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# Qingheiite-(Fe$^{2+}$), a new member of the wyllieite group

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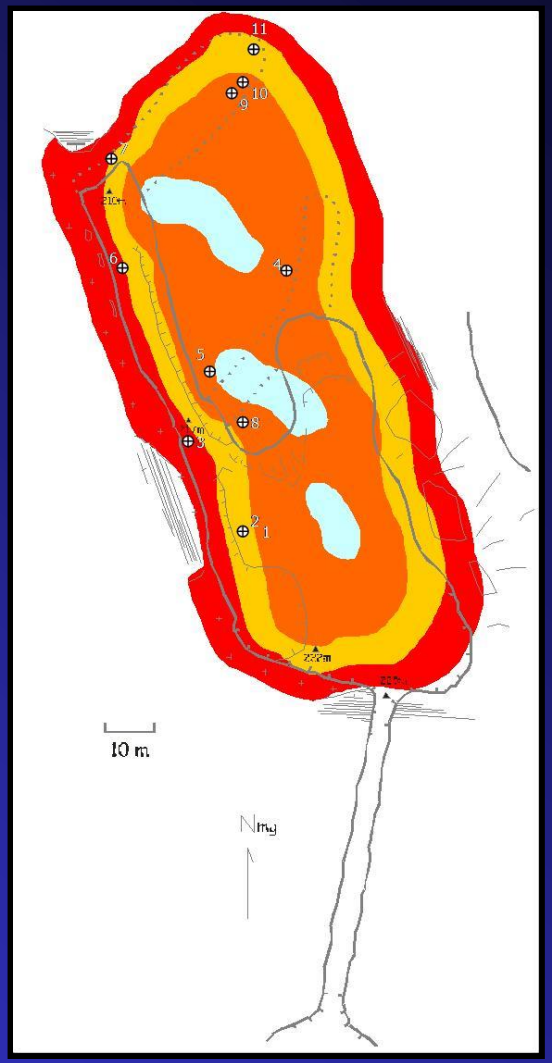
IMA 2010

Budapest, August 27$^{th}$, 2010


M. Baijot, F. Hatert, S. Philippo & J. Cassedanne (September 2008)

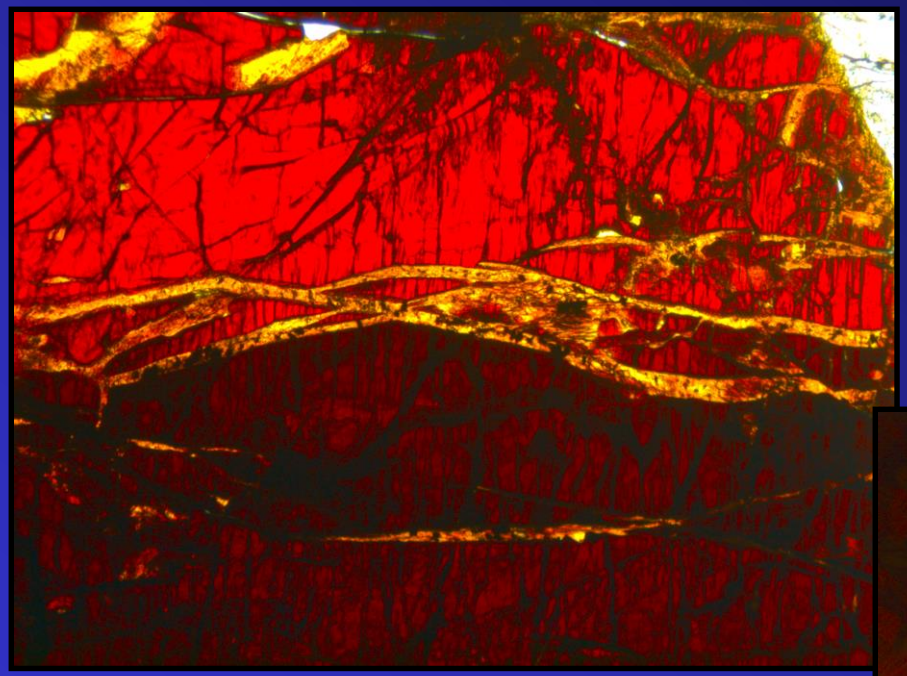
# The Conselheiro Pena disctrict

- **EBPP, Minas Gerais, Brazil**
- **15 new mineral species (Atencio, 2000, 2008)**
- **Sapucaia pegmatite**

