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The wyllieite group of minerals: crystal chemistry, nomenclature and stability

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The wyllieite group of pegmatitic phosphates

Mn-rich	Fe^{2+}-rich
Wyllieite[1]	**Ferrowyllieite**[2]
$Na_2MnFe^{2+}Al(PO_4)_3$	$Na_2Fe^{2+}{}_2Al(PO_4)_3$
↓ $Na^+ + Fe^{2+} \rightarrow \square + Fe^{3+}$	↓
Rosemaryite[1]	**Ferrorosemaryite**[3]
$\square NaMnFe^{3+}Al(PO_4)_3$	$\square NaFe^{2+}Fe^{3+}Al(PO_4)_3$

Qingheiite[4]

$Na_2MnMgAl(PO_4)_3$

1. Moore & Ito, 1979; 2. Moore & Molin-Case, 1974; 3. Hatert *et al*., 2005; 4. Zhesheng *et al*., 1983

The wyllieite structure

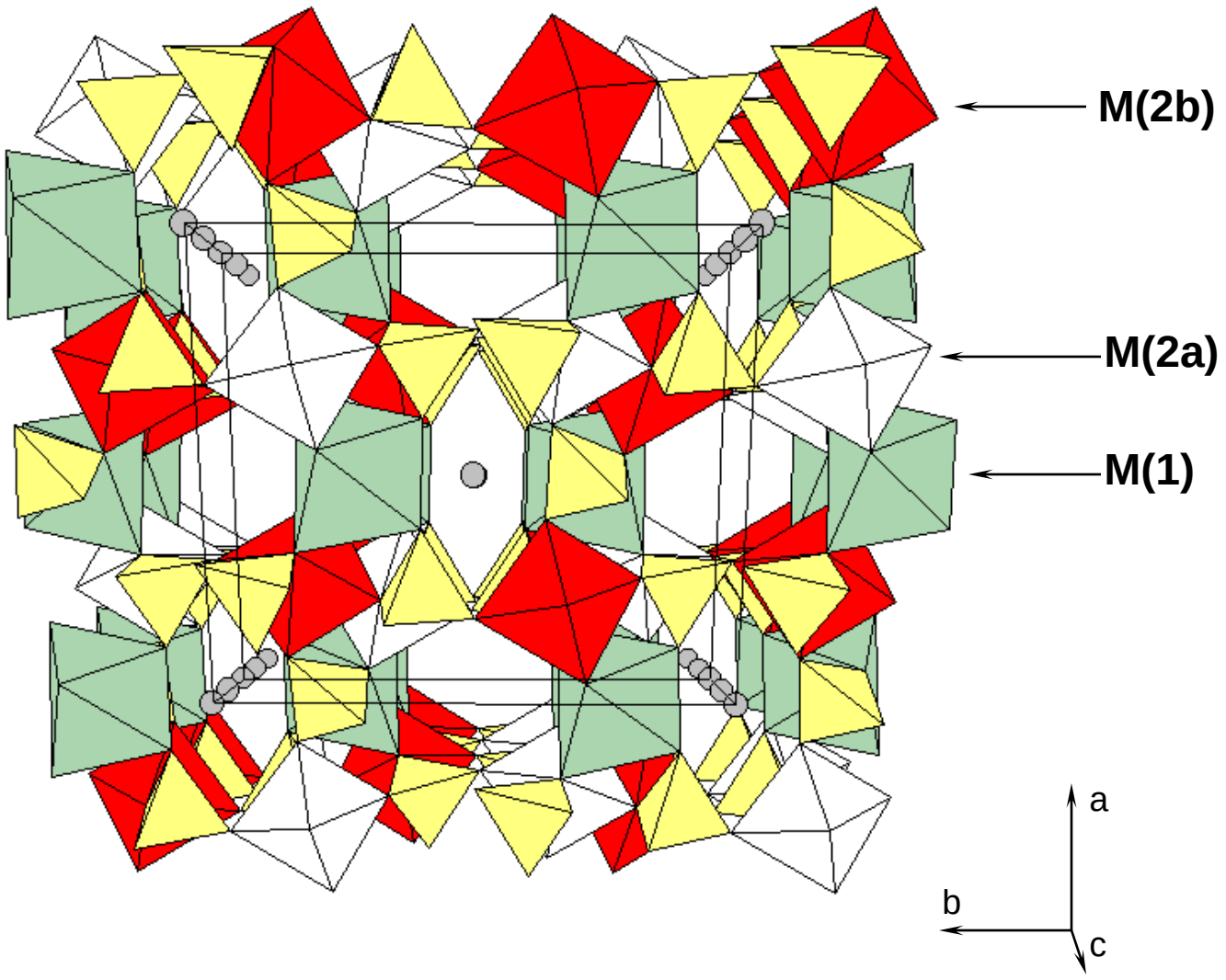
Topologically identical to the alluaudite structure, but due to ordering of cations, the space group *C*2/*c* of alluaudite becomes $P2_1/n$ in wyllieite

