BOBFERGUSONITE FROM THE NANCY PEGMATITE, SAN LUIS RANGE, ARGENTINA: CRYSTAL-STRUCTURE REFINEMENT AND CHEMICAL COMPOSITION

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Abstract

A second occurrence of bobfergusonite, ideally $Na_2 Mn^{2+}_5 Fe^{3+} Al (PO_4)_6$, has been discovered at the Nancy pegmatite, San Luis Range, Argentina. The Nancy pegmatite is a small, poorly evolved pegmatite of the beryl–columbite–phosphate subtype of rare-element pegmatites. Bobfergusonite from the Nancy pegmatite is monoclinic, a 12.796(3), b 12.465(2), c 11.001(2) Å, β 97.39(3) , V 1740.1(5) Å^3, $P2_1/n$, $Z = 4$, has been refined to an R-index of 2.6% for 2959 observed ($|F_o| \lozenge 4\sigma F$) reflections measured with Mo$K\alpha$ X-radiation on a Bruker $P4$ diffractometer equipped with a CCD detector. The crystal used for the collection of the X-ray intensity data was subsequently analyzed with an electron microprobe. The unit formula derived from the refined site-scattering values and electron-microprobe results is $(Na_{1.10} \square_{0.90}) (Na_{0.90} \square_{0.10}) Mn^{2+} (Mn^{2+}_{0.89} Ca_{0.11}) (Fe^{2+}_{0.91} Fe^{3+}_{0.49} Mn^{2+}_{0.32} Mg_{0.28}) (Fe^{3+}_{0.42} Fe^{2+}_{0.28} Mg_{0.30}) (Al_{0.94} Fe^{3+}_{0.06}) (PO_4)_6$. In bobfergusonite, there are six M sites, each coordinated by six O-atoms in an octahedral arrangement with $<M–O>$ distances ranging from 1.918 Å at $M(6)$ to 2.237 Å at $M(2)$. There is strong order between the divalent and trivalent cations over the six M sites, and there is also strong order between Al and Fe^{3+}. There are five X sites, $X(1)–X(5)$, each having a wide dispersion of X–O distances. The $X(1)$ site is mainly occupied by Mn^{2+} and has octahedral coordination. The $X(2)$ and $X(3)$ sites are each [8]-coordinated, the $X(4)$ and $X(5)$ sites are [7]-coordinated, and $X(2)–X(5)$ are all approximately half-occupied by Na. In all of the alluaudite-related structures, the M sites form linear edge-sharing trimers, and the alluaudite, wyllieite and bobfergusonite structures show subtly different patterns of cation order–disorder. Bobfergusonite crystals from both known localities, the Nancy pegmatite (Argentina) and the Cross Lake pegmatite (Manitoba), are considerably disordered.

Keywords: bobfergusonite, crystal structure, phosphate, Argentina.

Sommaire

Un deuxième exemple de bobfergusonite, de formule idéale $Na_2 Mn^{2+}_5 Fe^{3+} Al (PO_4)_6$, a été découvert, celui-ci dans la pegmatite de Nancy, chaîne de San Luis, en Argentine. Cette pegmatite est de taille restreinte, et constitue un exemple peu évolué du sous-type à béryl – columbite – phosphate des pegmatites à éléments rares. La bobfergusonite de cet indice est monoclinique, a 12.796(3), b 12.465(2), c 11.001(2) Å, β 97.39(3) , V 1740.1(5) Å^3, $P2_1/n$, $Z = 4$; nous en avons affiné la structure jusqu'à un résidu R de 2.6% pour 2959 réflexions observées ($|F_o| \lozenge 4\sigma F$), mesurées avec un diffractomètre Bruker $P4$ muni d'un détecteur CCD (rayonnement Mo$K\alpha$). Le cristal utilisé a ensuite été analysé avec une microsonde électronique. L'unité formulaire dérivée à partir des valeurs affinées de la dispersion des sites et des résultats des données obtenues à la microsonde électronique est $(Na_{1.10} \square_{0.90}) (Na_{0.90} \square_{0.10}) Mn^{2+} (Mn^{2+}_{0.89} Ca_{0.11}) (Fe^{2+}_{0.91} Fe^{3+}_{0.49} Mn^{2+}_{0.32} Mg_{0.28}) (Fe^{3+}_{0.42} Fe^{2+}_{0.28} Mg_{0.30}) (Al_{0.94} Fe^{3+}_{0.06}) (PO_4)_6$. La structure contient six sites M, chacun coordonné par six atomes d'oxygène dans un agencement octaédrique, avec les distances $<M–O>$ entre 1.918 Å pour $M(6)$ jusqu'à 2.237 Å pour $M(2)$. Il y a une forte mise en ordre entre les cations bivalents et trivalents sur les sites M, et il y a aussi une forte mise en ordre entre Al et Fe^{3+}. La structure contient cinq sites X, $X(1)–X(5)$, chacun faisant preuve d'une grande dispersion des distances X–O. Le site $X(1)$ est surtout rempli par le Mn^{2+} et possède une coordination octaédrique. Les sites $X(2)$ et $X(3)$ ont chacun une coordinance [8], et les sites $X(4)$ et $X(5)$, une coordinance [7]; les sites $X(2)$–$X(5)$ sont tous environ à moitié remplis par le Na. Dans tous les membres du groupe de l'alluaudite, les sites M forment des groupes trimériques linéaires d'octaèdres à arêtes partagées, et les structures de l'alluaudite, la wyllieïte et la bobfergusonite possèdent des degrés d'ordre et désordre subtilement différents. Les cristaux de bobfergusonite des deux localités, la pegmatite de Nancy, en Argentine, celle de Cross Lake, au Manitoba, sont considérablement désordonnés.

(Traduit par la Rédaction)

Mots-clés: bobfergusonite, structure cristalline, phosphate, Argentine.

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INTRODUCTION

Bobfergusonite is a phosphate mineral originally described by Ercit *et al.* (1986a, b) from pegmatite #22 at Cross Lake, Manitoba. It is closely related to wyllieite-group and alluaudite-group minerals, yet differs from all known members of these groups in both chemical composition and structure. There has been a lot of work on the minerals and synthetic compounds with structures related to that of alluaudite (Moore 1971). The structures of qingheiite (Ma *et al.* 1983), o'daniellite and johillerite (Keller & Hess 1988), caryinite (Ercit 1993), nickenichite (Auernhammer *et al.* 1993) and bradaczekite (Filatov *et al.* 2001, Krivovichev *et al.* 2001) have been refined. Many synthetic phosphates (Yakubovich *et al.* 1977, Antenucci *et al.* 1993, 1995, Hatert *et al.* 2000, Leroux *et al.* 1995a, b, Warner *et al.* 1993) and arsenates (Pertlik 1987, Khorari *et al.* 1997a, b, c) have been characterized structurally. Khorari *et al.* (1997b) have examined the compositional relations between the alluaudite and garnet structures, and it is particularly apparent from the work on synthetic compounds that the alluaudite structure, like the garnet structure, is extremely chemically compliant. Moore & Molin-Case (1974) showed that the crystal structure of wyllieite is a superstructure derivative of the structure of alluaudite, and Moore & Ito (1979) introduced a nomenclature for the minerals of the alluaudite and wyllieite groups. We recently discovered a new occurrence of bobfergusonite at the Nancy pegmatite in San Luis Province, Argentina. As part of a general study on the alluaudite-group minerals (*sensu lato*), we have examined the crystal structure of bobfergusonite from this new locality in order to derive detailed site-populations.

