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

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Natural and synthetic alluaudite-type phosphates: Crystal chemistry and applications

Frédéric Hatert & André-Mathieu Fransolet

BCS-4

Brussels, October 19th, 2005

Alluaudite, Buranga pegmatite, Rwanda

1. The alluaudite structure

- Moore (1971)

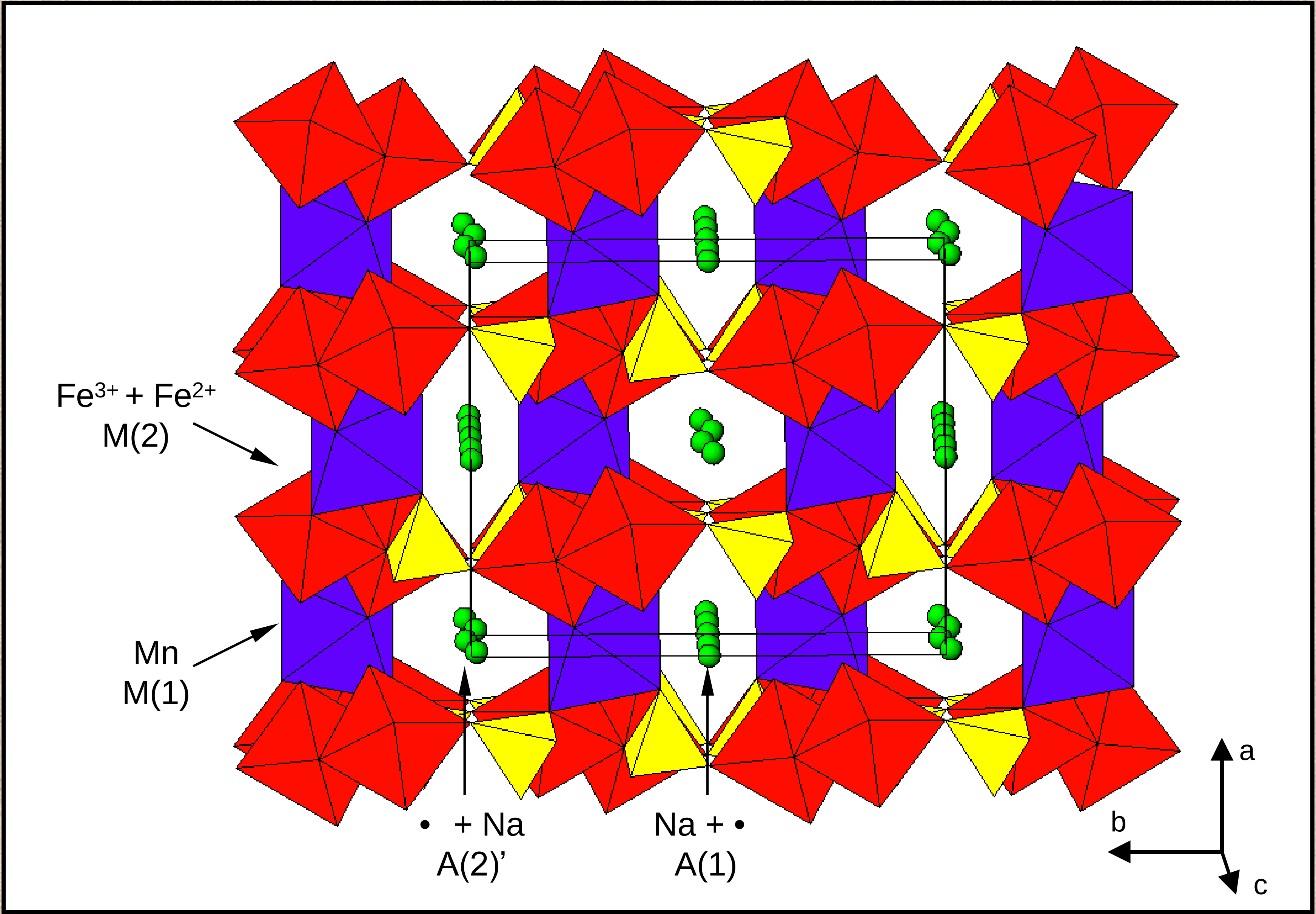
$C2/c$, $Z = 4$

$$X(2)X(1)M(1)M(2)_2(PO_4)_3$$

- Hatert *et al.* (2000)

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

-*A*(2)': gabled disphenoid
-*A*(1): distorted cube
-*M*(1): very distorted octahedron
-*M*(2): distorted octahedron


Fe3+ + Fe2+
M(2)
Mn
M(1)
• + Na
A(2)'
Na + •
A(1)
a
b
c

2. Crystal chemistry of natural alluaudites

- Moore & Ito (1979)