Moore & Molin-Case (1974)

$$X(1a)_2X(1b)_2X(2)_4M(1)_4M(2a)_4M(2b)_4(PO_4)_{12}$$

Alluaudite ⇒ Wyllieite

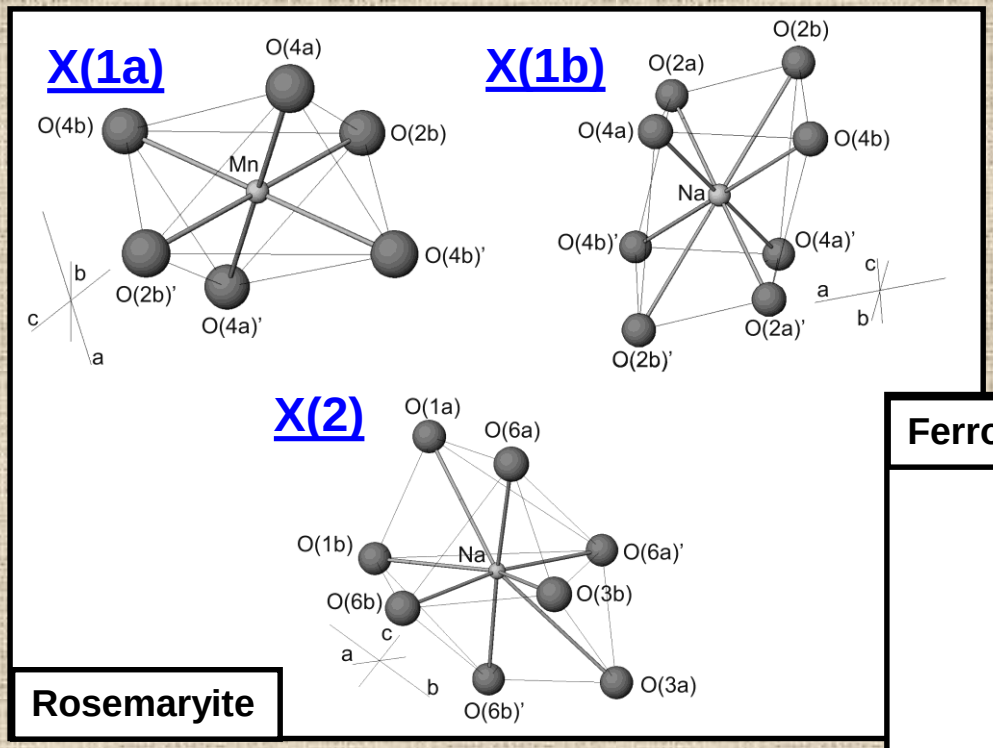
M(1) ⇒ M(1)
M(2) ⇒ M(2a), M(2b)
X(1) ⇒ X(1a), X(1b)
X(2) ⇒ X(2)