OCCURRENCE

Bobfergusonite occurs in the Nancy pegmatite; the NE stake of the mine property is located at 32 28'48"S and 65 16'42"W, 651 m a.s.l., in the Chacabuco Department, San Luis Province, Argentina (Fig. 1). The pegmatite belongs to the Conlara pegmatite field, situated in the northern part of the Eastern Pampean Ranges of San Luis (Galliski 1994). The crystalline basement of this part of the range is composed dominantly of pelitic and psammitic gneisses of the Conlara Metamorphic Complex (Sims *et al.* 1997) of Eopaleozoic age. These rocks were intruded by minor Paleozoic S-type granites and associated pegmatites. The host rock adjacent to the pegmatite is a medium-grade gray gneiss.

Old mining workings for beryl extend 140 m along strike, which varies from N 23 E in the southern half of the body to N 4 W in the northern part of the body. In the central part of the workings, there is a short branch 15 m long in the N 50 E direction. The width of the exposed pegmatite varies from 4 m at the southern end to 28 m at the northern end; the average width is about 7 m. The pegmatite is zoned, and its internal structure is best observed in a big broken block 30 m north of the southern end of the outcrop. The border zone is fine grained and is separated from the host rock by a layer of muscovite 2–3 mm thick parallel to the contact. A similar layer of muscovite separates the border and wall zones. The wall zone is 10 cm wide and contains elongate K-feldspar crystals (up to 5 cm) intergrown with minor albite, flakes of muscovite normal to the contact, and fine-grained quartz. There is a continuous layer (5 cm thick) of massive milky quartz between the wall zone and the intermediate zone. The intermediate zone consists of K-feldspar + albite + quartz + muscovite. The K-feldspar occurs as partly albitized crystals up to 1 to 2 m long, intergrown with coarse-grained milky quartz and 10-cm wide books of muscovite. There is no tourmaline in the pegmatite, but garnet is a common accessory as inclusions in K-feldspar or albite. Beryl occurs as yellowish cm-sized prismatic crystals associated with K-feldspar or albite + quartz. The pegmatite lacks a continuous core zone; instead, there are sporadic central masses of coarse-grained milky quartz.

In the dumps of the southern half of the pegmatite, one complete and several partly broken nodules of dark phosphates were found. The largest nodule (Fig. 2: 50 $\times$ 30 $\times$ 20 cm) is partly covered by quartz. Other nodules locally may be coated by quartz or "cleavelandite". The nodules consist of an intergrowth of very dark green to black crystals of bobfergusonite with apatite, Mn-rich apatite and Mn-rich wyllieite (Fig. 3), with minor accessory sulfides (mainly sphalerite and pyrite), quartz and secondary limonite and hematite. The relatively simple association of minerals is typical of a poorly evolved pegmatite of the beryl – columbite – phosphate subtype of rare-element pegmatites (Černý 1991). Geochemically, this subtype is characterized by P prevalent over B, and Mn^{2+} prevalent over Fe^{2+} in the transition-metal phosphate minerals.

EXPERIMENTAL

A crystal measuring 0.10 $\times$ 0.10 $\times$ 0.12 mm was attached to a glass fiber and mounted on a Bruker *P*4 diffractometer equipped with a CCD detector and Mo*K*α radiation. Intensity and unit-cell data (Table 1) were collected and processed according to the procedures described by Cooper & Hawthorne (2001). The data were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. A total of 13000 reflections was measured out to 60.10 2θ using 60 s per frame, with index ranges $\overline{17} \leq h \leq 17$, $\overline{17} \leq k \leq 17$, $\overline{15} \leq l \leq 15$. Of the 5035 unique reflections, 2959 reflections were considered as observed ($|F_o| \lozenge 4\sigma F$).

The crystal used for X-ray diffraction was mounted on a Perspex disc, ground, polished, carbon-coated and analyzed with a Cameca SX–50 electron-microprobe operating under the following conditions in wavelength-

TABLE 1. MISCELLANEOUS INFORMATION FOR BOBFERGUSONITE FROM THE NANCY PEGMATITE

a (Å)	12.796(3)	crystal size (mm)	0.10 x 0.10 x 0.12
b	12.465(2)	radiation/monochromator	Mo$K\alpha$/Gr
c	11.001(2)	No. of reflections	13000
V (Å^3)	1740.1(5)	No. unique reflections	5035
β	97.39(3)	No. $|F_o| > 4\sigma(|F_o|)$	2959
Sp. Gr.	$P2_1/n$	R_{merge} (%)	2.6
Z	4	R_1 ($|F_o| > 4\sigma F$) (%)	2.7
μ (mm^{-1})	4.73	wR_2 (F_o^2) (%)	6.4
D_{calc} (g/cm^3)	3.66		

$R = \Sigma(|F_o|-|F_c|) / \Sigma|F_o|$

$wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}, \; w = 1 / \sigma F_o^2$

TABLE 2. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA* (apfu) FOR BOBFERGUSONITE FROM THE NANCY AND CROSS LAKE PEGMATITES**

	Nancy	Cross Lake		Nancy	Cross Lake
P_2O_5	43.64	45.10	P	6.00	6.03
Al_2O_3	4.88	7.50			
Fe_2O_3	9.16	6.70	Fe^{3+}	1.05	0.80
FeO	7.73	0.30	Al	0.93	1.40
ZnO	–	0.40	Σ	1.98	2.20
MnO	23.48	31.60			
MgO	2.28	0.40	Mn^{2+}	3.23	4.23
CaO	0.65	1.10	Fe^{2+}	1.12	0.04
Na_2O	6.41	6.80	Zn	–	0.05
Σ	98.23	99.90	Mg	0.55	0.09
			Ca	0.11	1.19
			Σ	5.01	4.60
			Na	2.02	2.08

* calculated on the basis of 6 P cations, adjusting Fe^{3+}/Fe^{2+} for electroneutrality;
** taken from Ercit et al. (1986b)