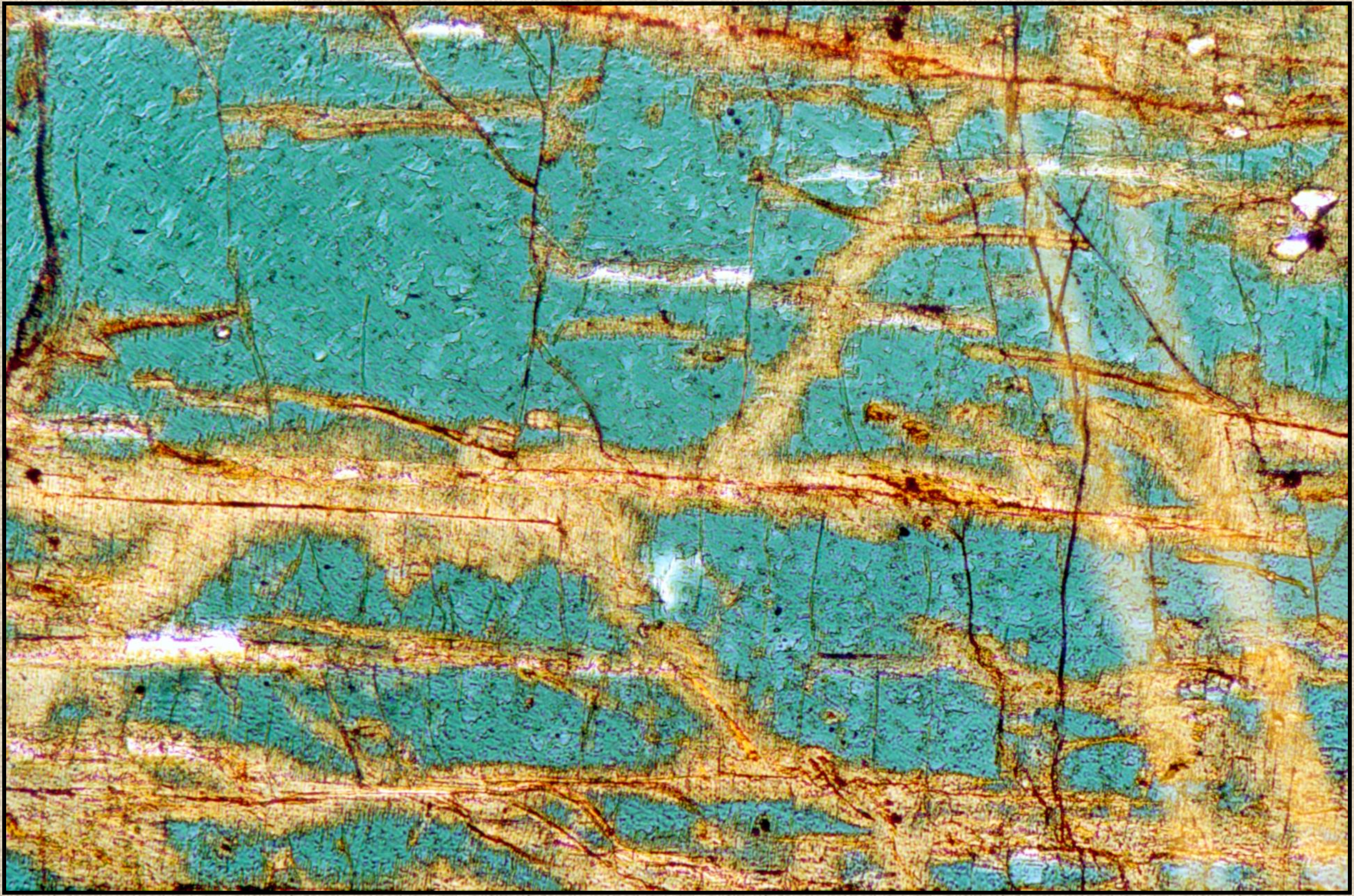
$A(2)' \Rightarrow Na^{+}$, •, K^{+}
$A(1) \Rightarrow Na^{+}, Mn^{2+}, Ca^{2+}$, •
$M(1) \Rightarrow Mn^{2+}, Fe^{2+}, Ca^{2+}, Mg^{2+}$
$M(2) \Rightarrow Fe^{3+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Li^{+}$

- Fransolet *et al*. (1985, 1986, 2004)

Oxidation mechanism:

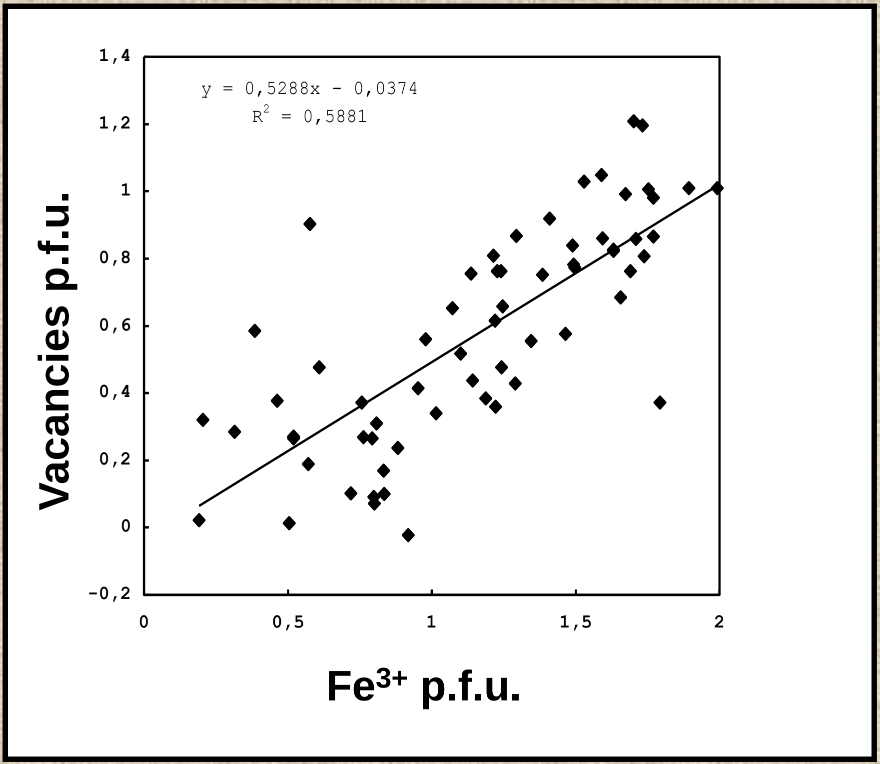
$Na^{+} + Fe^{2+} \Rightarrow$ • $+ Fe^{3+}$