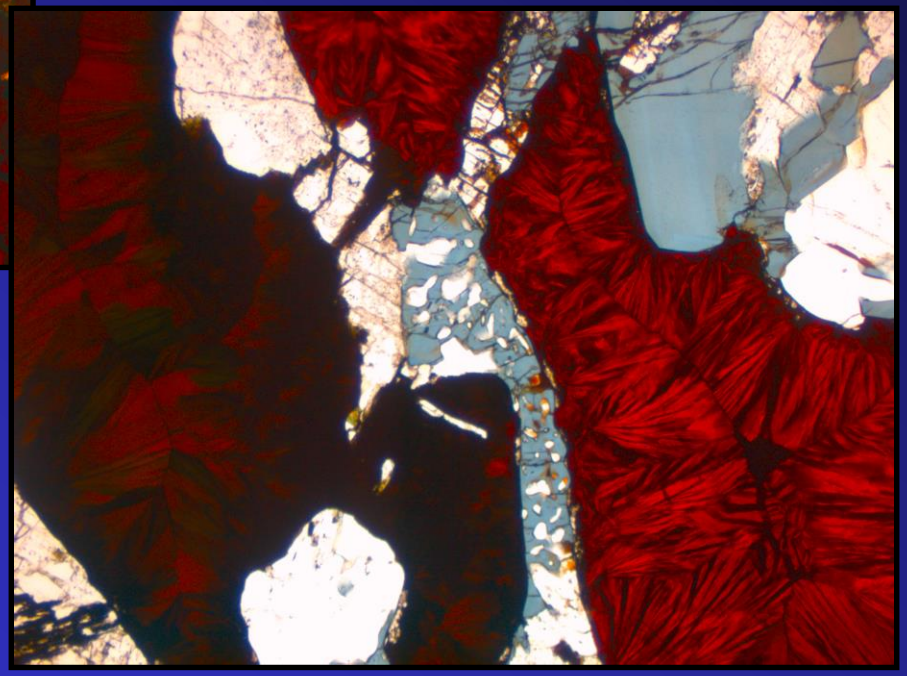


Dendritic phosphates, Sapucaia pegmatite, Minas Gerais, Brazil

# Dendritic phosphates



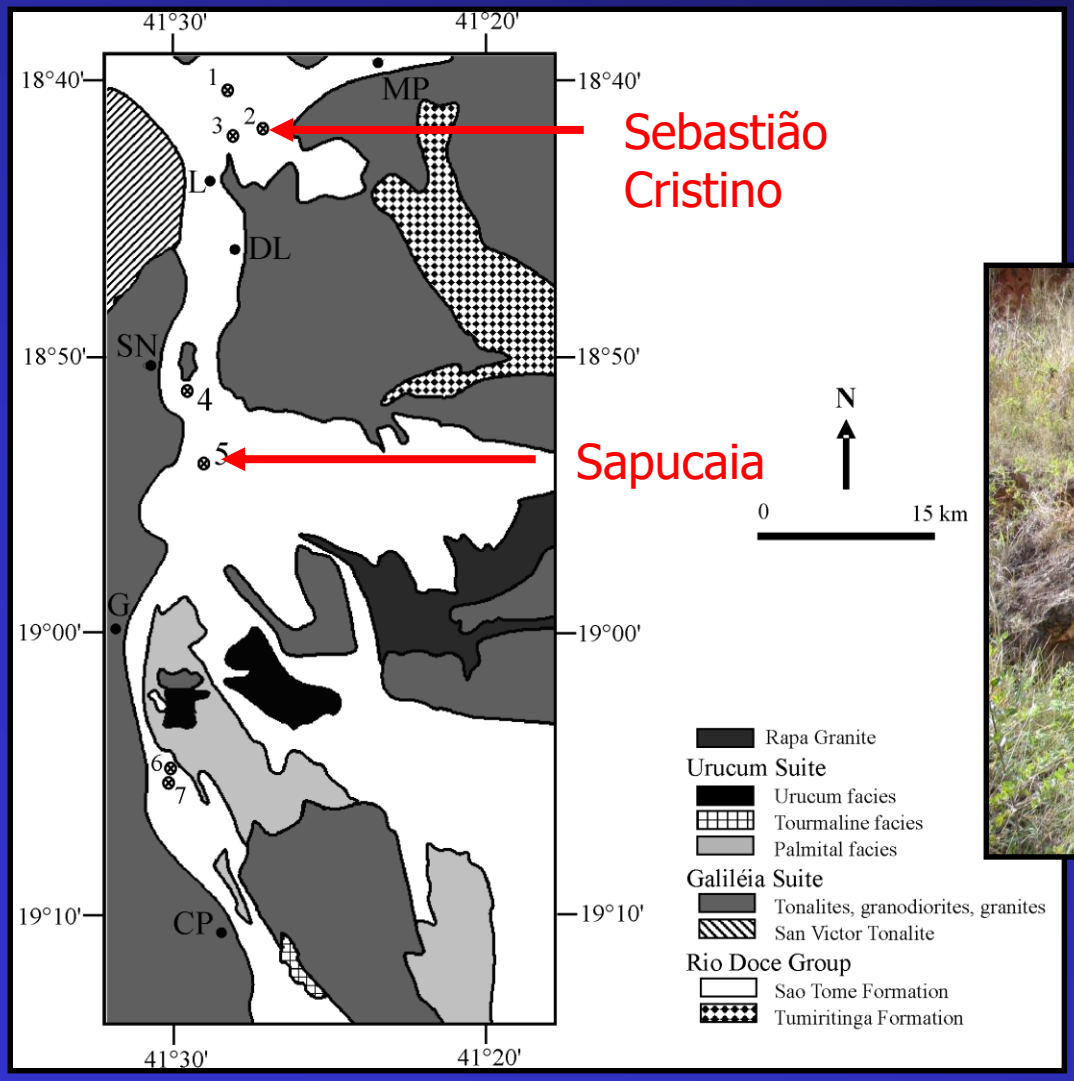
- Frondelite: $Mn^{2+}Fe^{3+}_4(PO_4)_3(OH)_5$
- Schorl
- Quartz and albite



