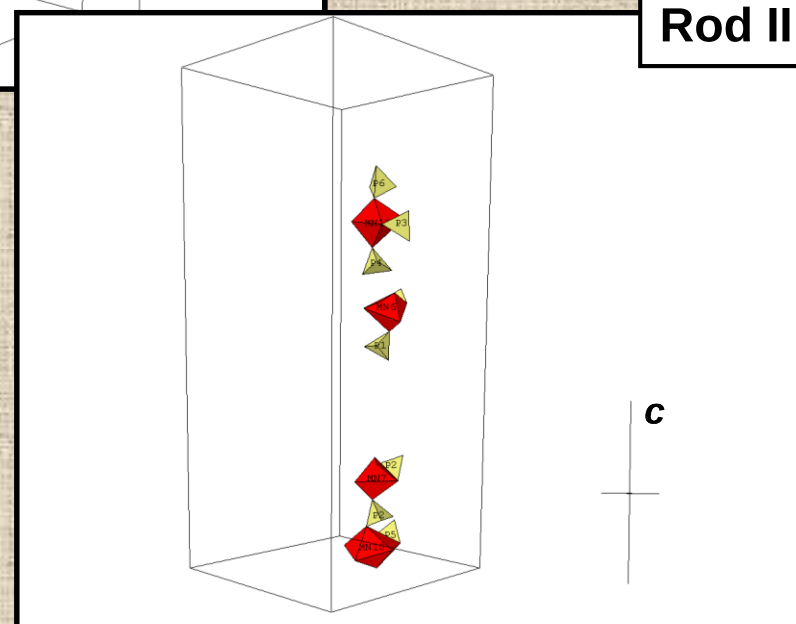
Rod I



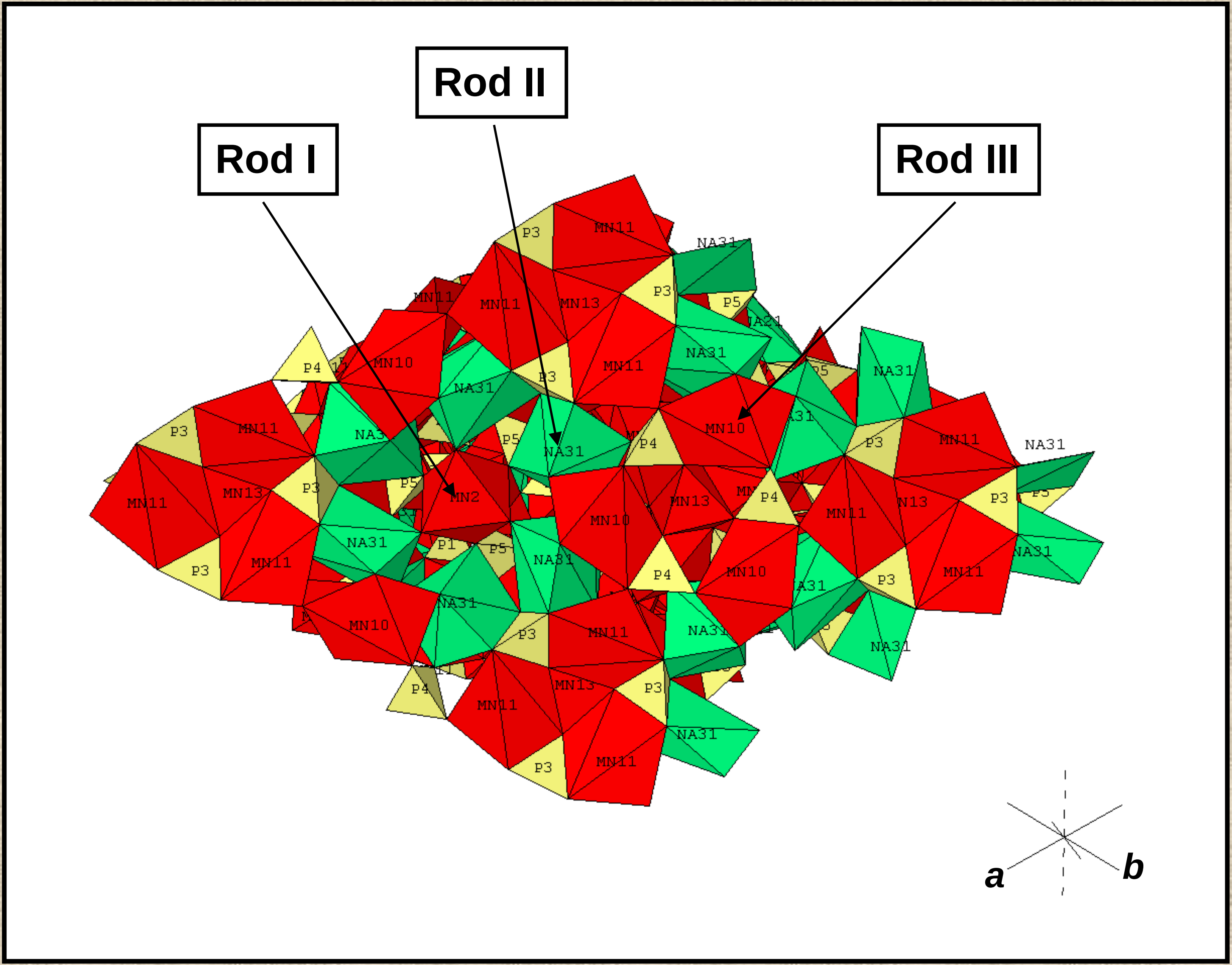
Rod II



Rod III



The fillowite structure



Literature data

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Fillowite, Branchville, Connecticut (Araki & Moore, 1981)

- $[Na_{11.96}Ca_{4.70}][Mn_{35.88}Fe^{2+}_{8.38}](PO_4)_{36}$
- *a* = 15.282(2) Å
- *b* = 43.507(3) Å
- R_1 = 6.9 %

Synthetic phosphate (Domanskii *et al*., 1982)

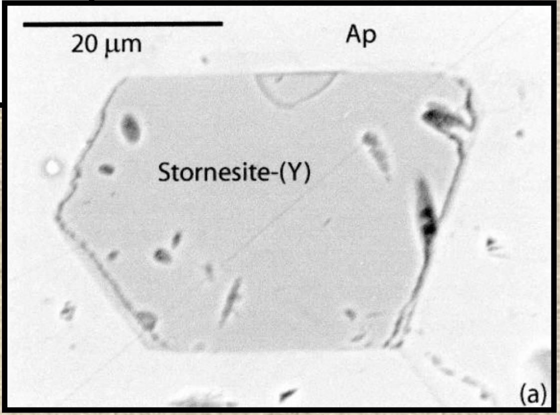
- $[Na_8Ca_8][Mg_{42}](PO_4)_{36}$