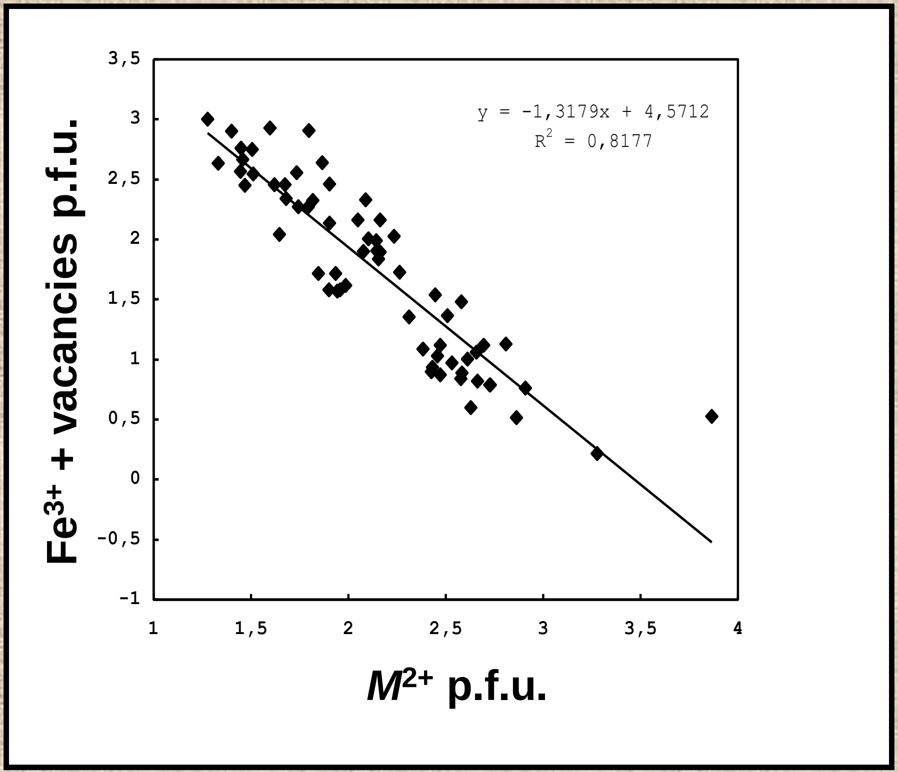
$Na_2MnFe^{2+}Fe^{3+}(PO_4)_3 \Rightarrow$ •$NaMnFe^{3+}_2(PO_4)_3$
$Na_2Fe^{2+}_2Fe^{3+}(PO_4)_3 \Rightarrow$ •$NaFe^{2+}Fe^{3+}_2(PO_4)_3$