TABLE 3. ATOM COORDINATES AND ANISOTROPIC-DISPLACEMENT PARAMETERS FOR BOBFERGUSONITE FROM THE NANCY PEGMATITE

|	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
$M(1)$	0.13420(4)	0.23941(4)	−0.00222(4)	0.0102(3)	0.0156(3)	0.0118(2)	0.00211(18)	−0.00031(19)	0.0004(2)	0.01269(15)
$M(2)$	0.63042(4)	0.23867(4)	0.00089(4)	0.0113(3)	0.0149(3)	0.0124(2)	−0.00105(19)	−0.00193(19)	0.0015(2)	0.01315(16)
$M(3)$	0.29672(3)	0.14728(4)	0.72252(3)	0.0102(3)	0.0099(3)	0.0108(2)	0.00094(18)	−0.00093(18)	−0.00120(18)	0.01049(15)
$M(4)$	0.79843(4)	0.14656(4)	0.72557(4)	0.0106(3)	0.0101(3)	0.0120(3)	0.00060(19)	−0.0003(2)	0.0001(2)	0.01102(16)
$M(5)$	0.46185(4)	0.16300(4)	0.28185(4)	0.0102(3)	0.0126(3)	0.0090(2)	−0.0020(2)	0.0002(2)	0.0010(2)	0.01071(16)
$M(6)$	0.96010(6)	0.16394(6)	0.28144(6)	0.0078(5)	0.0092(4)	0.0081(4)	−0.0006(3)	0.0009(3)	0.0004(3)	0.0084(2)
$X(1)$	0.24917(5)	0.00113(4)	−0.00326(4)	0.0354(3)	0.00972(19)	0.0228(2)	−0.00134(15)	0.01923(18)	−0.00170(16)	0.02130(14)
$X(2)$	0	0	0	0.0329(15)	0.0137(12)	0.0340(12)	0.0028(9)	0.0211(10)	0.0016(10)	0.0254(7)
$X(3)$	½	0	0	0.0380(16)	0.0143(13)	0.0462(15)	−0.0001(10)	0.0304(12)	0.0021(10)	0.0306(8)
$X(4)$	0.3713(2)	0.0174(2)	0.49650(18)	0.060(2)	0.0295(16)	0.0199(13)	−0.0015(10)	0.0122(12)	0.0008(13)	0.0352(10)
$X(5)$	0.8762(2)	0.0160(2)	0.50243(19)	0.060(2)	0.0296(18)	0.0211(14)	−0.0001(11)	0.0154(14)	0.0048(14)	0.0359(11)
$P(1)$	0.38358(6)	0.21696(6)	0.00290(6)	0.0078(4)	0.0086(4)	0.0078(3)	−0.0001(3)	0.0015(3)	−0.0002(3)	0.00802(16)
$P(2)$	0.88391(6)	0.21205(6)	0.00852(6)	0.0074(4)	0.0081(4)	0.0075(3)	0.0004(3)	0.0017(3)	0.0002(3)	0.00757(16)
$P(3)$	0.20062(6)	0.11529(6)	0.25736(6)	0.0075(4)	0.0080(4)	0.0081(3)	−0.0001(3)	0.0014(3)	0.0002(3)	0.00783(17)
$P(4)$	0.70687(6)	0.11406(6)	0.26218(6)	0.0077(4)	0.0075(4)	0.0092(3)	0.0001(3)	0.0021(3)	0.0006(3)	0.00805(17)
$P(5)$	0.06085(6)	0.09455(6)	0.73786(6)	0.0070(4)	0.0088(4)	0.0081(3)	0.0004(3)	0.0012(3)	0.0001(3)	0.00796(17)
$P(6)$	0.56023(6)	0.10271(6)	0.74000(6)	0.0079(4)	0.0082(4)	0.0098(3)	0.0002(3)	0.0019(3)	−0.0007(3)	0.00857(17)
$O(1)$	0.29738(15)	0.21362(14)	0.54446(15)	0.0120(12)	0.0127(11)	0.0108(9)	0.0000(8)	0.0032(9)	−0.0023(9)	0.0117(5)
$O(2)$	0.79913(14)	0.20976(14)	0.54512(15)	0.0067(11)	0.0129(11)	0.0099(9)	−0.0002(8)	0.0026(8)	−0.0021(8)	0.0097(4)
$O(3)$	0.46853(15)	0.22141(14)	0.45476(15)	0.0102(11)	0.0104(10)	0.0101(9)	−0.0010(8)	0.0046(8)	0.0017(8)	0.0100(4)
$O(4)$	0.96558(15)	0.21419(14)	0.44520(15)	0.0071(11)	0.0120(10)	0.0077(8)	−0.0004(8)	0.0013(8)	0.0022(8)	0.0089(4)
$O(5)$	0.33192(15)	0.37396(15)	0.41874(15)	0.0166(12)	0.0108(10)	0.0117(9)	0.0015(8)	0.0028(8)	0.0033(9)	0.0129(4)
$O(6)$	0.82928(15)	0.36872(15)	0.41534(15)	0.0162(12)	0.0121(11)	0.0125(9)	0.0008(8)	0.0034(9)	0.0089(9)	0.0135(4)
$O(7)$	0.44212(15)	0.35398(14)	0.61396(15)	0.0168(12)	0.0111(10)	0.0087(8)	−0.0013(8)	0.0027(8)	−0.0043(9)	0.0121(4)
$O(8)$	0.94709(15)	0.34870(15)	0.60403(15)	0.0194(12)	0.0123(11)	0.0092(9)	−0.0016(8)	0.0010(8)	−0.0072(9)	0.0137(5)
$O(9)$	0.11059(14)	0.17153(14)	0.31505(14)	0.0084(10)	0.0088(10)	0.0109(9)	−0.0010(8)	0.0035(8)	0.0006(8)	0.0092(4)
$O(10)$	0.62192(15)	0.17581(15)	0.32160(15)	0.0123(11)	0.0094(10)	0.0122(9)	−0.0006(8)	0.0030(8)	0.0010(8)	0.0112(4)
$O(11)$	0.13403(14)	0.15220(14)	0.65739(16)	0.0106(11)	0.0122(11)	0.0181(10)	0.0045(9)	0.0083(9)	0.0023(9)	0.0131(4)
$O(12)$	0.63820(15)	0.15597(14)	0.66157(15)	0.0133(11)	0.0106(10)	0.0168(9)	0.0012(9)	0.0073(9)	0.0004(9)	0.0131(4)
$O(13)$	0.11172(15)	0.40832(14)	0.37427(15)	0.0136(12)	0.0131(11)	0.0112(9)	−0.0013(8)	−0.0016(9)	−0.0001(9)	0.0129(5)
$O(14)$	0.61316(15)	0.41262(14)	0.37201(15)	0.0138(12)	0.0138(11)	0.0092(9)	−0.0013(8)	−0.0033(9)	−0.0004(9)	0.0127(5)
$O(15)$	0.17331(15)	0.39990(14)	0.62261(15)	0.0125(12)	0.0123(11)	0.0088(9)	0.0022(8)	0.0015(8)	0.0006(8)	0.0112(5)
$O(16)$	0.67093(15)	0.39784(14)	0.61741(14)	0.0132(12)	0.0119(11)	0.0078(9)	0.0012(8)	0.0001(8)	−0.0006(9)	0.0111(5)
$O(17)$	0.29979(15)	0.18730(15)	0.27910(15)	0.0086(11)	0.0149(11)	0.0102(9)	−0.0018(8)	−0.0004(8)	−0.0025(9)	0.0114(4)
$O(18)$	0.80896(15)	0.18240(15)	0.27782(15)	0.0098(10)	0.0106(10)	0.0099(9)	−0.0005(8)	0.0016(8)	−0.0012(8)	0.0101(4)
$O(19)$	0.46212(14)	0.17609(14)	0.73756(14)	0.0088(10)	0.0116(10)	0.0118(9)	0.0005(8)	0.0022(8)	0.0012(8)	0.0106(4)
$O(20)$	0.95903(15)	0.16093(15)	0.73393(15)	0.0106(11)	0.0131(10)	0.0140(9)	0.0011(8)	0.0017(8)	0.0022(8)	0.0125(4)
$O(21)$	0.27858(15)	0.50788(15)	0.18067(16)	0.0176(12)	0.0110(11)	0.0221(10)	−0.0065(9)	0.0041(9)	−0.0058(9)	0.0168(5)
$O(22)$	0.77610(15)	0.50661(15)	0.17456(16)	0.0168(12)	0.0102(11)	0.0209(10)	−0.0026(9)	0.0057(9)	−0.0030(9)	0.0157(5)
$O(23)$	0.46455(15)	0.48170(14)	0.81566(15)	0.0159(11)	0.0093(10)	0.0105(9)	−0.0011(8)	−0.0001(8)	0.0024(8)	0.0120(4)
$O(24)$	0.97240(16)	0.49340(15)	0.81578(16)	0.0165(11)	0.0109(10)	0.0200(10)	0.0034(9)	0.0023(9)	0.0045(9)	0.0158(4)
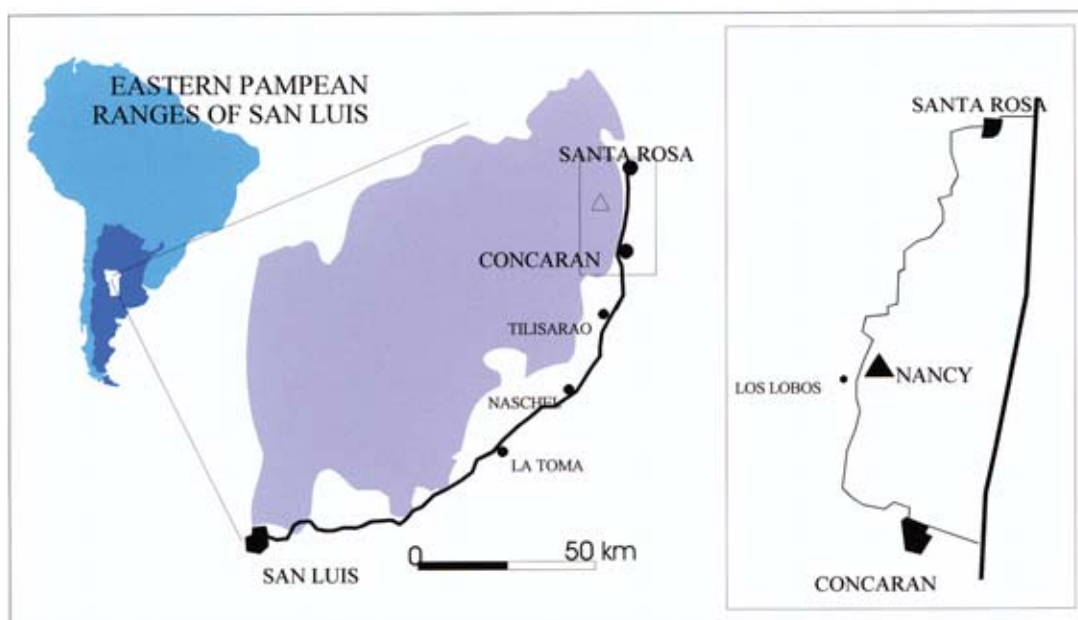
FIG. 1.   The Nancy pegmatite (denoted by a triangle) belongs to the Conlara pegmatite field, situated in the northern part of the
           Eastern Pampean Ranges of San Luis, Argentina.