- *a* = 14.974(4) Å
- *b* = 42.74(1) Å
- R_1 = 3.8 %

Fillowite, Quinghe County, China (Zhesheng *et al*., 2005)

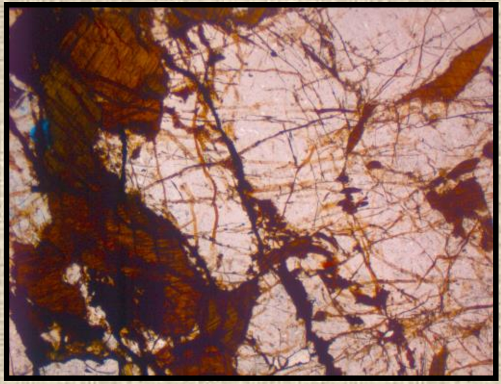
- $[Na_{10.86}Ca_{6.36}][Mn_{24.24}Mg_{10.92}Fe^{2+}_{5.34}Zn_{0.96}](PO_4)_{36}$
- *a* = 15.143(3) Å
- *b* = 43.191(2) Å
- R_1 = 7.76 %

Stornesite-(Y) (Grew *et al*., 2006)

- $[Y_{0.68}Yb_{0.06}Na_{8.69}Ca_{5.40}][Mg_{30.71}Fe^{2+}_{11.57}Mn_{0.18}](PO_4)_{36}$
- *a* = 14.963(3) Å
- *b* = 42.76(1) Å
- R_1 = 8.57 %