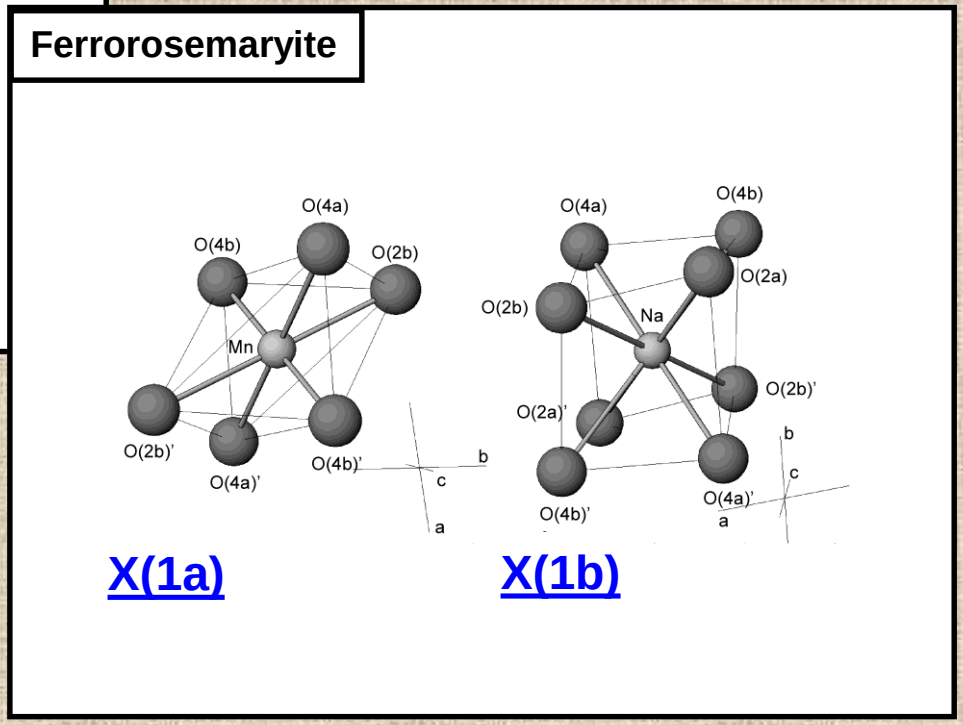

M(2b)
M(2a)
M(1)
a
b
c

New single-crystal structure refinements

	FERROROSEMARYITE (Hatert *et al.* 2005)	ROSEMARYITE (Hatert *et al.* 2006)
S.G.:	$P2_1/n$	$P2_1/n$
a:	11.838(1) Å	12.001(2) Å
b:	12.347(1) Å	12.396(1) Å
c:	6.2973(6) Å	6.329(1) Å
β:	114.353(6)°	114.48(1)°
R_1 (all):	0.0300	0.0532
S:	1.082	1.081