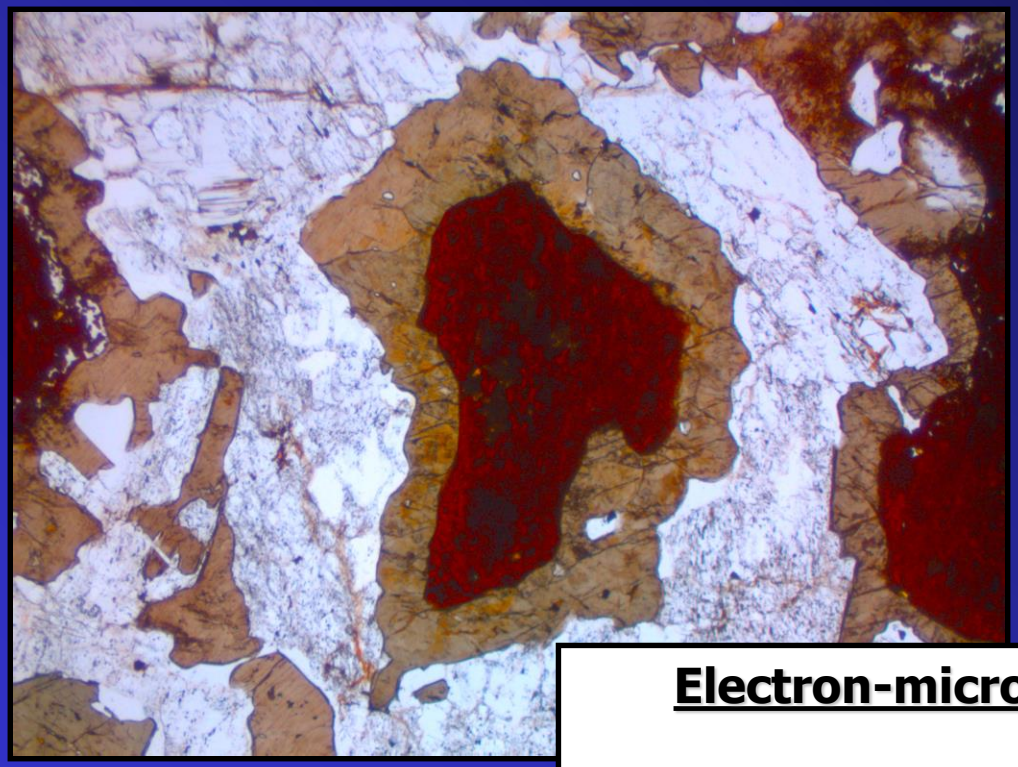
- Ferrisicklerite, $Li_{1-x}(Fe^{3+},Mn^{2+})PO_4$
- Heterosite, $(Fe^{3+},Mn^{3+})PO_4$
- Jahnsite-(CaMnMg): $CaMn^{2+}Mg_2Fe^{3+}_2(PO_4)_4(OH)_2.8H_2O$

Dendritic phosphates, Sapucaia pegmatite, Minas Gerais, Brazil

# The Sebastião Cristino pegmatite




# A new mineral species?



- Green-brown mineral forming rims around frondelite grains
- X-ray powder diffraction pattern similar to those of alluaudites and wyllieites

- $Na_2Fe^{2+}MgAl(PO_4)_3$
- New member of the wyllieite group (IMA 2009-076)

**Electron-microprobe analyses**

- X sites: 0.93 Na + 0.40 Mn + 0.02 Ca + 0.65 □
- M(1): 0.68 $Fe^{2+}$ + 0.32 Mn
- M(2a): 0.72 Mg + 0.23 $Fe^{3+}$ + 0.05 $Fe^{2+}$
- M(2b): 0.62 Al + 0.38 $Fe^{3+}$

# Phosphates of the wyllieite group

| 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] | **Qingheiite-($Fe^{2+}$)**[5] |
| $Na_2MnMgAl(PO_4)_3$ | $Na_2Fe^{2+}MgAl(PO_4)_3$ |

1. Moore & Ito, 1979; 2. Moore & Molin-Case, 1974; 3. Hatert *et al*., 2005;
4. Zhesheng *et al*., 1983; 5. Hatert *et al*., 2010