New data: Natural samples

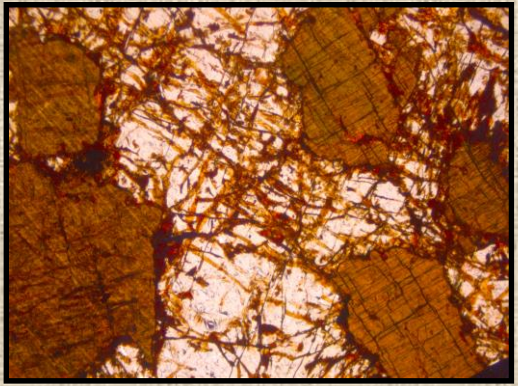


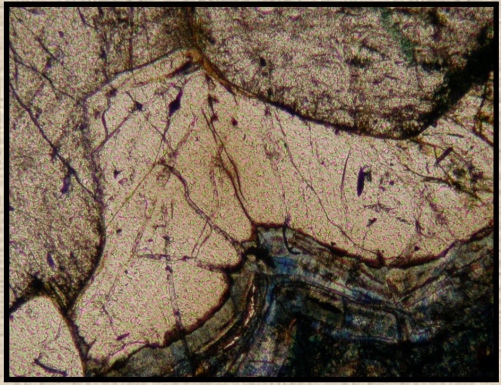
Fillowite, Kabira, Uganda

- $[K_{0.26}Na_{11.42}Ca_{5.38}][Mn_{23.42}Fe^{2+}_{16.94}Fe^{3+}_{1.56}](PO_4)_{36}$
- *a* = 15.125(1) Å
- *b* = 43.195(3) Å
- R_1 = 3.52 %

Fillowite, Buranga, Rwanda

- $[Na_{10.78}Ca_{4.94}][Mn_{24.46}Fe^{2+}_{14.92}Fe^{3+}_{2.16}Mg_{0.34}](PO_4)_{36}$
- *a* = 15.122(1) Å
- *b* = 43.258(4) Å
- R_1 = 3.79 %

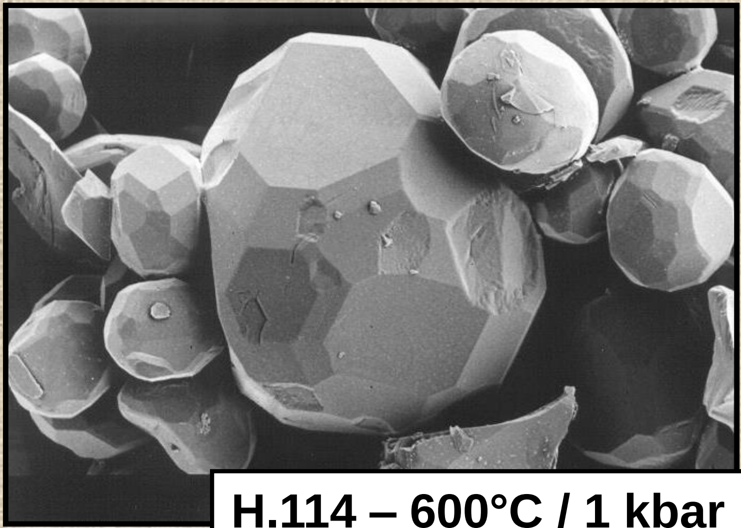


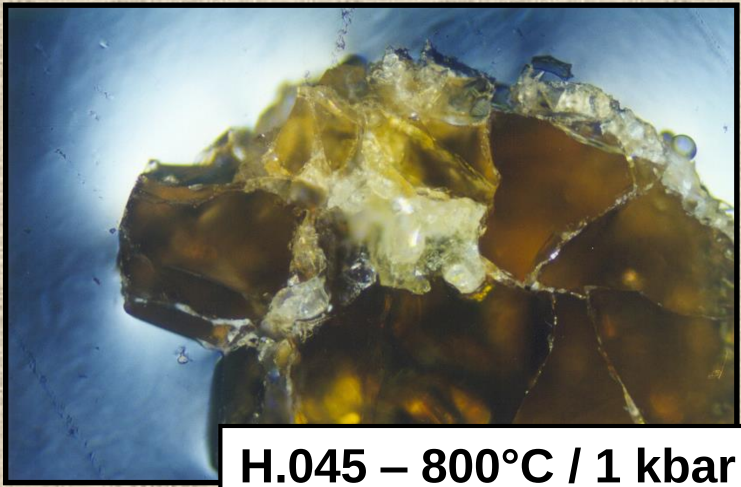


Johnsomervilleite, Loch Quoich, Scotland

- $[Na_{8.48}Ca_{6.42}][Fe^{2+}_{20.96}Mg_{17.84}Mn_{4.00}](PO_4)_{36}$
- *a* = 15.036(2) Å
- *b* = 42.972(9) Å
- R_1 = 4.14 %