Hagendorfite and alluaudite, Kibingo pegmatite, Rwanda

2.1. Correlations on natural alluaudites

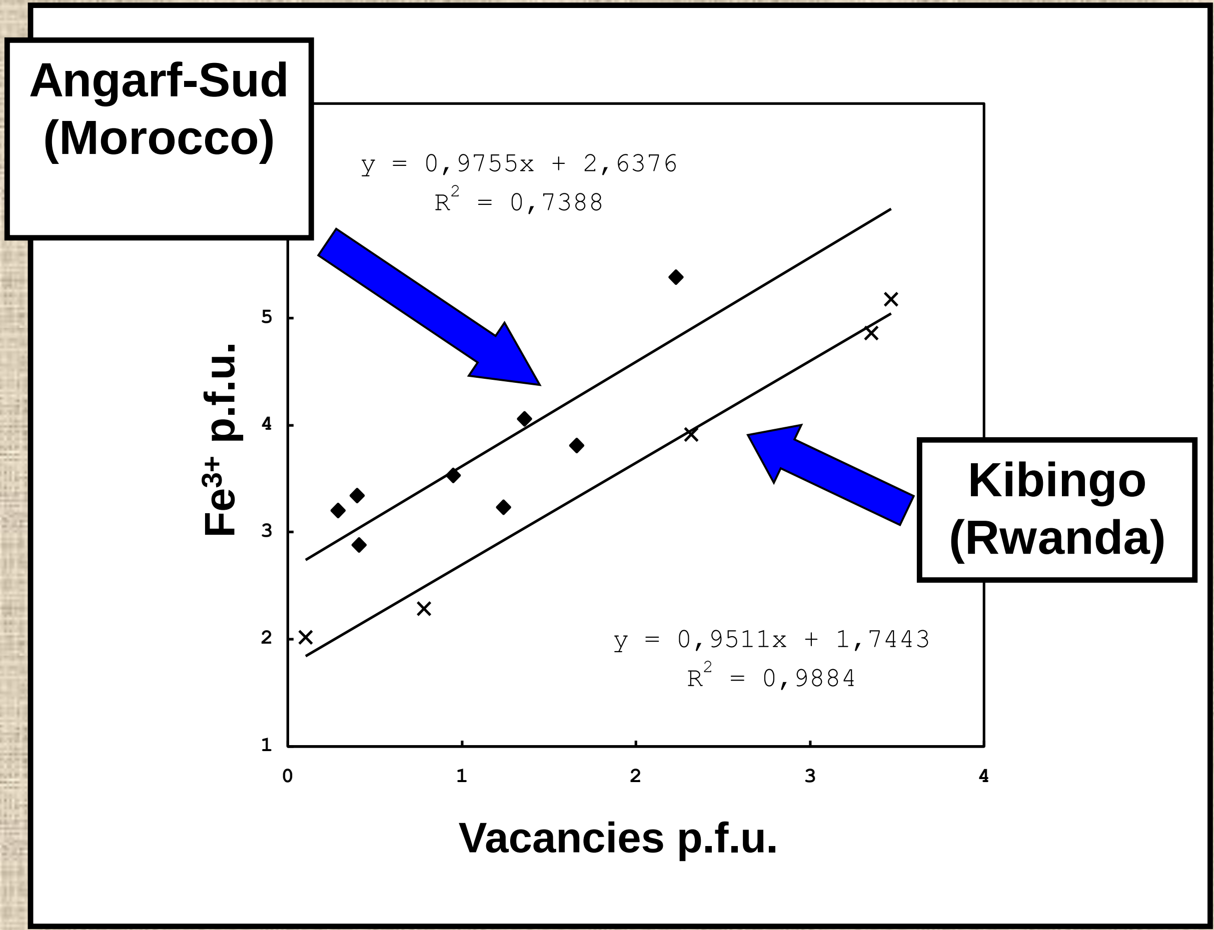




$Na^{+} + Fe^{2+} \Rightarrow \square + Fe^{3+}$

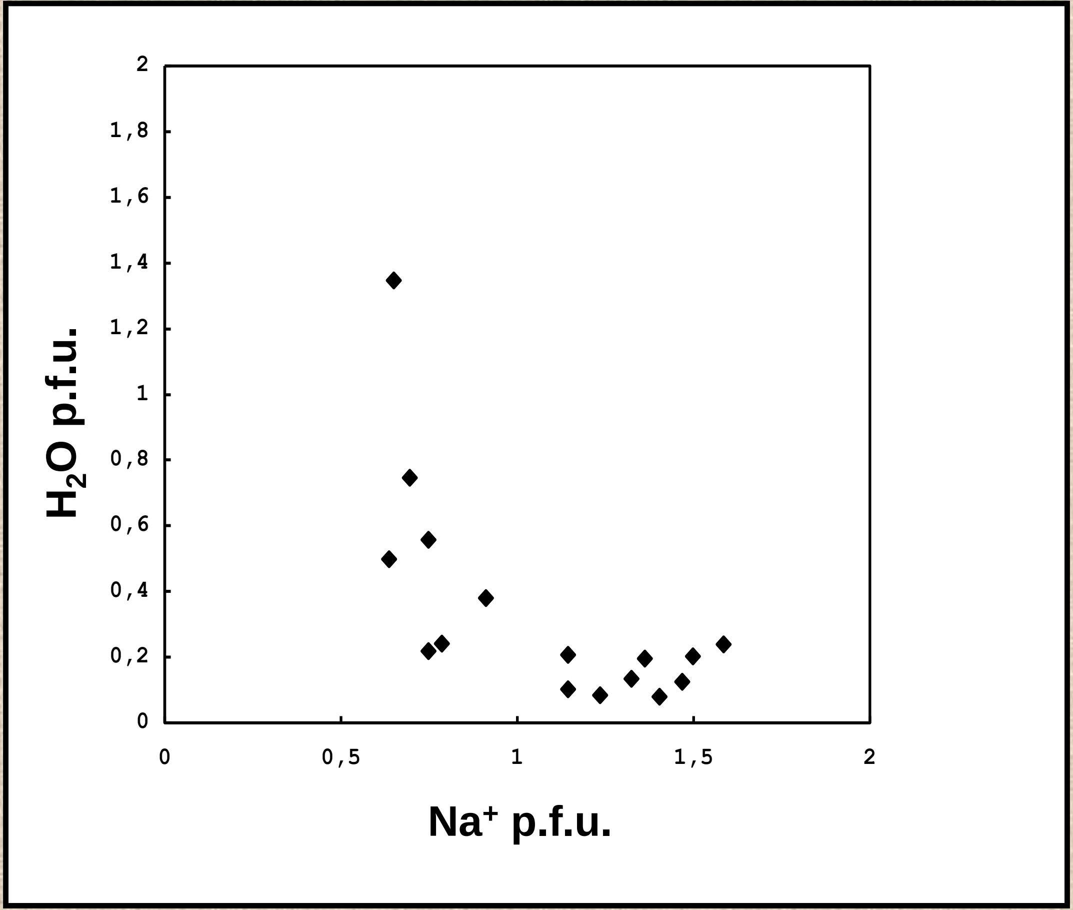
$(Ca,Mn)^{2+} + 2Fe^{2+} \Rightarrow \square + 2Fe^{3+}$