# Crystal structure

**Qingheiite-($Fe^{2+}$) shows the wyllieite structure, which is topologically identical to the alluaudite structure.**

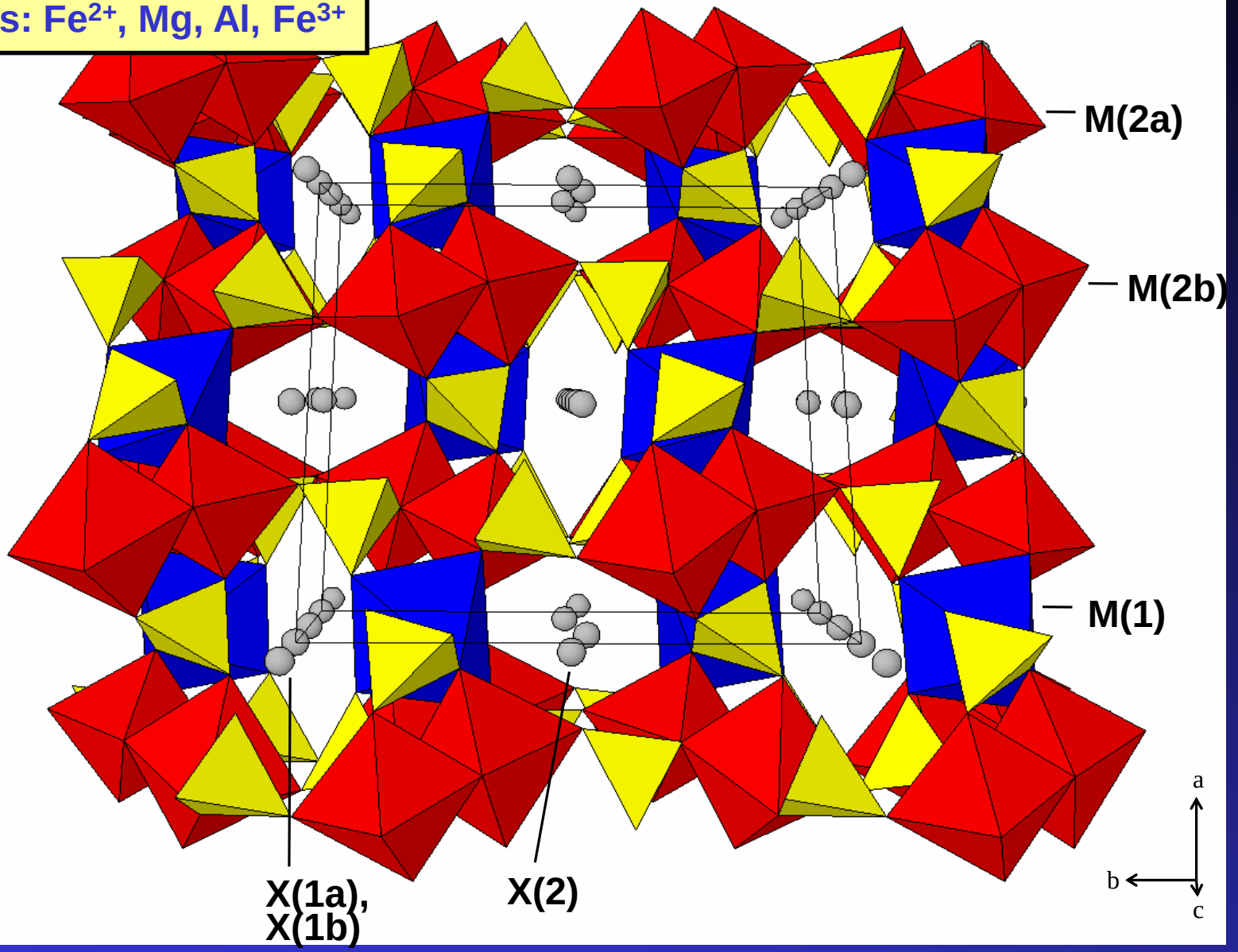
Moore & Molin-Case (1974)

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

Alluaudite $\Rightarrow$ Wyllieite

M(1) $\Rightarrow$ M(1)
M(2) $\Rightarrow$ M(2a), M(2b)
X(1) $\Rightarrow$ X(1a), X(1b)
X(2) $\Rightarrow$ X(2)

X sites: Na, Mn, []
M(1): Mn, $Fe^{2+}$
M(2) sites: $Fe^{2+}$, Mg, Al, $Fe^{3+}$



# Previous single-crystal structure refinements

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| | Ferrowyllieite | Qingheiite | Synthetic compound |
|---|---|---|---|
| **References** | [1] | [2] | [3] |
| **Ideal formula** | $Na_2Fe^{2+}{}_2Al(PO_4)_3$ | $Na_2MnMgAl(PO_4)_3$ | $Na_2Mn^{2+}{}_2Mn^{3+}(PO_4)_3$ |
| **Space group** | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ |
| ***a* (Å)** | 11.868(15) | 11.856(3) | 6.5291(6) |
| ***b* (Å)** | 12.382(12) | 12.411(3) | 12.653(1) |
| ***c* (Å)** | 6.354(9) | 6.421(1) | 10.952(1) |
| ***β* (°)** | 114.52(8) | 114.45(2) | 97.18(1) |
| **M(2a)** | **$1.00Fe^{2+}$** | **$0.42Al^{3+}$** + $0.26Fe^{2+}$ + $0.18Mg^{2+}$ + $0.13Fe^{3+}$ + $0.01Zn^{2+}$ | $1.00Mn^{2+}$ |
| **M(2b)** | **$0.75Al^{3+}$** + $0.25Fe^{2+}$ | **$0.95Mg^{2+}$** + $0.05Mn^{2+}$ | $0.79Mn^{3+}$ + $0.21Mn^{2+}$ |
| **M(1)** | $0.75Fe^{2+}$ + $0.25Mg^{2+}$ | $1.00Mn^{2+}$ | $1.00Mn^{2+}$ |
| **X(1a)** | $0.46Na^{+}$ + 0.04[] | $0.50Mn^{2+}$ | $0.41Na^{+}$ + 0.09[] |
| **X(1b)** | $0.25Ca^{2+}$ + $0.25Mn^{2+}$ | $0.50Na^{+}$ | $0.48Mn^{2+}$ + 0.02[] |
| **X(2)** | $0.70Na^{+}$ + 0.30[] | $0.81Na^{+}$ + $0.08Ca^{2+}$ + 0.11[] | $0.85Na^{+}$ + 0.15[] |