New data: Synthetic samples


H.114 – 600°C / 1 kbar


H.045 – 800°C / 1 kbar

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

- Hydrothermal synthesis
- Tuttle-type cold-seal bombs
- T = 600-800 °C
- P = 1 – 3.5 kbar
- Oxygen fugacity: Ni/NiO (NNO)

New data: Synthetic samples

Sample H.053 (800°C / 1 kbar; Keller *et al*., 2006)

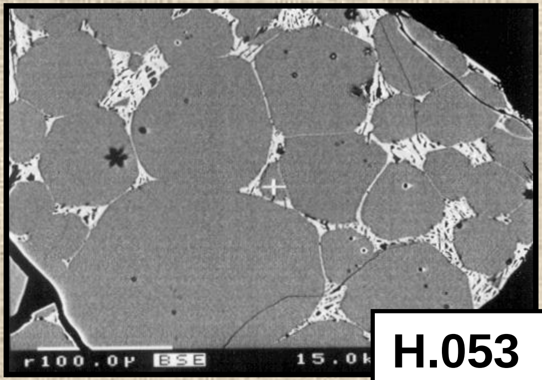
- $Na_2(Na,Mn)_{14}Mn_{44}(PO_4)_{36}.H_2O$
- a = 15.274(1) Å
- b = 43.334(3) Å
- R_1 = 5.46 %

Sample H.042 (600°C / 3.5 kbar)

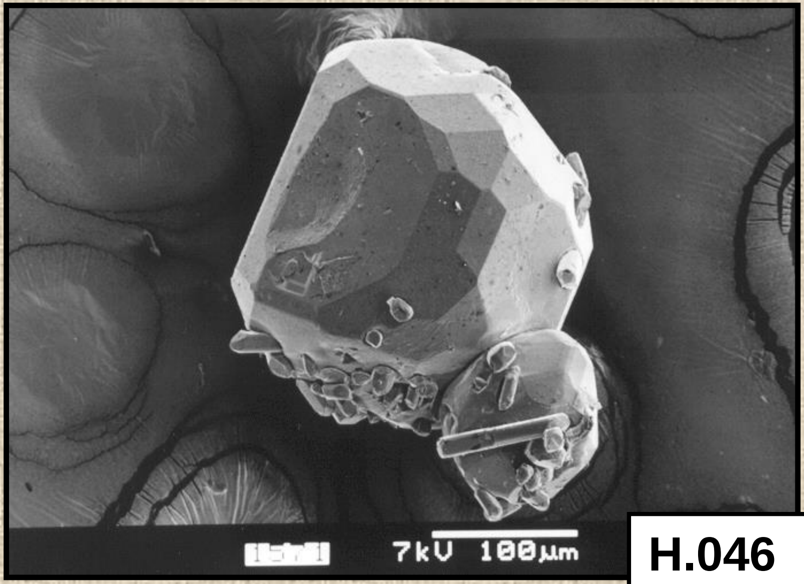
- $Na_{14.36}Mn_{44.51}(PO_4)_{36}$
- a = 15.305(1) Å
- b = 43.672(3) Å
- R_1 = 3.84 %

Sample H.046 (700°C / 3.5 kbar)

- $Na_{15.66}Mn_{37.21}Fe^{3+}_{4.80}Fe^{2+}_{1.86}(PO_4)_{36}$
- a = 15.216(1) Å
- b = 43.291(3) Å
- R_1 = 5.12 %