FIG. 2.   Phosphate nodule from the Nancy pegmatite; a dark phosphate center is surrounded
           by quartz; note the hammer for scale.

FIG. 3. Phosphatic nodule from the Nancy pegmatite; a dark phosphate center is surrounded by quartz.

dispersion mode: excitation voltage 15 kV, specimen current 20 nA, beam size 15 μm, peak count-time 20 s, background count-time 10 s. The following standards and crystals were used for $K\alpha$ X-ray lines for the elements sought: Na: marićite, TAP; Mg: forsterite, TAP; Si: diopside, PET; P: marićite, PET; Ca: apatite, PET; Mn: spessartine, LiF; Fe: marićite, LiF; Zn: gahnite, LiF; As: mimetite, TAP. Ten points were analyzed, and the mean chemical composition is given in Table 2. The resulting unit formula is $Na_{2.02}$ ($Mn^{2+}_{3.23}$ $Fe^{2+}_{1.12}$ $Mg_{0.55}$ $Ca_{0.11}$) ($Fe^{3+}_{1.05}$ $Al_{0.93}$) (PO_4)$_6$, calculated on the basis of 6 P cations and 24 anions, with Fe^{3+}/Fe^{2+} adjusted for electroneutrality.

CRYSTAL-STRUCTURE REFINEMENT

All calculations were done with the SHELXTL PC (Plus) system of programs; R indices are of the form given in Table 1 and are expressed as percentages. Crystal-structure refinement was initiated with the atom coordinates of Ercit *et al.* (1986b). Note that the orientation is conformable with the $I2/a$ orientation adopted for caryinite (Ercit 1993) and arseniopleite (Tait & Hawthorne 2003).

The sum of the medium-sized divalent and trivalent cations in the unit formula is 7.03 *apfu* (atoms per formula unit), and the sum of the large univalent cations is 2.02 *apfu*. These sums are in accord with (Mn + Mg + Fe + Al) ordered at the $M(1)$ to $M(6)$ and $X(1)$ sites, and Na ordered at the $X(2)$ to $X(5)$ sites, as found by Ercit *et al.* (1986b). Accordingly, the $M(1)$ to $M(5)$ and $X(1)$ sites were considered as occupied by Mn and Mg, $M(6)$

was considered as fully occupied by Al and Fe, and the $X(2)$ to $X(6)$ sites were considered as half-occupied by Na at the start of the refinement. Full-matrix least-squares refinement of all positional, anisotropic-displacement and site-occupancy variables converged to an R_1 index of 2.7%. Refined coordinates and anisotropic-displacement factors are listed in Table 3, selected interatomic distances are given in Table 4, and site-scattering values and assigned site populations are given in Table 5. Observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