**1. Moore & Molin-Case, 1974; 2. Zhesheng *et al*., 1983; 3. Yakubovich *et al*., 2005**

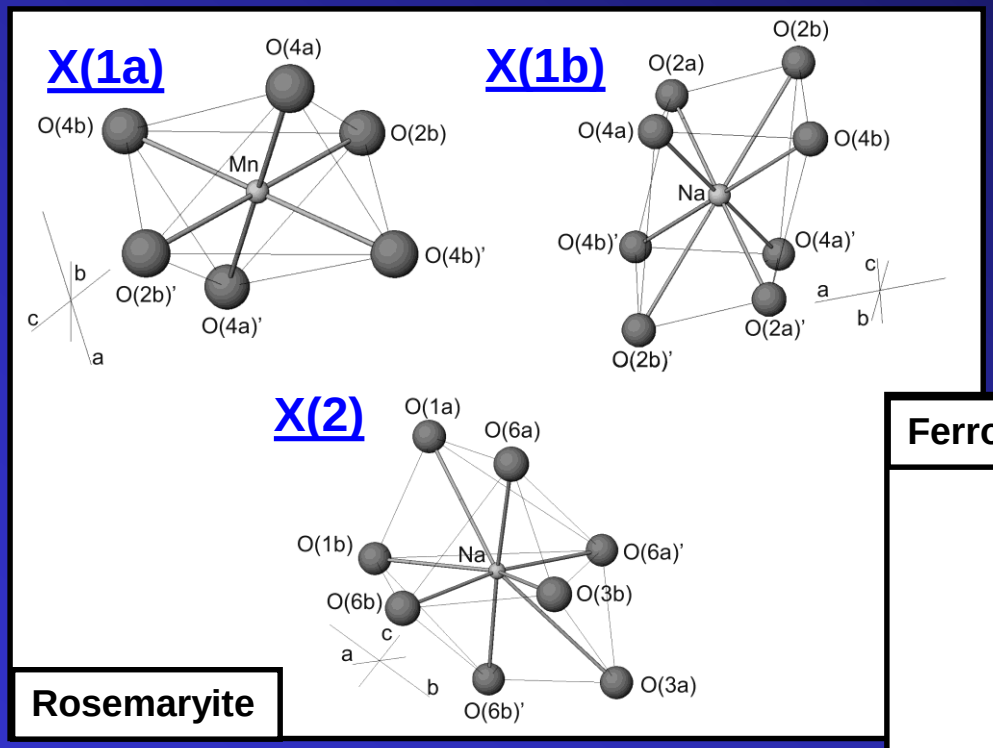
# New single-crystal structure refinements

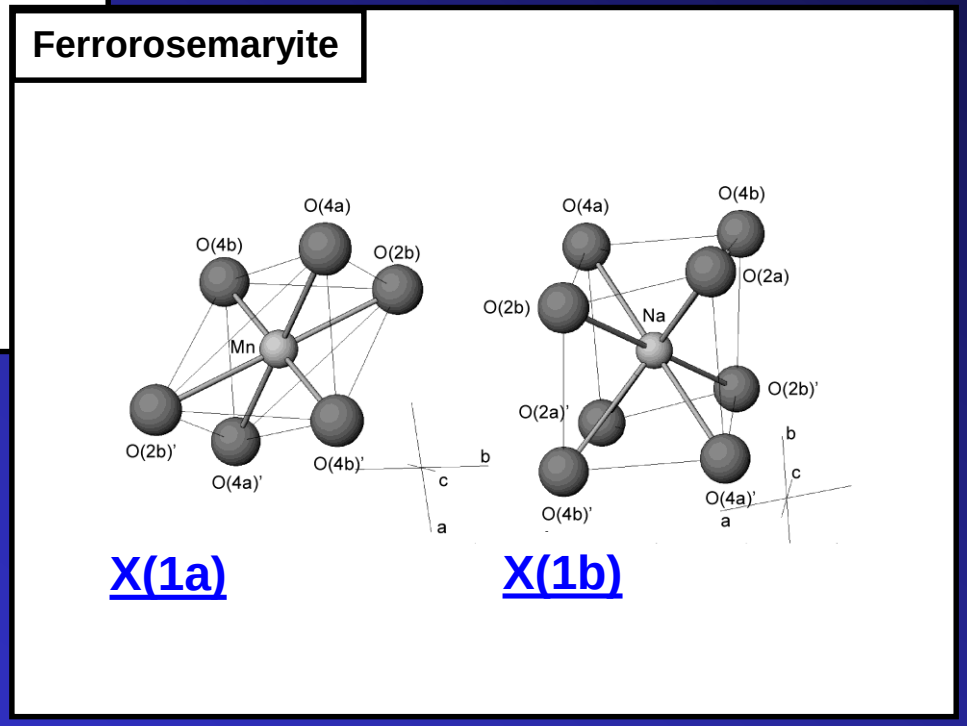
| | Ferrorosemaryite | Rosemaryite | Qingheiite-($Fe^{2+}$) | Wyllieite | Qingheiite |
|---|---|---|---|---|---|
| References | [1] | [2] | [3] | This work | This work |
| Locality | Rubindi, Rwanda | Buranga, Rwanda | Sebastião Cristino, Brazil | Buranga, Rwanda | Santa Ana, Argentina |
| Ideal formula | $NaFe^{2+}Fe^{3+}Al(PO_4)_3$ | $NaMn^{2+}Fe^{3+}Al(PO_4)_3$ | $Na_2Fe^{2+}MgAl(PO_4)_3$ | $Na_2MnFe^{2+}Al(PO_4)_3$ | $Na_2MnMgAl(PO_4)_3$ |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| *a* (Å) | 11.838(1) | 12.001(2) | 11.910(2) | 11.954(2) | 11.878(3) |
| *b* (Å) | 12.347(1) | 12.396(1) | 12.383(3) | 12.439(2) | 12.448(2) |
| *c* (Å) | 6.2973(6) | 6.329(1) | 6.372(1) | 6.406(1) | 6.438(2) |
| *β* (°) | 114.353(6) | 114.48(1) | 114.43(3) | 114.54(1) | 114.49(1) |
| M(2a) | **$0.72Al^{3+}$** + $0.14Fe^{2+}$ + $0.14Fe^{3+}$ | **$0.69Al^{3+}$** +$0.24Fe^{3+}$ + $0.08Fe^{2+}$ | **$0.62Al^{3+}$** + $0.28Mg^{2+}$ + $0.10Fe^{3+}$ | **$0.70Al^{3+}$** + $0.25Fe^{2+}$ + $0.05Mn^{2+}$ | **$0.47Al^{3+}$** + $0.34Mg^{2+}$ + $0.19Fe^{3+}$ |
| M(2b) | **$0.88Fe^{3+}$** + $0.10Al^{3+}$ + $0.02Mg$ | **$0.80Fe^{3+}$** + $0.10Al^{3+}$ + $0.10Mn^{2+}$ | **$0.44Mg^{2+}$** + $0.35\ Fe^{3+}$ + $0.21Fe^{2+}$ | **$0.55Fe^{2+}$** + $0.20Fe^{3+}$ + $0.20Mg^{2+}$ + $0.05Al^{3+}$ | **$0.60Mg^{2+}$** + $0.40Fe^{2+}$ |
| M(1) | $0.57Fe^{2+}$ + $0.20Fe^{3+}$ + $0.18Na^{+}$ + $0.05Mn^{2+}$ | $0.75Mn^{2+}$ + $0.10Ca^{2+}$ + $0.08Mg^{2+}$ + $0.07Fe^{2+}$ | $0.52\ Fe^{2+}$ + $0.25\ Na^{+}$ + $0.07Mn^{2+}$ + $0.16Fe^{3+}$ | $0.75Mn^{2+}$ + $0.20Na^{+}$ + $0.05Ca^{2+}$ | $0.93Mn^{2+}$ + $0.07Fe^{3+}$ |
| X(1a) | $0.43Mn^{2+}$ + $0.07Na^{+}$ | $0.45Mn^{2+}$ + $0.05Na^{+}$ | $0.50Mn^{2+}$ | $0.50Mn^{2+}$ | $0.50Mn^{2+}$ |
| X(1b) | $0.17Na^{+}$ + $0.04Mn^{2+}$ + $0.04Ca^{2+}$ + 0.25[] | $0.10Na^{+}$ + $0.07Mn^{2+}$ + 0.33[] | $0.50Na^{+}$ | $0.50Na^{+}$ | $0.50Na^{+}$ |
| X(2) | 1.0[] | $0.44Na^{+}$ + 0.56[] | $0.18Na^{+}$ + $0.15\ Mn^{2+}$ + $0.02Ca^{2+}$ + 0.65 [] | $1.00Na^{+}$ | $0.95Na^{+}$ + $0.05Ca^{2+}$ |