Morphology of the X sites

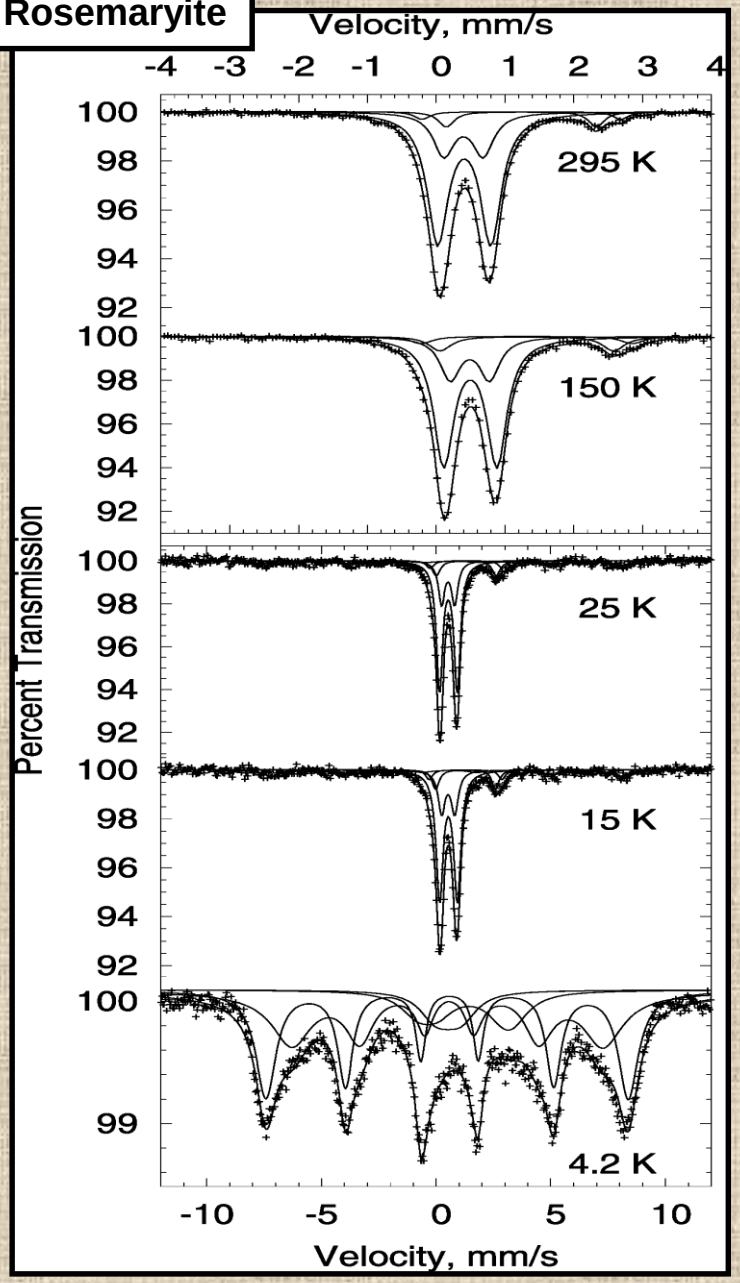




X(1a): Distorted octahedron [6]
X(1b): Distorted cube [4+4]
X(2): Distorted gable disphenoid [7+1]

Mössbauer spectroscopy

Rosemaryite



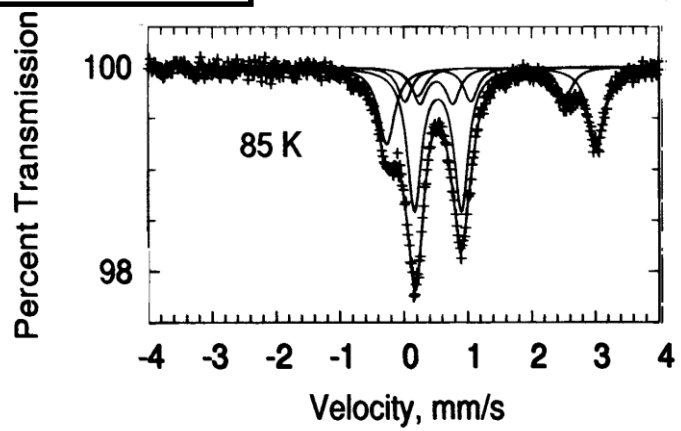
- Rosemaryite

Fe^{2+} ⇒ 0.050 *a.p.f.u.* on M(1) and 0.098 on M(2a)
Fe^{3+} ⇒ 0.259 *a.p.f.u.* on M(2a) and 0.775 on M(2b)