Site populations

There are six M sites, each of which is coordinated by six O-atoms in an octahedral arrangement, with <M–O> distances ranging from 2.216 Å at $M(1)$ to 1.918 Å at $M(6)$ and refined site-scattering values from 14.1 to 25.3 *epfu* (electrons per formula unit). In addition, one of the X sites is octahedrally coordinated by six O-atoms with a <$X(1)$–O> distance of 2.236 Å and a refined site-scattering value of 25.4 *epfu*. These sites must be occupied by the small- to medium-sized divalent (Mg, Fe^{2+}, Mn^{2+}) and trivalent (Al, Fe^{3+}) cations. There are approximately two trivalent cations in the unit formula (0.94 Al + 0.98 Fe^{3+}) *apfu* (Table 2). However, there is only one site that is obviously dominated by small trivalent cations: the $M(6)$ site has a refined site-scattering

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) IN
BOBFERGUSONITE FROM THE NANCY PEGMATITE

M(1)–O(2)a	2.201(2)		M(2)–O(1)b	2.210(2)
M(1)–O(3)a	2.168(2)		M(2)–O(4)a	2.199(2)
M(1)–O(10)a	2.195(2)		M(2)–O(9)b	2.316(2)
M(1)–O(12)a	2.220(2)		M(2)–O(11)b	2.190(2)
M(1)–O(14)a	2.341(2)		M(2)–O(13)b	2.295(2)
M(1)–O(16)a	2.173(2)		M(2)–O(15)b	2.211(2)
<M(1)–O>	2.216		<M(2)–O>	2.237
M(3)–O(1)	2.127(2)		M(4)–O(2)	2.137(2)
M(3)–O(6)c	2.118(2)		M(4)–O(5)d	2.129(2)
M(3)–O(11)	2.113(2)		M(4)–O(12)	2.084(2)
M(3)–O(18)c	2.208(2)		M(4)–O(17)d	2.153(2)
M(3)–O(19)	2.132(2)		M(4)–O(20)	2.053(2)
M(3)–O(22)c	1.998(2)		M(4)–O(21)d	1.996(2)
<M(3)–O>	2.116		<M(4)–O>	2.092
M(5)–O(3)	2.028(2)		M(6)–O(4)	1.900(2)
M(5)–O(8)a	1.946(2)		M(6)–O(7)b	1.841(2)
M(5)–O(10)	2.045(2)		M(6)–O(9)e	1.916(2)
M(5)–O(17)	2.092(2)		M(6)–O(18)	1.943(2)
M(5)–O(20)a	2.256(2)		M(6)–O(19)b	2.053(2)
M(5)–O(24)a	1.986(2)		M(6)–O(23)b	1.853(2)
<M(5)–O>	2.059		<M(6)–O>	1.918
X(1)–O(5)f	2.168(2)		X(2)–O(5)a ×2	2.720(2)
X(1)–O(6)a	2.173(2)		X(2)–O(7)a ×2	2.382(2)
X(1)–O(13)f	2.423(2)		X(2)–O(14)a ×2	2.406(2)
X(1)–O(14)a	2.335(2)		X(2)–O(16)a ×2	2.711(2)
X(1)–O(15)f	2.153(2)		<X(2)–O>	2.555
X(1)–O(16)a	2.166(2)			
<X(1)–O>	2.236		X(4)–O(1)	2.698(3)
			X(4)–O(3)	2.893(3)
X(3)–O(6)a ×2	2.792(2)		X(4)–O(12)g	2.767(3)
X(3)–O(8)a ×2	2.350(2)		X(4)–O(21)f	2.555(3)
X(3)–O(13)b ×2	2.402(2)		X(4)–O(22)c	2.454(3)
X(3)–O(15)b ×2	2.743(2)		X(4)–O(24)a	2.511(3)
<X(3)–O>	2.572		X(4)–O(24)h	2.700(3)
			<X(3)–O>	2.654
X(5)–O(2)	2.673(3)			
X(5)–O(4)	2.827(3)			
X(5)–O(11)g	2.728(3)			
X(5)–O(21)d	2.475(3)			
X(5)–O(22)i	2.574(3)			
X(5)–O(23)b	2.469(3)			
X(5)–O(23)h	2.700(3)			
<X(5)–O>	2.635			
P(1)–O(2)a	1.532(2)		P(4)–O(10)	1.544(2)
P(1)–O(4)a	1.553(2)		P(4)–O(15)b	1.550(2)
P(1)–O(6)a	1.542(2)		P(4)–O(18)	1.551(2)
P(1)–O(8)a	1.528(2)		P(4)–O(22)i	1.512(2)
<P(1)–O>	1.539		<P(4)–O>	1.539
P(2)–O(1)b	1.534(2)		P(5)–O(11)	1.546(2)
P(2)–O(3)b	1.541(2)		P(5)–O(14)c	1.543(2)
P(2)–O(5)b	1.549(2)		P(5)–O(20)j	1.539(2)
P(2)–O(7)b	1.535(2)		P(5)–O(23)k	1.543(2)
<P(2)–O>	1.54		<P(5)–O>	1.543
P(3)–O(9)	1.552(2)		P(6)–O(12)	1.550(2)
P(3)–O(16)a	1.546(2)		P(6)–O(13)d	1.544(2)
P(3)–O(17)	1.548(2)		P(6)–O(19)	1.551(2)
P(3)–O(21)f	1.510(2)		P(6)–O(24)h	1.530(2)
<P(3)–O>	1.539		<P(6)–O>	1.544

a: x–1/2, –y+1/2, z–1/2; b: x+1/2, –y+1/2, z–1/2; c: x–1/2,
–y+1/2, z+1/2; d: x+1/2, –y+1/2, z+1/2; d: x+1, y, z; f: –x+1/2,
y–1/2, –z+1/2; g: –x+1, –y, –z+1; h: –x+3/2, y–1/2, –z+3/2;
i: –x+3/2, y–1/2, –z+1/2; j: x–1, y, z; k: –x+1/2, y–1/2, –z+3/2

value of 14.1 *epfu* (Table 5) and a <M(6)–O> bond-length of 1.918 Å (Table 4). Hence M(6) must be occupied predominantly by Al ($^{[6]}$r = 0.535 Å, Z = 13), with a small amount of Fe^{3+} ($^{[6]}$r = 0.645 Å, Z = 26). The balance of the Fe^{3+} in the unit formula must occur at one or more of the M(1–5) and X(1) sites.

There is one aspect that remains unclear about the unit formula: the assignment of Ca to the M(1) to M(6), X(1) or the X(2) to X(5) sites. The sum of the cations assigned to M(1)–M(6) and X(1) is 7.03 *apfu* including Ca and 6.92 *apfu* excluding Ca; the sum of the cations assigned to the X(2)–X(5) sites is 2.02 *apfu* excluding Ca and 2.13 *apfu* including Ca. Thus the cation sums are in favor of Ca being assigned to the M(1)–M(6) and X(1) sites (Table 2). We may also examine this issue *via* the refined site-scattering values at these two groups of sites (Table 6). Where Ca is assigned to the M(1)–M(6) and X(1) sites, the agreement between the refined and assigned (from the unit formula) site-scattering values is much closer than where Ca is assigned to the X(2)–X(5) sites (2.5 and 0.1 *versus* 4.7 and 2.3 *epfu*, respectively, Table 6). Hence all indications are that Ca must occur at the M(1)–M(6) and X(1) sites. Six-coordinated Ca (r = 1.00 Å; Shannon 1976) is much larger than the next largest cation in the unit formula, [6]-coordinated Mn^{2+} (r = 0.83 Å). The two largest octahedra in the structure are M(2) and X(1) at 2.237 and 2.236 Å, respectively. The sizes of these octahedra give us no indication of preferential occupancy of Ca. However, the refined site-scattering values at these two sites are 24.8 and 25.4 *epfu*, respectively; as the atomic number of Ca (Z = 20) is less than that of Mn (Z = 25), the refined site-scattering values support the view that Ca occurs at M(2), and we have assigned the site populations accordingly.