2.2. Correlation between Fe^{3+} and vacancies



$Na^{+} + Fe^{2+} \Rightarrow \bullet + Fe^{3+}$

2.3. Correlation between H_2O and the Na-content



H_2O occurs in the channels of the structure, when the Na-content is low

3. Crystal chemistry of synthetic alluaudite-type compounds

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- Solid state synthesis in air
- T = 800-950 °C
- P = 1 bar

→ Na-Mn-Fe^{3+} (+ PO_4) system
→ Role of Li^+
→ Role of Cd^{2+} and Zn^{2+}
→ Role of In^{3+} and Ga^{3+}

Experimental

- Hydrothermal synthesis
- Tuttle-type cold-seal bombs
- T = 400-800 °C
- P = 1-5 kbar

→ Na-Mn-Fe^{2+}-Fe^{3+} (+ PO_4) system
→ Stability of alluaudites
→ Stability of alluaudite + triphylite

Cation	Ionic radius (Å) [VI]	[VIII]	Site *A*(2)'	*A*(1)	*M*(1)	*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

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3.1. Cationic distribution

3.2. The role of lithium

- $(Na_{1-x}Li_x)MnFe^{3+}_2(PO_4)_3$

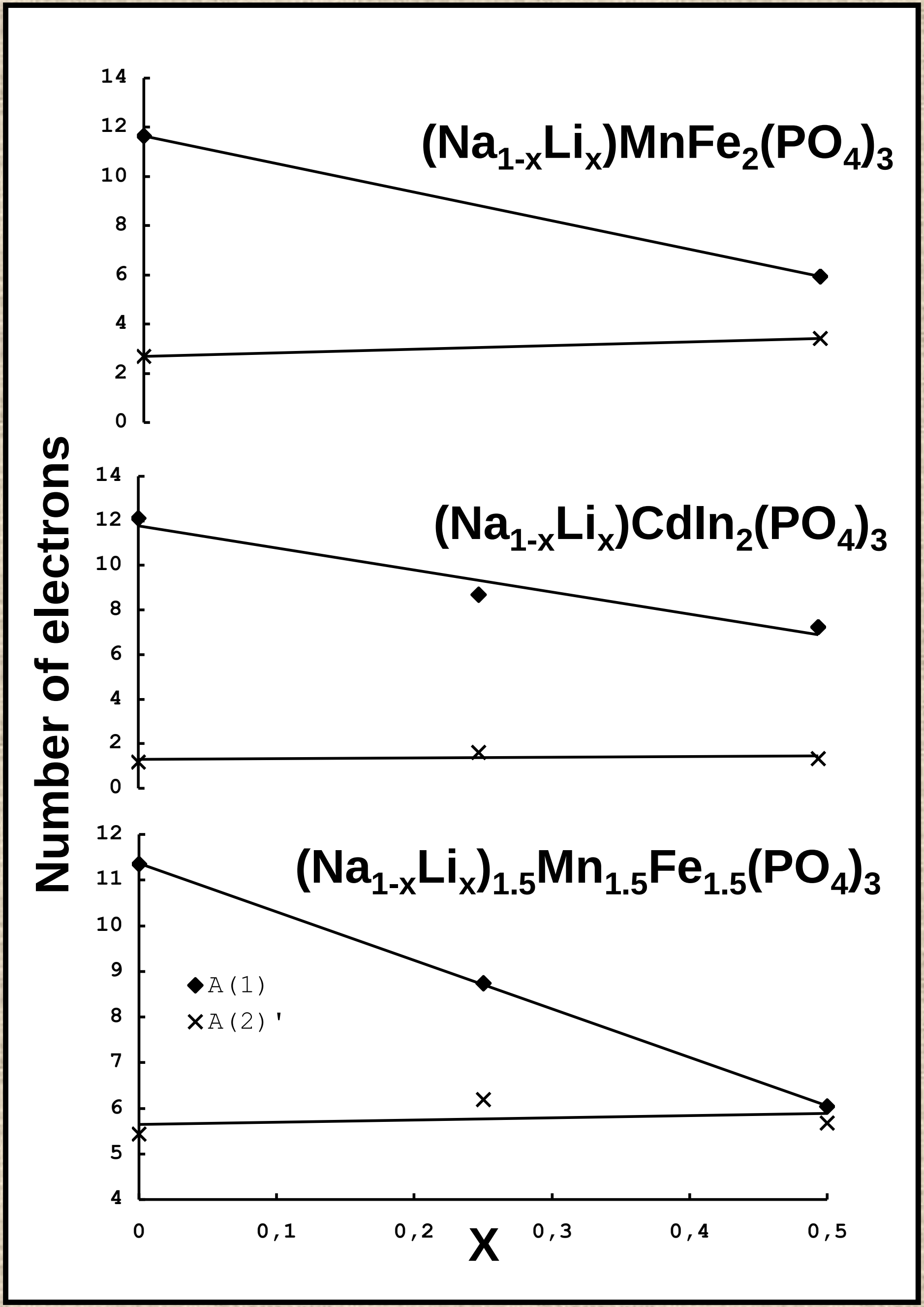
  Single-crystal structure refinements
  Variations of the unit-cell parameters
  Mössbauer spectroscopy