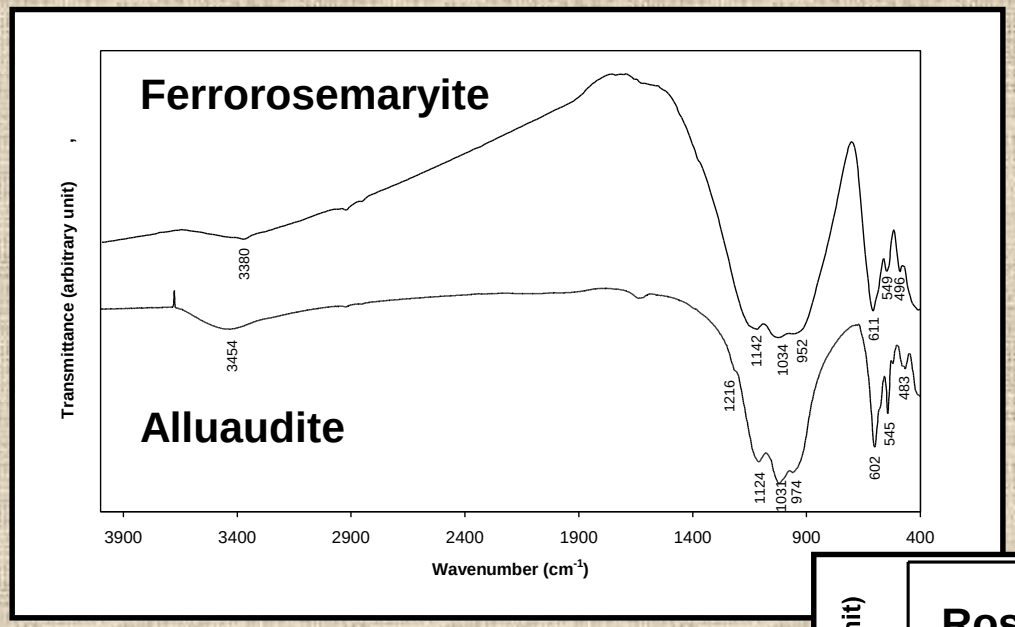
- Ferrorosemaryite

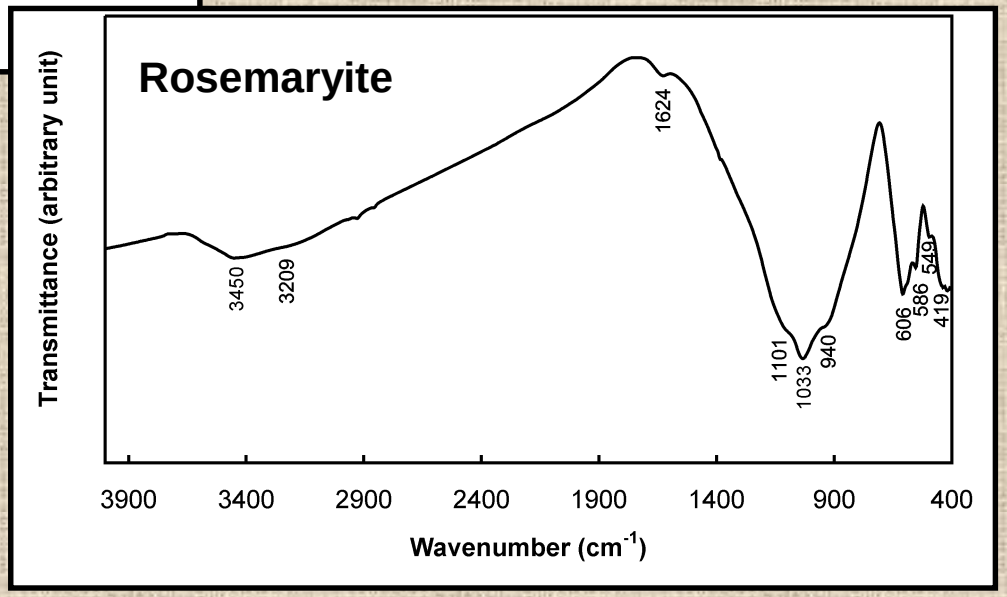
Fe^{2+} ⇒ 0.519 *a.p.f.u.* on M(1) and 0.192 on M(2a)
Fe^{3+} ⇒ 0.211 *a.p.f.u.* on M(2a), 0.807 on M(2b) and 0.192 on M(1)

Ferrorosemaryite



Infrared spectroscopy





- Similarity between the wyllieite and alluaudite structures
- Presence of H_2O in the channels