The M(1) site has a refined site-scattering value of 25.3 *epfu* and a <M(1)–O> distance of 2.216 Å, indicating that this site is also fully occupied by Mn^{2+}. This leaves three sites, M(3) to M(5), that must be occupied by the remaining unassigned cations in the unit formula: Fe^{2+}, Mn^{2+}, Mg and Fe^{3+}. As Mg (Z = 13) scatters X-rays very differently from Mn (Z = 25) or Fe (Z = 26), we may assign Mg and (Fe + Mn) contents of these three sites directly from the refined site-scattering values (Table 5). The Fe^{2+}, Mn^{2+} and Fe^{3+} contents were then assigned on the basis of mean bond-lengths, using the unit formula of the crystal (Table 2) as a constraint.

There are five X sites, X(1)–X(5), each having a wide dispersion of X–O distances. The X(1) site is occupied by Mn^{2+} and is discussed above. The X(2) and X(3) sites are each surrounded by eight O-atoms, with <X–O> distances of 2.550 and 2.572 Å, respectively. The X(4) and X(5) sites are actually [7]-coordinated, as is also the case in caryinite (Ercit 1993) and arseniopleite (Tait & Hawthorne 2003), with <X–O> distances of 2.654 and 2.635 Å, respectively. At first sight, it seems unusual that the mean bond-lengths of the [8]-coordinated X–O polyhedra are less than the mean bond-lengths of the

TABLE 5. REFINED SITE-SCATTERING VALUES AND ASSIGNED SITE-POPULATIONS FOR BOBFERGUSONITE FROM THE NANCY PEGMATITE

	Refined site-scattering (*epfu*)	$<M, X–O>$ Å	Site population (*apfu*)	Calculated site-scattering	$<M,X–O>_{calc}$* Å
$M(1)$	25.25(4)	2.216	1.00 Mn^{2+}	25	2.207
$M(2)$	24.84(4)	2.237	0.89 Mn^{2+} + 0.11 Ca	24.5	2.226
$M(3)$	25.22(4)	2.116	0.38 Fe^{2+} + 0.32 Mn^{2+} + 0.24 Fe^{3+} + 0.06 Mg	24.8	2.130
$M(4)$	23.31(7)	2.092	0.53 Fe^{2+} + 0.25 Fe^{3+} + 0.22 Mg	22.9	2.106
$M(5)$	22.09(7)	2.059	0.28 Fe^{2+} + 0.42 Fe^{3+} + 0.30 Mg	21.8	2.072
$M(6)$	14.14(3)	1.918	0.94 Al + 0.06 Fe^{3+}	13.8	1.942
$X(1)$	25.42(5)	2.236	1.00 Mn^{2+}	25	2.207
$X(2)$	5.06(3)	2.550	0.46 Na + 0.04 □	5	–
$X(3)$	4.87(3)	2.572	0.44 Na + 0.06 □	4.8	–
$X(4)$	6.31(6)	2.654	0.57 Na + 0.43 □	6.3	–
$X(5)$	5.81(6)	2.635	0.53 Na + 0.47 □	5.8	–

* radii from Shannon (1976)

TABLE 6. AGGREGATE SITE-SCATTERING VALUES (*epfu*) FROM CRYSTAL-STRUCTURE REFINEMENT (SREF) AND FROM THE UNIT FORMULA

Σ sites	SREF	Unit formula* [Ca^M]	[Ca^X]
$M(1)$–$M(6)$ + $X(1)$	160.3	157.8	155.6
$X(2)$–$X(5)$	22.1	22.2	24.2

* calculated from electron-microprobe analysis

[7]-coordinated polyhedra. However, the polyhedra are only approximately half-occupied, and hence their sizes do not completely reflect the size of their constituent cation(s), as we do not know the "effective size" of a vacancy at each of these sites. Furthermore, the [7]-coordinated nature of the $X(4)$ and $X(5)$ sites is a result of positional disorder of their constituent cations, indicating that the polyhedra may be ideally somewhat large to accommodate such cations, with the result that the cations are (statically or dynamically) displaced from the center of the polyhedron.

All Na was assigned to $X(1)$–$X(5)$ on the basis of the refined site-scattering values; the sum of the resulting site-populations (2.00 Na *apfu*) is in close accord with the Na content of the crystal derived from the chemical composition (2.02 Na *apfu*, Table 2), with the remainder of each site vacant. The sum of the bond valences incident at the M site is in reasonable agreement with the aggregate formal charges at these sites (Table 7), further supporting the site populations assigned in Table 5.

Structure topology

The six M octahedra share edges to form two linear trimers [$M(5) = M(1) = M(4)$] and [$M(6) = M(2) = M(3)$] (Fig. 4). The trimers are linked in the a and c directions

by sharing corners with (PO_4) tetrahedra to form a layer parallel to (101). The $X(1)$, $X(2)$ and $X(3)$ polyhedra share edges to form chains extending in the a direction; the $X(4)$ and $X(5)$ polyhedra also form chains parallel to a (Fig. 4). These chains link through (PO_4) tetrahedra to form sheets parallel to (101) (Fig. 4). These sheets are seen "edge-on" in Figure 5, and they alternate with the sheet of M polyhedra in the b direction.

