MANITOBAITE, Na₁₆ Mn²⁺₂₅ Al₈ (PO₄)₃₀, A NEW PHOSPHATE MINERAL SPECIES FROM CROSS LAKE, MANITOBA, CANADA

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Abstract

Manitobaite, ideally $Na_{16} Mn^{2+}_{25} Al_8 (PO_4)_{30}$, is a new mineral species from Cross Lake, Manitoba, Canada. It occurs as large crystals or cleavage masses intergrown with other phosphate minerals in a phosphate pod in the intermediate and core zones of pegmatite #22 on the southeastern shoreline of a small unnamed island in Cross Lake, Manitoba, about 5 km north–northwest of the Cross Lake settlement, longitude 54° 41' N, latitude 97° 49' W. Associated minerals are fluorapatite, chlorapatite, bobfergusonite, eosphorite, dickinsonite, fillowite, triploidite, goyazite, perloffite, beusite, triplite, as well as quartz, K-feldspar, muscovite, schorl, beryl, spessartine, gahnite and (Nb,Ta,Sn) oxides. Manitobaite is opaque in large crystals (up to 4 cm), and transparent to translucent in small (<1 mm) grains. Color varies from green to brown, with a colorless to very pale green or very pale greenish brown streak and a vitreous to resinous luster; manitobaite does not fluoresce under ultraviolet light. The cleavage is perfect on {010}, there is no parting, the tenacity is brittle, and the fracture is hackly. The following properties were measured on the green variety of manitobaite. The measured and calculated densities are 3.621(6) and 3.628 g cm⁻³, respectively. Manitobaite is biaxial negative with α 1.682, β 1.691, γ 1.697 (all ±0.001), with X ∧ **a** = 31.7° (in β obtuse), Y ‖ **b**, Z ∧ **c** = 20.2° (in β acute); $2V_{obs}$ = 78.1(6)°, $2V_{calc}$ = 77.9°. It is pleochroic X = orange brown, Y = green, Z = greenish brown, with absorption Y ≥ Z > X and dispersion *r* > *v*, medium. Manitobaite is monoclinic, *Pc*, *a* 13.4516(15), *b* 12.5153(16), *c* 26.661(3) Å, β 101.579(10)°, *V* 4397.1(6) Å³, Z = 2, *a*:*b*:*c* = 1.07482:1:2.13027. The strongest seven lines in the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 2.715(100)(242), 2.730(50)(404), 3.494(47)(313), 3.078(27)(3̄17), 2.518(22)(5̄15), 2.881(21)(1̄19), and 6.260(20)(020). A chemical analysis with an electron microprobe gave P₂O₅ 44.19, Al₂O₃ 6.91, FeO 7.79, MnO 27.57, ZnO 0.54, MgO 0.73, CaO 1.71, Na₂O 9.97, for a total of 99.58 wt%. The resulting empirical formula, using the valence states of Fe determined by Mössbauer spectroscopy, is $Na_{15.55} Ca_{1.47} Mg_{0.88} Fe^{2+}_{4.19} Mn^{2+}_{18.78} Zn_{0.32} Al_{6.54} Fe^{3+}_{1.05} P_{30.08} O_{120}$ based on 120 O²⁻ anions *pfu*. The general formula is $(\mathbf{Na},Ca,\square)_{16} (\mathbf{Mn^{2+}},Fe^{2+},Ca,Al,Fe^{3+},Mg,Zn)_{25} (\mathbf{Al},Fe^{3+},Mg,Mn^{2+}, Fe^{2+})_8 (PO_4)_{30}$, and the end-member formula is $Na_{16} Mn^{2+}_{25} Al_8 (PO_4)_{30}$. The crystal structure of manitobaite is an ordered superstructure of the alluaudite arrangement with a cell volume five times that of alluaudite.

Keywords: manitobaite, new mineral species, phosphate, alluaudite superstructure, granitic pegmatite, electron-microprobe analysis, Mössbauer spectroscopy, optical properties, X-ray powder-diffraction pattern, Cross Lake, Manitoba, Canada.

Sommaire

La manitobaïte, de formule idéale $Na_{16} Mn^{2+}_{25} Al_8 (PO_4)_{30}$, est une nouvelle espèce minérale découverte au lac Cross, au Manitoba, Canada. Elle se présente en gros cristaux ou en masses clivables en intercroissance avec d'autres minéraux phosphatés dans une lentille de phosphate chevauchant les zones intermédiaire et du noyau de la pegmatite #22, exposée sur la rive sud–est d'une petite île sans nom dans le lac Cross, environ 5 km au nord–nord-ouest de la communauté de Cross Lake, longitude 54° 41' N, latitude 97° 49' O. Lui sont associés fluorapatite, chlorapatite, bobfergusonite, éosphorite, dickinsonite, fillowite, triploïdite, goyazite, perloffite, beusite, triplite, ainsi que quartz, feldspath potassique, muscovite, schorl, béryl, spessartine, gahnite et oxydes de (Nb,Ta,Sn). La manitobaïte est opaque en gros cristaux (jusqu'à 4 cm), et transparents à translucides en petits grains (<1 mm).