**1. Hatert *et al*., 2005; 2. Hatert *et al*., 2006; 3. Hatert *et al*., 2010**

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

# Morphology of the X sites




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

# The X sites in qingheiite-($Fe^{2+}$)

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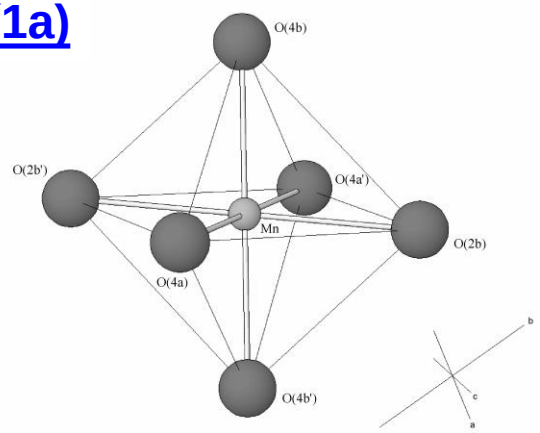
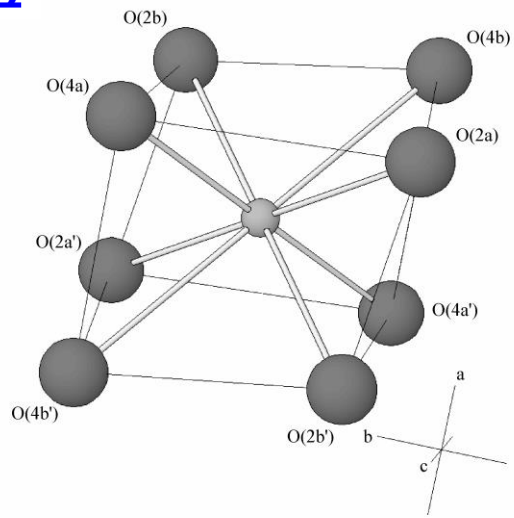
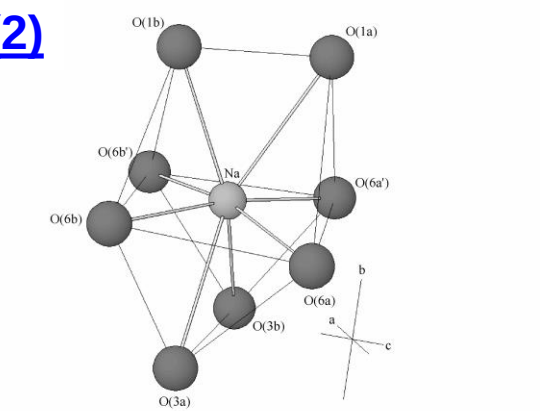
**X(1a)**