- $(Na_{1-x}Li_x)CdIn_2(PO_4)_3$

  X-ray Rietveld refinements

- $(Na_{1-x}Li_x)_{1.5}Mn_{1.5}Fe^{3+}_{1.5}(PO_4)_3$

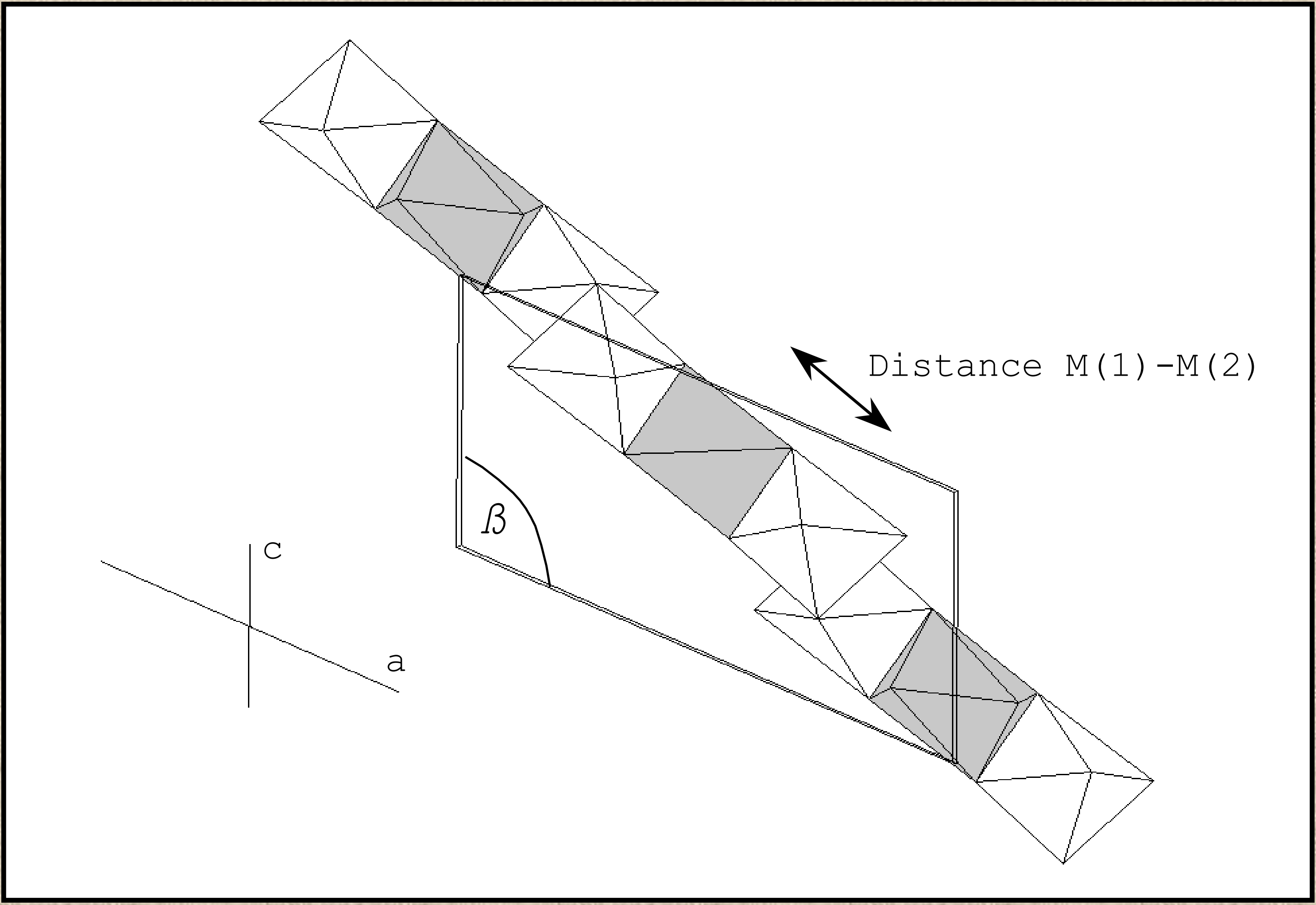
  X-ray Rietveld refinements



Number of electrons on *A*(1) and *A*(2) '