H.053



H.046

Site occupancies: Natural samples

	Fillowite Branchville	Stornesite-(Y) Prydz Bay	Fillowite Buranga	Fillowite Kabira	Johnsomervilleite Loch Quoich
M1	0.62 Mn + 0.38 Ca	0.26 Ca + 0.68 Y + 0.06 Yb	0.93 Mn	0.54 Mn + 0.46 Ca	0.89 Mg + 0.11 Fe
M2	Mn	0.51 Fe + 0.49 Mg	0.67 Ca + 0.33 Mn	0.94 Mn	0.66 Fe + 0.34 Mg
M3	Fe	0.98 Mg + 0.02 Fe	0.86 Fe	0.98 Fe	0.88 Mg + 0.12 Fe
M4	Fe	0.97 Mg + 0.03 Fe	0.98 Na	0.87 Fe	0.38 Na
M5	Mn	Mg	0.75 Fe + 0.29 Mn	0.93 Fe	0.88 Mg + 0.12 Fe
M6	Mn	0.55 Mg + 0.45 Fe	Mn	0.56 Fe + 0.42 Mn	0.56 Fe + 0.44 Mg
M7	Mn	0.89 Mg + 0.11 Fe	0.69 Fe + 0.29 Mn	0.69 Fe + 0.30 Mn	0.65 Fe + 0.35 Mg
M8	0.67Fe + 0.33 Mn	0.67 Mg + 0.33 Fe	0.63 Mn + 0.36 Fe	0.62 Fe + 0.36 Mn	0.56 Mg + 0.44 Fe
M9	Mn	0.72 Mg + 0.28 Fe	0.49 Mn + 0.49 Fe	Mn	0.68 Fe + 0.32 Mg
M10	Mn	0.62 Mg + 0.37 Fe	0.52 Fe + 0.48 Mn	Mn	0.58 Fe + 0.42 Mg
M11	Mn	0.79 Mg + 0.21 Fe	0.67 Mn + 0.33 Fe	0.61 Mn + 0.39 Fe	0.73 Fe + 0.27 Mg
Na1	0.91 Na + 0.09 Ca	0.06 Na	0.93 Fe	Na	0.62 Na + 0.38 Ca
Na2	0.90 Ca + 0.10 Ca	0.75 Ca + 0.25 Na	Na	0.88 Na	0.72 Na + 0.28 Ca
Na3	Na	Na	0.67 Ca + 0.33 Na	Na	0.79 Ca
Ca	0.65 Ca + 0.35 Na	0.58 Ca + 0.42 Na	Na	0.67 Ca + 0.33 Na	0.97 Na

M3 and M5-M11 are occupied by Fe, Mn, Mg
Na2, Na3, and Ca are occupied by (Na,Ca)
M1 can be occupied by (Y,Yb,Ca)
M2 can be occupied by Ca
M4 can be occupied by Na
Na1 can be occupied by Fe

Site occupancies: Synthetic samples

	H.053	H.042	H.046
M1	Mn	Mn	Mn
M2	Mn	0.67 Mn + 0.33 Na	0.91 Mn
M3	Mn	0.89 Mn	0.56 Fe + 0.43 Mn
M4	Mn	0.98 Na	0.95 Na
M5	Mn	Mn	0.88 Fe + 0.10 Mn
M6	Mn	Mn	Mn
M7	Mn	Mn	Mn
M8	Mn	Mn	Mn
M9	Mn	Mn	Mn
M10	Mn	Mn	Mn
M11	Mn	Mn	0.89 Fe + 0.09 Mn
Na1	0.84 Na + 0.16 Mn	0.98 Mn	0.67 Fe + 0.33 Mn
Na2	Na	Na	0.95 Na + 0.05 Mn
Na3	0.93 Na + 0.07 Mn	0.65 Na + 0.35 Mn	0.90 Na + 0.10 Mn
Ca	0.58 Na + 0.42 Mn	0.98 Na	0.98 Na

M4 can be occupied by Na
Na1 can be occupied by (Fe,Mn)

Conclusions

- New structural data on natural and synthetic fillowite-type phosphates show that the cationic distributions are extremely complex.
- The M3 and M5-M11 sites have a similar crystal-chemical role (Fe,Mn,Mg), as well as the Na2, Na3, and Ca sites (Ca,Na).
- However, the M1, M2, M4, and Na1 sites have a mixed crystal-chemical role.
- A nomenclature scheme should take into account general compositional criteria and not detailed cationic distributions, in order to avoid the proliferation of new mineral species in the fillowite group.

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