Cationic distribution

	Ferrowyllieite	Ferrorosemaryite	Rosemaryite	Qingheiite
References	1	2	3	4
Ideal formula	$Na_2Fe^{2+}{}_2Al(PO_4)_3$	$\square NaFe^{2+}Fe^{3+}Al(PO_4)_3$	$\square NaMn^{2+}Fe^{3+}Al(PO_4)_3$	$Na_2MnMgAl(PO_4)_3$
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
***a* (Å)**	11.868(15)	11.838(1)	12.001(2)	11.856(3)
***b* (Å)**	12.382(12)	12.347(1)	12.396(1)	12.411(3)
***c* (Å)**	6.354(9)	6.2973(6)	6.329(1)	6.421(1)
***β* (°)**	114.52(8)	114.353(6)	114.48(1)	114.45(2)
M(2a)	**$1.00Fe^{2+}$**	**$0.72Al^{3+}$** + $0.14Fe^{2+}$ + $0.14Fe^{3+}$	**$0.69Al^{3+}$** +$0.24Fe^{3+}$ + $0.08Fe^{2+}$	**$0.42Al^{3+}$** + $0.26Fe^{2+}$ + $0.18Mg^{2+}$ + $0.13Fe^{3+}$ + $0.01Zn^{2+}$
M(2b)	**$0.75Al^{3+}$** + $0.25Fe^{2+}$	**$0.88Fe^{3+}$** + $0.10Al^{3+}$ + 0.02Mg	**$0.80Fe^{3+}$** + $0.10Al^{3+}$ + $0.10Mn^{2+}$	**$0.95Mg^{2+}$** + $0.05Mn^{2+}$
M(1)	$0.75Fe^{2+}$ + $0.25Mg^{2+}$	$0.57Fe^{2+}$ + $0.20Fe^{3+}$ + $0.18Na^{+}$ + $0.05Mn^{2+}$	$0.75Mn^{2+}$ + $0.10Ca^{2+}$ + $0.08Mg^{2+}$ + $0.07Fe^{2+}$	$1.00Mn^{2+}$
X(1a)	$0.46Na^{+}$ + 0.04□	$0.43Mn^{2+}$ + $0.07Na^{+}$	$0.45Mn^{2+}$ + $0.05Na^{+}$	$0.50Mn^{2+}$
X(1b)	$0.25Ca^{2+}$ + $0.25Mn^{2+}$	$0.17Na^{+}$ + $0.04Mn^{2+}$ + $0.04Ca^{2+}$ + 0.25□	$0.10Na^{+}$ + $0.07Mn^{2+}$ + 0.33□	$0.50Na^{+}$
X(2)	$0.70Na^{+}$ + 0.30□	1.0□	$0.44Na^{+}$ + 0.56□	$0.81Na^{+}$ + $0.08Ca^{2+}$ + 0.11□

1. Moore & Molin-Case (1974); 2. Hatert *et al.* (2005); 3. Hatert *et al.* (2006); 4. Zhesheng *et al.* (1983).

Variation in the distribution of Al and Fe on the M(2a) and M(2b) sites

Nomenclature problem

Moore & Ito (1979)

Generic name	M(2a)	M(1)	Specific name
Wyllieites	Fe^{2+}	Fe^{2+}	Ferrowyllieite
	Fe^{2+}	Mn^{2+}	Wyllieite
Unnamed	Mn^{2+}	Mn^{2+}	Unnamed
Rosemaryites	Fe^{3+}	Fe^{2+}	Unnamed (ferrorosemaryite)
	Fe^{3+}	Mn^{2+}	Rosemaryite