**X(1b)**



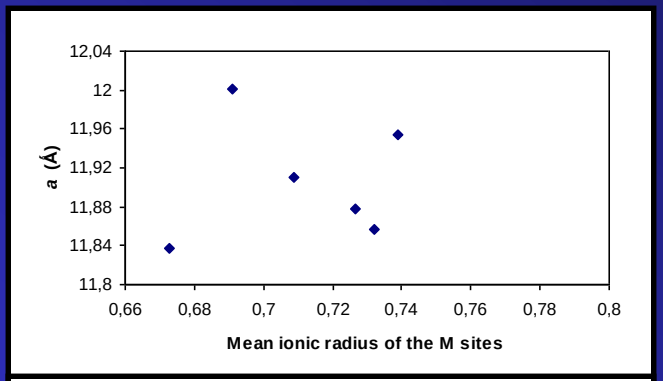

**X(2)**

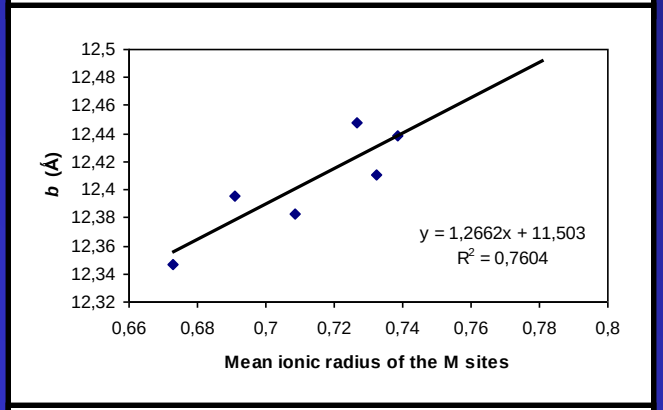


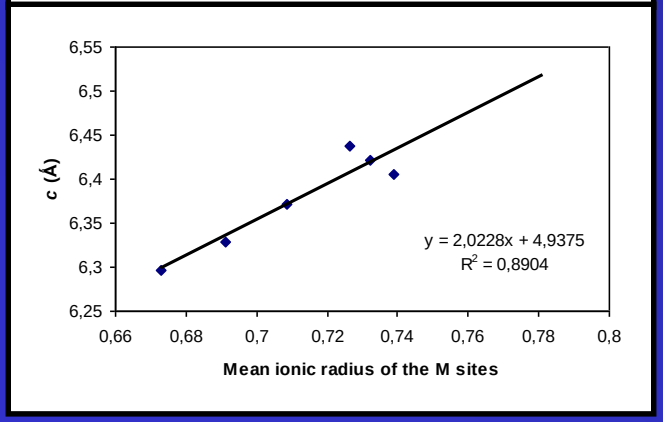

**BLD coefficients:**

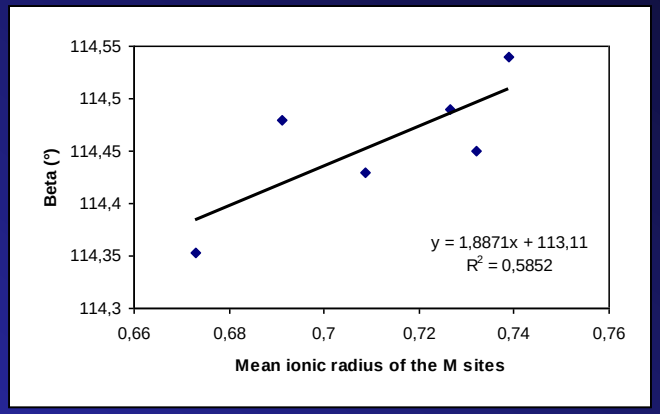
- **Rosemaryite: 8.07 %**
- **Ferrorosemaryite: 7.76 %**
- **Qingheiite-($Fe^{2+}$): 6.72 %**

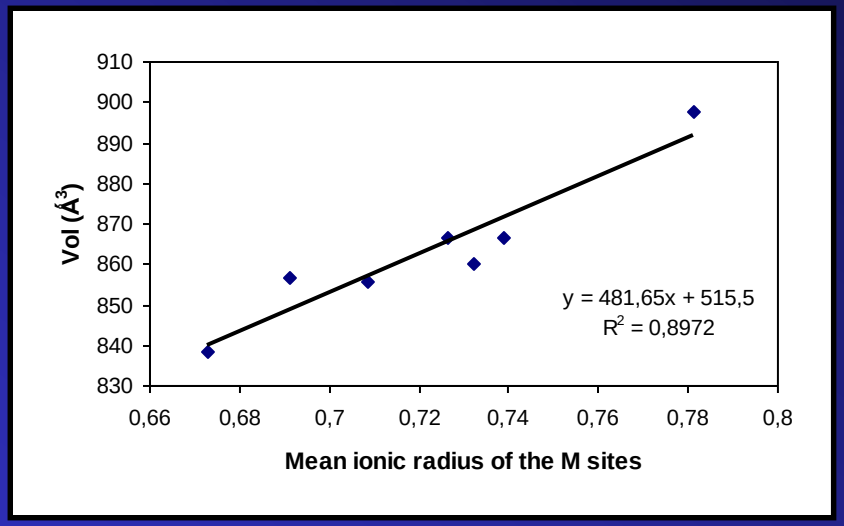
# Variations of the unit-cell parameters