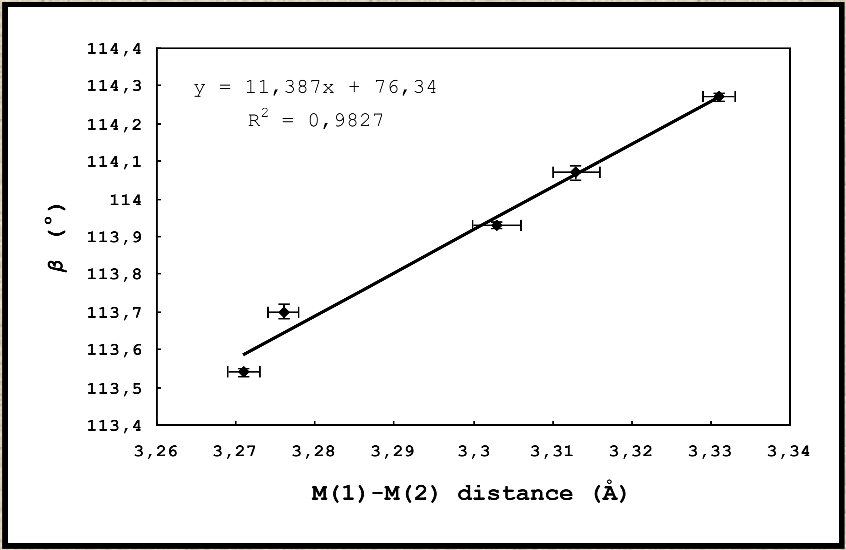
Li localized on the large *A*(1) site

3.3. The role of the *M* cations

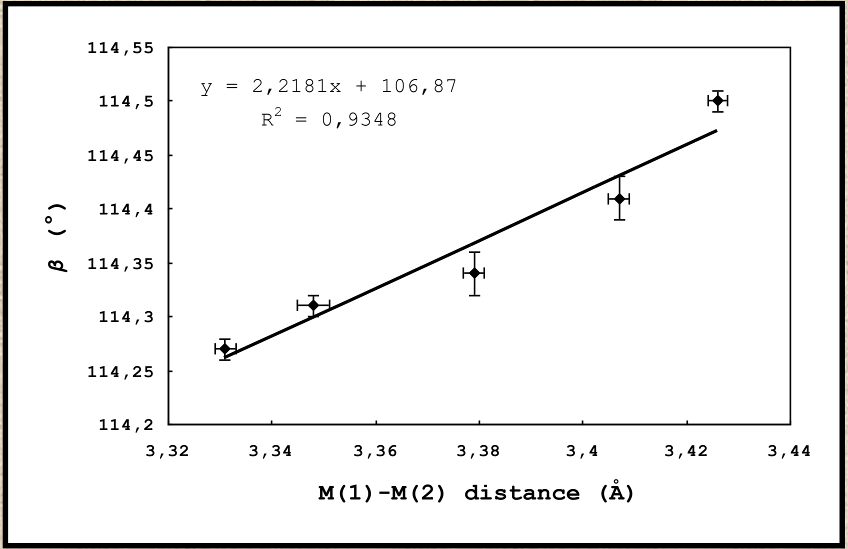


Structure | Natural | Synthetic | Applications

$Na_{1.5}(Mn_{1-x}Zn_x)_{1.5}Fe^{3+}_{1.5}(PO_4)_3$



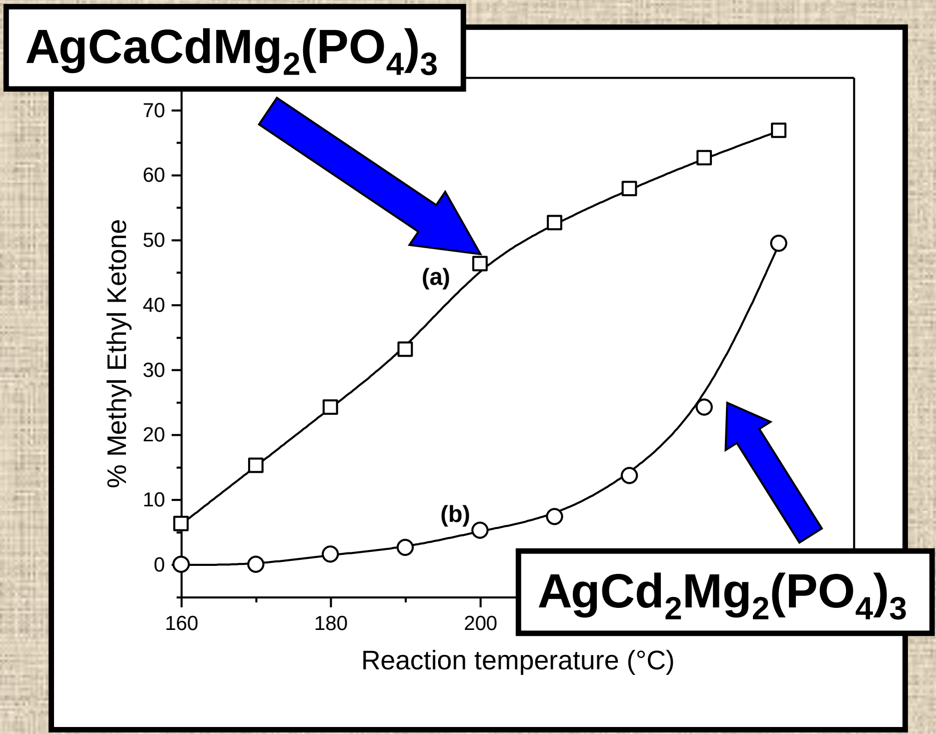
$Na_{1.5}(Mn_{1-x}Cd_x)_{1.5}Fe^{3+}_{1.5}(PO_4)_3$