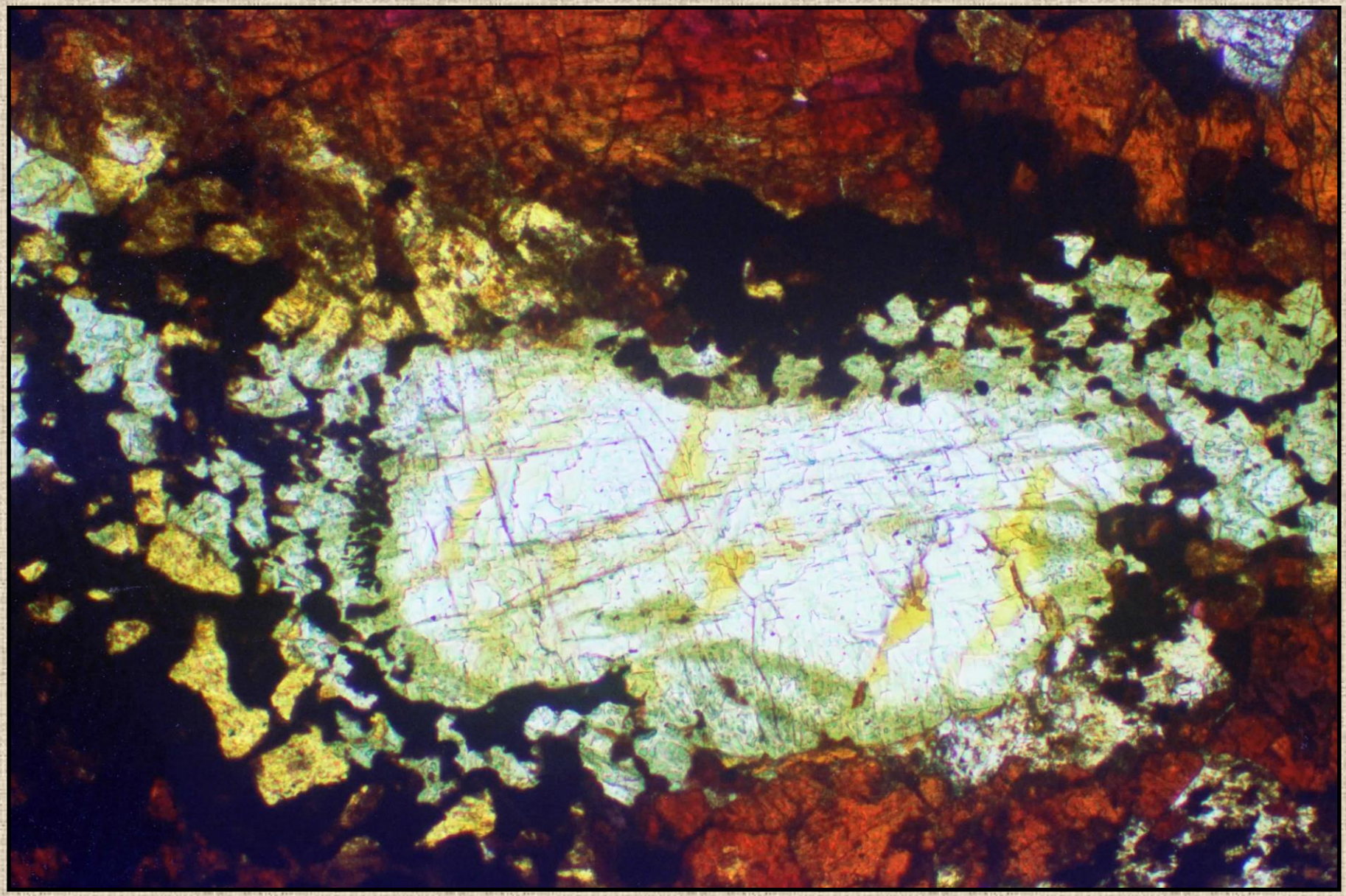
The structure refinements of rosemaryite and ferrorosemaryite show that Al, and not Fe^{3+}, predominantly occurs on the M(2a) site

New nomenclature necessary for the wyllieite group

Suggested nomenclature

Generic name	M(2a)	M(2b)	M(1)	Specific name
Wyllieites	Fe^{2+}	Al	Fe^{2+}	Ferrowyllieite
	Fe^{2+}	Al	Mn^{2+}	Wyllieite (?)
Rosemaryites	Al	Fe^{3+}	Fe^{2+}	Ferrorosemaryite
	Al	Fe^{3+}	Mn^{2+}	Rosemaryite
Qingheiites	Al	Mg	Fe^{2+}	« Ferroqingheiite »
	Al	Mg	Mn^{2+}	Qingheiite