CATION ORDER IN BOBFERGUSONITE

Why does bobfergusonite exhibit the pattern of cation order given in Table 5? This is related to the connectivity of the structure and its effect on the incident bond-valence sums at the anions coordinating each of the M sites. The sets of anions coordinating each M site have to receive a total of 12 *vu* (valence units) in order to satisfy the valence-sum rule (Brown 1981, Hawthorne 1994, 1997). For each M polyhedron, we may divide this aggregate bond-valence into two parts: (1) bond-valence incident from the central cation, and (2) bond-valence incident from the nearest-neighbor cations. The total bond-valence supplied by the central cation to its coordinating anion is equal to the aggregate formal valence of the cations occupying the central M site. The total bond-valence supplied by the nearest-neighbor cations is a function of the number of those bonds, and to a larger extent, the charges at those cation sites. The number of bonds received by each polyhedron may be represented by the mean coordination number of its coordinating anions. The lower the (aggregate) formal charge of the central cation, the greater the number of incident bonds required by the coordinating anions (*i.e.*, the higher their aggregate coordination-number). This relation is examined in Figure 6. There is an inverse correlation between aggregate formal charge and mean anion-coordination number for the M sites in bobfergusonite, in accord with above discussion, indicating that it is the connectivity (bond topology) of the struc-
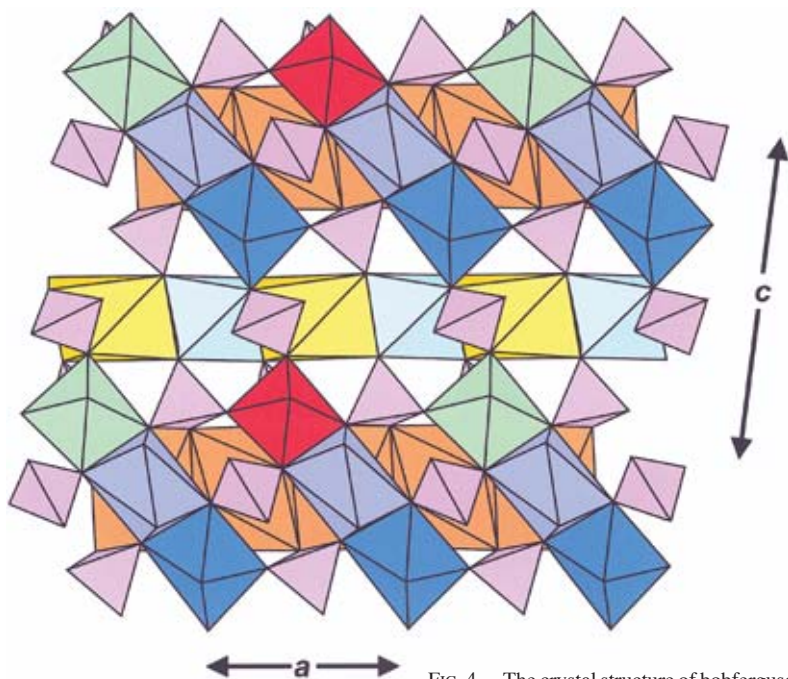
FIG. 4.   The crystal structure of bobfergusonite projected down [010]; the poly-
hedra are colored as follows: P: mauve; $^{[6]}X(1)$; pale blue; $^{[8]}X(2)$, $^{[8]}X(3)$:
yellow; $^{[7]}X(4)$, $^{[7]}X(5)$: orange; $^{[8]}M(1)$, $^{[8]}M(2)$: gray; $^{[8]}M(3)$, $^{[8]}M(4)$: dark
blue; $^{[8]}M(5)$: green; $^{[8]}M(6)$: red. The $M(1)$ (gray) and $M(4)$ (dark blue)
polyhedra belong to the trimer containing $M(5)$ (green); the $M(2)$ (gray) and
$M(3)$ (dark blue) polyhedra belong to the trimer containing the $M(6)$ (red)
polyhedron.

FIG. 5.   The crystal structure of
bobfergusonite projected onto
(100), showing the linkage be-
tween the X polyhedra and the
tetrahedra [omitting the M and
$X(1)$ polyhedra]; legend as in
Figure 4, with the $X(4)$ and $X(5)$
cations shown as orange circles.
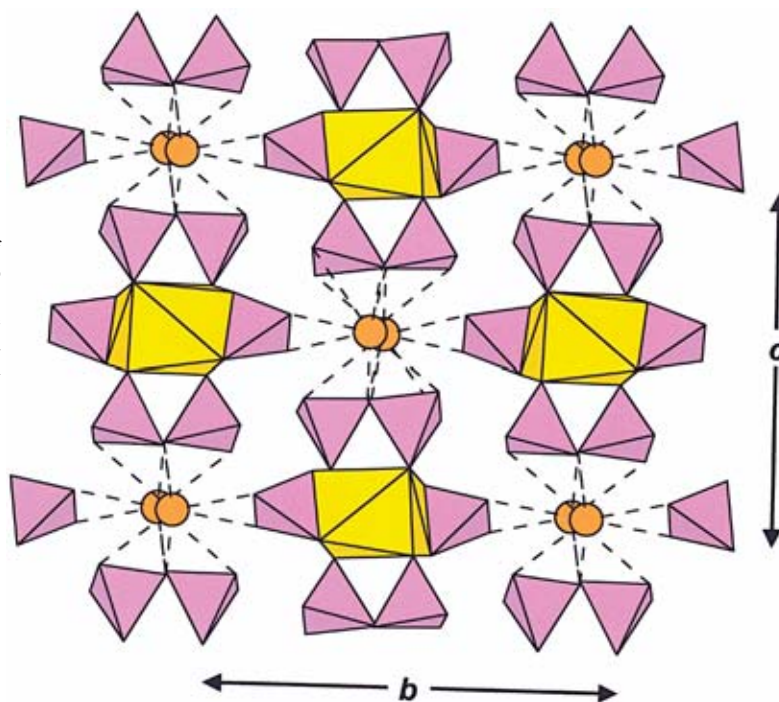
TABLE 7. BOND-VALENCE TABLE* (*vu*) FOR BOBFERGUSONITE FROM THE NANCY PEGMATITE

	X(1)	X(2)	X(3)	X(4)	X(5)	M(1)	M(2)	M(3)	M(4)	M(5)	M(6)	P(1)	P(2)	P(3)	P(4)	P(5)	P(6)	Σ
O(1)				0.09			0.33	0.37					1.27					2.06
O(2)						0.10	0.32		0.34			1.28						2.04
O(3)			0.06				0.35			0.45		1.25						2.10
O(4)				0.07			0.34				0.52	1.20						2.14
O(5)	0.35	0.09×2↓							0.35				1.22					1.91
O(6)	0.51		0.08×2↓					0.37					1.24					2.20
O(7)		0.19×2↓									0.61		1.27					2.07
O(8)			0.21×2↓							0.56			1.29					2.06
O(9)							0.25				0.50			1.21				1.96
O(10)						0.33				0.43					1.24			1.99
O(11)				0.09			0.35	0.38								1.23		2.04
O(12)			0.08				0.31		0.39								1.21	1.99
O(13)	0.19		0.19×2↓				0.27										1.24	1.88
O(14)	0.23	0.18×2↓				0.23									1.24			1.88
O(15)	0.37		0.09×2↓				0.33							1.21				2.00
O(16)	0.35	0.09×2↓				0.35							1.23					1.93
O(17)										0.33	0.38		1.22					1.93
O(18)							0.30			0.46					1.21			1.97
O(19)							0.36			0.35							1.21	1.92
O(20)									0.42	0.25						1.25		1.92
O(21)				0.13	0.16				0.49					1.36				2.14
O(22)				0.16	0.13			0.52							1.35			2.16
O(23)					0.16						0.59					1.24		2.08
					0.09													
O(24)					0.14						0.50						1.28	2.02
					0.19													
Σ	2	1.03	1.12	0.77	0.80	1.89	1.87	2.30	2.32	2.56	3.03	5.01	5.01	5.02	5.01	4.96	4.94	
Σ**	2	1	1	1	1	2	2	2.24	2.25	2.42	3	5	5	5	5	5	5	

* calculated from the curves of Brown (1981);
** sum of the aggregate formal charges at each site.

ture (as manifest in the anion-coordination numbers) that is the dominant factor controlling the pattern of order of the heterovalent cations.