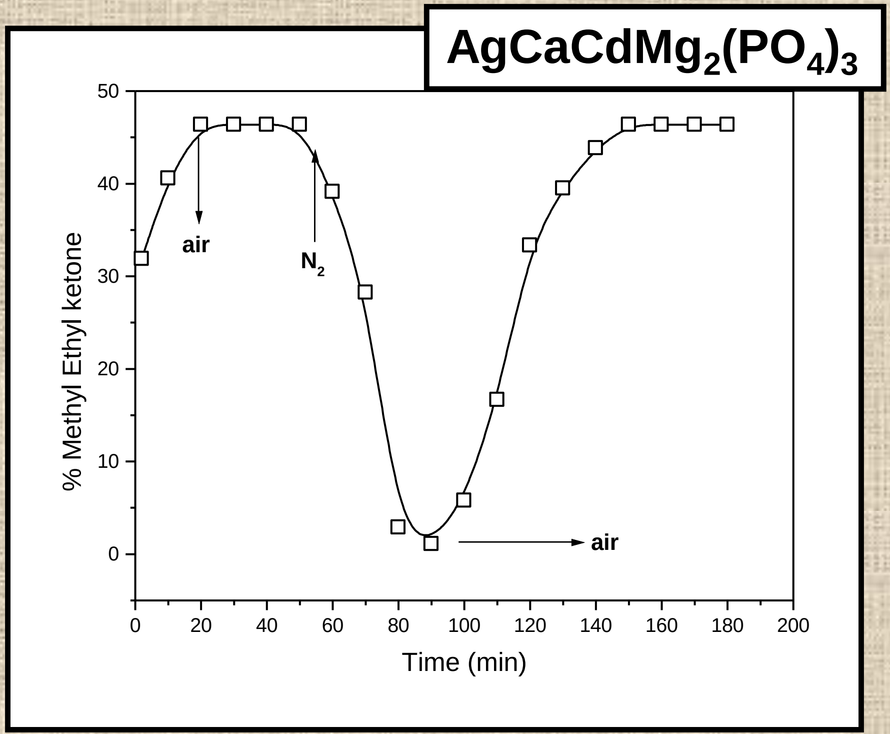


Correlations between the *M*(1)-*M*(2) distance and the beta angle

4. Applications
4.1. Catalytic properties

Probe reaction: Butan-2-ol ⇒ Methyl ethyl ketone + butenes + CO_2



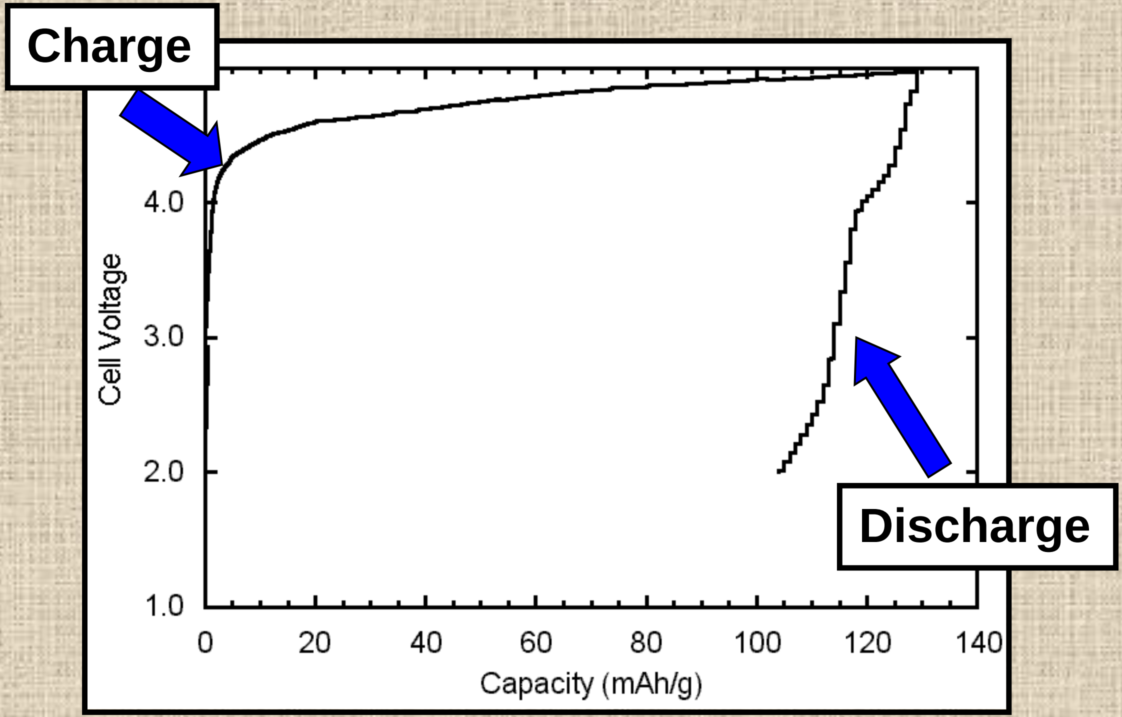


⇒ Catalytic activity comparable to that of nasicon-type phosphates

Kacimi *et al*. (2005), Materials Research Bulletin, 40, 682-693

4.2. The Li-batteries

$Li_xNa_{2-x}Mn_2Fe^{3+}(PO_4)_3$



Poor performance, but possibility of improvement (sample preparation, other chemical compositions)

Richardson (2003), J. Power Sources, 119-121, 262-265

5. Conclusions

- The alluaudite structure is extremely flexible, and accommodate trivalent cations on *M*(2), divalent cations on *M*(1) and *M*(2), and monovalent cations in the channels

- In natural alluaudites, two main substitution mechanisms were observed, and small amounts of H_2O probably occur in the channels of the structure

- The insertion of Li, Ag and Cu in the channels of synthetic alluaudite-type compounds makes possible their use as electrode materials for Li-batteries or as catalysts