Crystal chemistry of wyllieite-type phosphates

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Introduction

- The wyllieite group comprises Na-Mn-Fe-Mg-Al-bearing phosphate minerals, which occur in granitic pegmatites.
- Structural formula of wyllieite-type phosphates [1]:

X(2)X(1a)X(1b)M(1)M(2a)M(2b)$(PO_4)_3$
***Z* = 4, S.G. $P2_1/n$**

- New structure refinements were performed on rosemaryite, ferrorosemaryite, wyllieite, and qingheiite, in order to shed some light on the crystal chemistry of these phosphates.

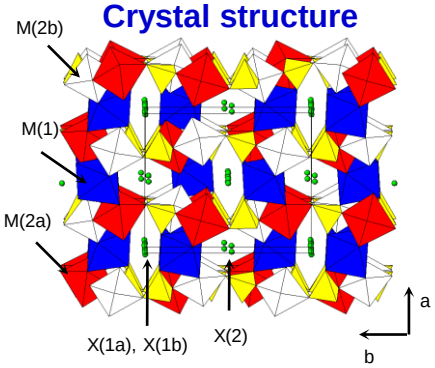
Previous structure refinements

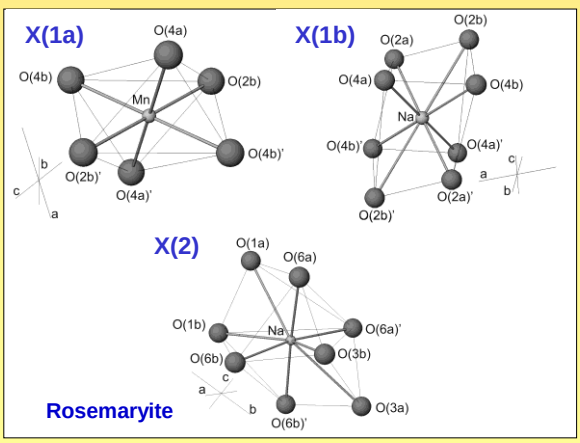
	Ferrowyllieite	Qingheiite	Synthetic compound
References	[2]	[3]	[4]
Ideal formula	$Na_2Fe^{2+}{}_2Al(PO_4)_3$	$Na_2MnMgAl(PO_4)_3$	$Na_2Mn^{2+}{}_2Mn^{3+}(PO_4)_3$
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	11.868(15)	11.856(3)	6.5291(6)
b (Å)	12.382(12)	12.411(3)	12.653(1)
c (Å)	6.354(9)	6.421(1)	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□

New structure refinements

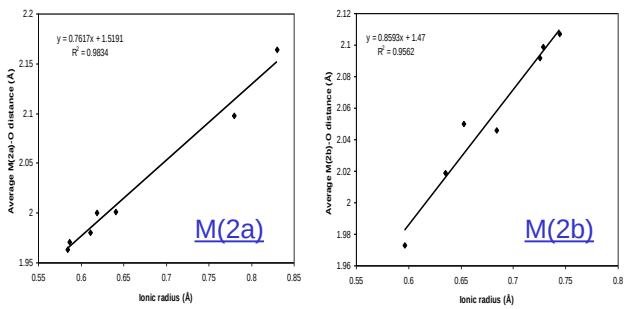
	Ferrorosemaryite	Rosemaryite	Wyllieite	Qingheiite
References	[5]	[6]	This work	This work
Locality	Rubindi, Rwanda	Buranga, Rwanda	Buranga, Rwanda	Santa Ana, Argentina
Ideal formula	□$NaFe^{2+}Fe^{3+}Al(PO_4)_3$	□$NaMn^{2+}Fe^{3+}Al(PO_4)_3$	$Na_2MnFe^{2+}Al(PO_4)_3$	$Na_2MnMgAl(PO_4)_3$
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	11.838(1)	12.001(2)	11.954(2)	11.878(3)
b (Å)	12.347(1)	12.396(1)	12.439(2)	12.448(2)
c (Å)	6.2973(6)	6.329(1)	6.406(1)	6.438(2)
β (°)	114.353(6)	114.48(1)	114.54(1)	114.49(1)
M(2a)	**$0.72Al^{3+}$** + $0.14Fe^{2+}$ + $0.14Fe^{3+}$	**$0.69Al^{3+}$** + $0.24Fe^{3+}$ + $0.08Fe^{2+}$	**$0.70Al^{3+}$** + $0.25Fe^{2+}$ + $0.05Mn^{2+}$	**$0.47Al^{3+}$** + $0.34Mg^{2+}$ + $0.19Fe^{3+}$
M(2b)	**$0.88Fe^{3+}$** + $0.10Al^{3+}$ + 0.02Mg	**$0.80Fe^{3+}$** + $0.10Al^{3+}$ + $0.10Mn^{2+}$	**$0.55Fe^{2+}$** + $0.20Fe^{3+}$ + $0.20Mg^{2+}$ + $0.05Al^{3+}$	**$0.60Mg^{2+}$** + $0.40Fe^{2+}$
M(1)	$0.57Fe^{2+}$ + $0.20Fe^{3+}$ + $0.18Na^{+}$ + $0.05Mn^{2+}$	$0.75Mn^{2+}$ + $0.10Ca^{2+}$ + $0.08Mg^{2+}$ + $0.07Fe^{2+}$	$0.75Mn^{2+}$ + $0.20Na^{+}$ + $0.05Ca^{2+}$	$0.93Mn^{2+}$ + $0.07Fe^{3+}$
X(1a)	$0.43Mn^{2+}$ + $0.07Na^{+}$	$0.45Mn^{2+}$ + $0.05Na^{+}$	$0.50Mn^{2+}$	$0.50Mn^{2+}$
X(1b)	$0.17Na^{+}$ + $0.04Mn^{2+}$ + $0.04Ca^{2+}$ + 0.25□	$0.10Na^{+}$ + $0.07Mn^{2+}$ + 0.33□	$0.50Na^{+}$	$0.50Na^{+}$
X(2)	1.0□	$0.44Na^{+}$ + 0.56□	$1.00Na^{+}$	$0.95Na^{+}$ + $0.05Ca^{2+}$

Crystal structure





Variations of M(2)-O bond lengths



Conclusions

- In natural wyllieite-type phosphates, aluminum generally occupies the M(2a) crystallographic site.
- In ferrowyllieite, aluminum occupies the M(2b) site, and M(2a) is filled by Fe^{2+}.
- The good correlations between the M(2)-O bond distances, and the ionic radius of the cations occurring on this site, confirm the reliability of the cation distributions in wyllieite-type phosphates.

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