CATION ORDER IN ALLUAUDITE, WYLLIEITE AND BOBFERGUSONITE

The patterns of cation order in the alluaudite (Moore 1971), wyllieite (Moore & Ito 1973, Moore & Molin-Case 1974) and bobfergusonite structures were examined in some detail by Ercit *et al.* (1986b), and Figure 7 is reproduced (in a modified form) from their paper. Ercit *et al.* (1986b) remarked on the need for "additional structure-refinements of wyllieite and bobfergusonite" to further characterize the patterns of cation order in these structures. In the alluaudite structure, the dominant trivalent cation is Fe^{3+}, and cation order may range from complete disorder of M^{2+} and Fe^{3+} (Fig. 7a) to complete order of Fe^{3+} at one site (Fig. 7b). In the wyllieite structure, both Al *and* Fe^{3+} are significant and show different patterns of order. Cation order ranges from order of Al at one site and disorder of M^{2+} and Fe^{3+} over two sites (Fig. 7c) to order of Al at one site,

Fe^{3+} (+ M^{2+}) at a second site, and M^{2+} at a third site (Fig. 7d).

In the structure of bobfergusonite, there are two distinct edge-sharing trimers of octahedra (Fig. 7e). In one trimer, $[M(6) = M(2) = M(3)$; here, "=" indicates edges sharing], one site is completely occupied by trivalent cations, dominantly Al, one site is completely occupied by divalent cations, and the third site is occupied primarily by divalent cations but with significant (~20%) trivalent cations. In the other trimer, $[M(5) = M(1) = M(4)]$, one site is occupied primarily by both trivalent and divalent cations, the central site is occupied completely by divalent cations, and the third site is occupied primarily by divalent cations but with significant (~25%) trivalent cations. The patterns of order in both refinements of bobfergusonite are compared with the ideal pattern of order in end-member bobfergusonite in Figure 8. In both the structures, the site populations in the $[M(6) = M(2) = M(3)]$ trimer are closer to those in ideally ordered end-member bobfergsonite than the site populations in the $[M(5) = M(1) = M(4)]$ trimer: the $M(6)$ site is completely occupied by trivalent cations in both structures, whereas the $M(5)$ site has dominant trivalent
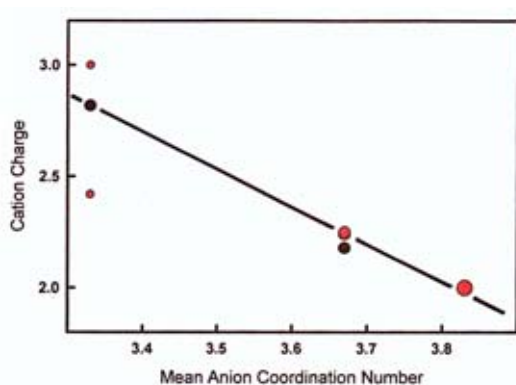
cations but with significant divalent cations. In addition,
both structures contain significant trivalent cations at the
$M(3)$ and $M(4)$ sites, which contain only divalent cat-
ions in the ideally ordered end-member (Fig. 8). Only
the $M(1)$ and $M(2)$ sites are totally in accord with the
ideally ordered end-member in that they are occupied
only by divalent cations.

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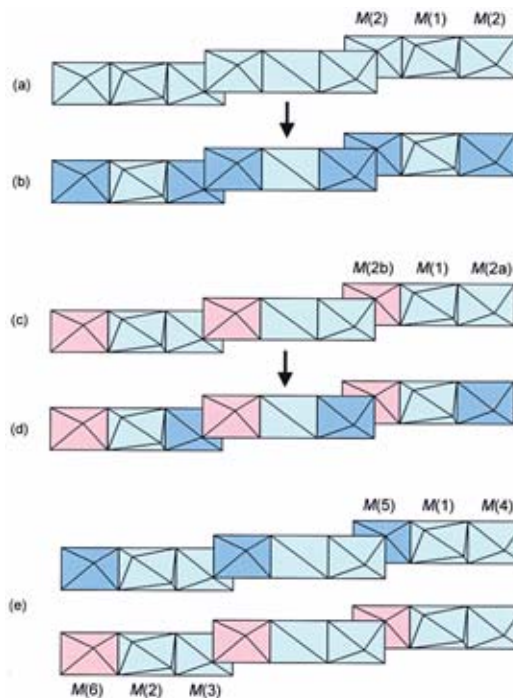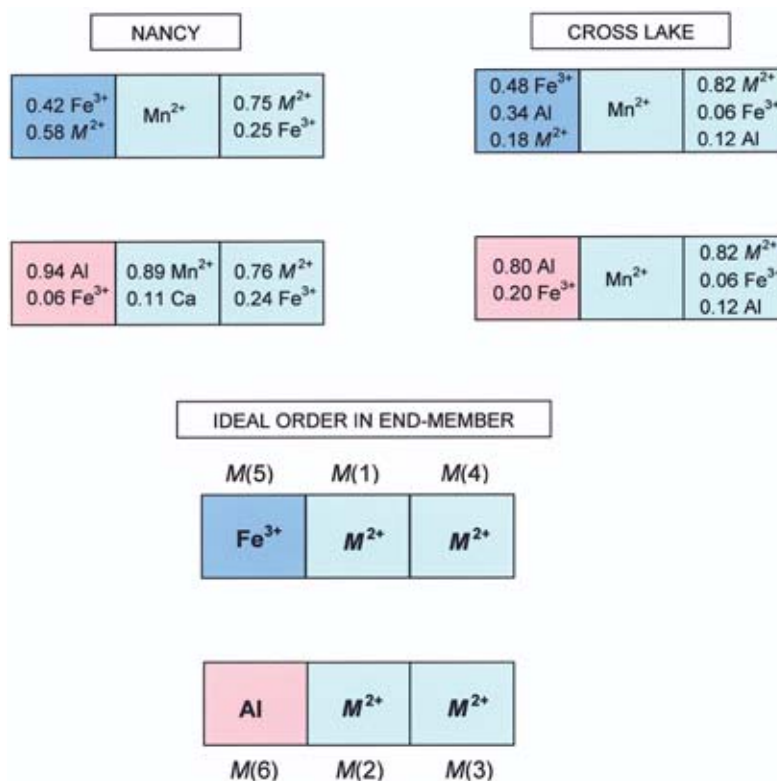   604.

FIG. 8.   Patterns of cation order in (a) Nancy bobfergusonite, (b) Cross Lake bobfergusonite, (c) ideal-ordered end-member bobfergusonite; legend as in Figure 5. Note that the trimers have been shifted in their relative position (*cf*. Fig. 4) for ease of comparison of site populations.

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