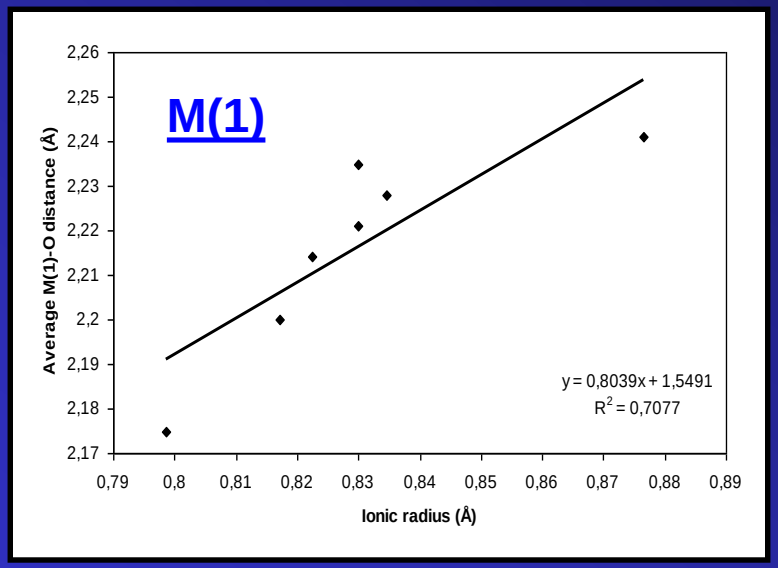



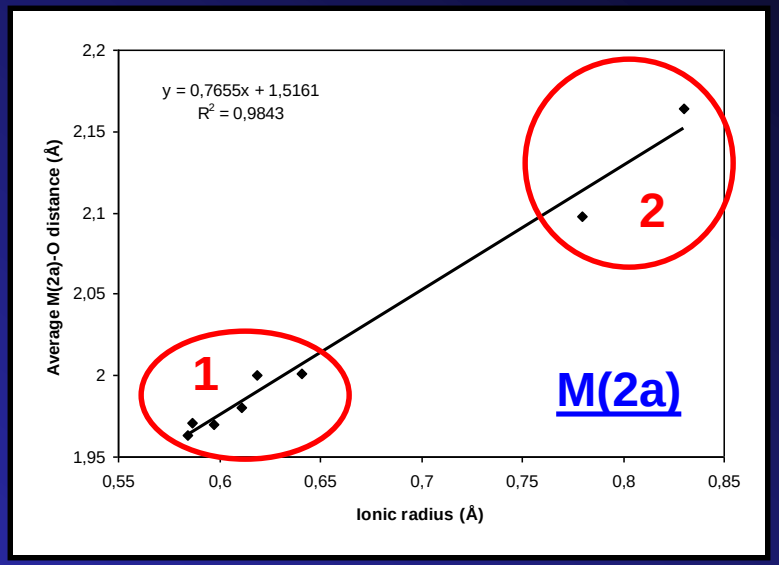



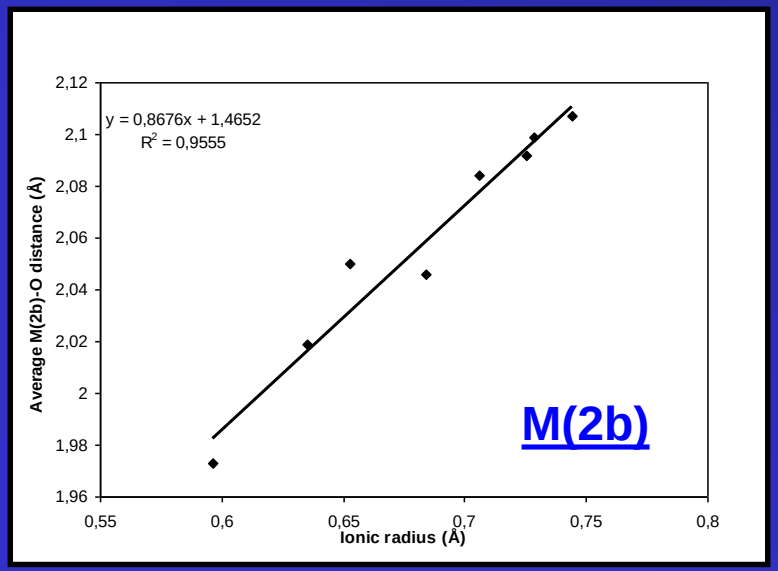




**Good correlations between *b*, *c*, Vol., and the mean ionic radius of the cations occurring on the M sites**

# Variations of the M-O bond lengths




- When the M(2) sites contain Al and a cation with an *e.i.r.* smaller than 0.75 Å ($Fe^{3+}$, Mg), then Al occupies the M(2a) site (zone 1).
- When the M(2) sites contain a cation with an *e.i.r.* larger than 0.75 Å ($Fe^{2+}$, $Mn^{2+}$), this cation occupies the M(2a) site (zone 2) and the small cations (Al, $Mn^{3+}$) occupy the M(2b) site.

M(2a) can accomodate larger cations than M(2b)

# Conclusions

- Qingheiite-($Fe^{2+}$) is a new phosphate mineral of the wyllieite group, which occurs in the Sebastião Cristino pegmatite, Minas Gerais, Brazil

- A comparison of the structural data of qingheiite-($Fe^{2+}$), with those of other minerals of the wyllieite group, indicates: (I) that the distortion coefficients calculated for the X(1b) sites show significant variations. (II) that the M(2a) site can accommodate larger cations than M(2b).

- Investigations are in progress in order to better understand the genesis of qingheiite-($Fe^{2+}$), and of other phosphates from pegmatites of the Conselheiro Pena district.