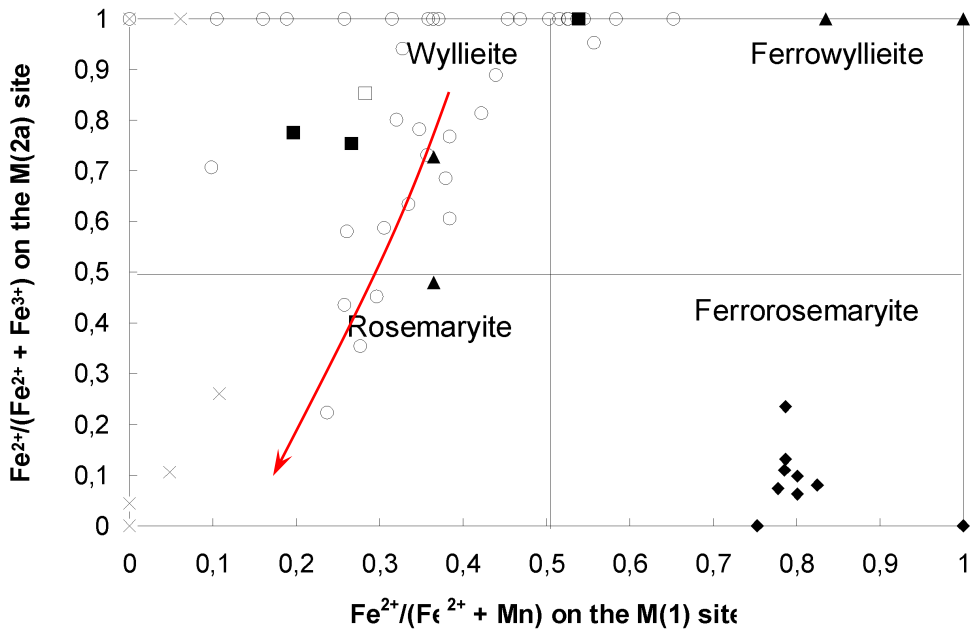
If some samples show Al predominant on the M(2a) site, and Fe^{2+} on M(2b), a new generic name should be created, if the « predominant cation » rule is strictly applied. Is it really necessary??



Wyllieite, rosemaryite and staněkite, Albères, France

Chemical composition

$Na^{+} + Fe^{2+} \rightarrow \square + Fe^{3+}$



Wyllieites are primary, and rosemaryites are secondary

♦: Hatert *et al*. (2005)
■: Ek & Nysten (1990)
×: Fransolet (1995)
▲: Moore & Ito (1979)
O: Roda *et al*. (1996)

Stability of wyllieite-type phosphates

Moore & Molin-Case (1974)

- **Ferrowyllieite is a primary phosphate**
  - ⇒ In accordance with petrographic observations
  - ⇒ Yakubovich *et al.* (2005) synthesized a wyllieite-type compound at 400°C/0.1 kbar

- **Al stabilizes the wyllieite structure, whereas alluaudites do not contain significant amounts of this element**
  - ⇒ The synthetic wyllieite-type compound $Na_{1.265}Mn^{2+}_{2.690}Mn^{3+}_{0.785}(PO_4)_3$ (Yakubovich *et al*., 2005) does not contain Al
  - ⇒ The alluaudite-type compound $Na_{1.50}Mn_{2.48}Al_{0.85}(PO_4)_3$ (Hatert, 2006), synthesized at 800°C/1 kbar, contains Al in significant amounts

Further experimental investigations of Al-rich compositions at low temperatures are necessary

Conclusions

- Structural investigations of ferrorosemaryite and rosemaryite show that Al is localized on M(2a), not on M(2b)
- A new nomenclature for the wyllieite group is necessary, which takes into account these new data
- Experimental investigations are necessary to better understand the transition mechanism from the alluaudite to the wyllieite structure