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La couleur varie de vert à brun, avec une rayure incolore ou vert ou brun verdâtre très pâle, et un éclat vitreux à résineux; la manitobaïte ne montre aucune fluorescence en lumière ultraviolette. Le clivage est parfait sur {010}, il n'y a aucun plan de séparation, la tenacité est cassante, et la fracture est crochue. Nous avons mesuré les propriétés suivantes de la manitobaïte verte. La densité mesurée est 3.621(6), et la densité calculée est 3.628 g cm⁻³. La manitobaïte est biaxe négative, avec α 1.682, β 1.691, γ 1.697 (dans chaque cas, ±0.001), avec X $\wedge$ **a** = 31.7° (dans l'angle β obtus), Y ∥ **b**, Z $\wedge$ **c** = 20.2° (dans l'angle β aigu); $2V_{obs}$ = 78.1(6)°, $2V_{calc}$ = 77.9°. Elle est pléochroïque, X = orange brun, Y = vert, Z = brun verdâtre, avec un schéma d'absorption Y ≥ Z > X, et une dispersion $r > v$, modérée. La manitobaïte est monoclinique, Pc, a 13.4516(15), b 12.5153(16), c 26.661(3) Å, β 101.579(10)°, V 4397.1(6) Å³, Z = 2, $a{:}b{:}c$ = 1.07482:1:2.13027. Les sept raies les plus intenses du spectre de diffraction (méthode des poudres) [d en Å(I)(hkl)] sont: 2.715(100)(242), 2.730(50)(404), 3.494(47)(313), 3.078(27)($\overline{3}$17), 2.518(22)($\overline{5}$15), 2.881(21)($\overline{1}$19), et 6.260(20)(020). Une analyse chimique avec une microsonde électronique a donné P_2O_5 44.19, Al_2O_3 6.91, FeO 7.79, MnO 27.57, ZnO 0.54, MgO 0.73, CaO 1.71, Na_2O 9.97, pour un total de 99.58% (poids). La formule empirique qui en résulte, avec les proportions de Fe^{2+} et Fe^{3+} établies par spectroscopie Mössbauer, serait $Na_{15.55}$ $Ca_{1.47}$ $Mg_{0.88}$ $Fe^{2+}_{4.19}$ $Mn^{2+}_{18.78}$ $Zn_{0.32}$ $Al_{6.54}$ $Fe^{3+}_{1.05}$ $P_{30.08}$ O_{120} sur une base de 120 anions O^{2-} par formule unitaire. La formule générale serait (**Na**,Ca,$\square$)$_{16}$ (**Mn²⁺**,Fe^{2+},Ca,Al,Fe^{3+},Mg,Zn)$_{25}$ (**Al**,Fe^{3+},Mg,Mn^{2+}, Fe^{2+})$_8$ $(PO_4)_{30}$, et la formule du pôle est Na_{16} Mn^{2+}_{25} Al_8 $(PO_4)_{30}$. Du point de vue structural, la manitobaïte est une surstructure ordonnée de l'arrangement de l'alluaudite, avec un volume de la maille cinq fois le volume de l'alluaudite.

(Traduit par a Rédaction)

Mots-clés: manitobaïte, nouvelle espèce minérale, phosphate, surstructure de l'alluaudite, pegmatite granitique, analyse avec une microsonde électronique, spectroscopie Mössbauer, propriétés optiques, diffraction X, méthode des poudres, lac Cross, Manitoba, Canada.

Introduction

The alluaudite structure-type can accommodate a wide variety of cations, giving rise to many minerals (Damour 1848, Moore 1971, Keller *et al.* 1981, 1982, Keller & Hess 1988, Ercit 1993, Auernhammer *et al.* 1993, Filatov *et al.* 2001, Tait & Hawthorne 2003, Redhammer *et al.* 2005, Sarp & Černý 2005) and a large number of synthetic analogues (Yakubovich *et al.* 1977, Warner *et al.* 1993, Antenucci *et al.* 1993, 1995, Leroux *et al.* 1995a, 1995b, Khorari *et al.* 1997a, 1997b, 1997c, Hatert 2008, Hatert *et al.* 2000, 2003, 2006a). Ordering of cations in the anion framework of this structure type gives rise to superstructures: wyllieite-group minerals (Moore & Ito 1973, Moore & Molin-Case 1974, Hatert *et al.* 2005, 2006b), and bobfergusonite (Ercit *et al.* 1986a, 1986b, Tait *et al.* 2004). During a systematic examination of the mineralogy of granitic pegmatites at Cross Lake, Manitoba, two new phosphate minerals were discovered that are ordered superstructures of the alluaudite structure, bobfergusonite (Ercit *et al.* 1986a, 1986b) and the mineral that is described here.

This mineral is named *manitobaite* after the province of Manitoba (Canada) in which the mineral was discovered. Both the mineral and the name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2008–064). The holotype specimen of manitobaite has been deposited in the mineral collection of the Royal Ontario Museum [100 Queens Park, Toronto, Ontario M5S 2C6, Canada, catalogue number M53321].

Occurrence

Manitobaite was found in pegmatite #22 on the southeastern shoreline of a small unnamed island in Cross Lake, Manitoba, about 5 km north–northwest of the Cross Lake settlement (Anderson 1984), longitude 54° 41' N, latitude 97° 49' W. This locality is notable in also being the type locality for bobfergusonite (Ercit *et al.* 1986a, 1986b). The pegmatite is a member of the Northern pegmatite series of the Cross Lake pegmatite field that is hosted by the Cross Lake greenstone belt in the Sachigo Subprovince of the Superior Province, Canadian Shield (Corkery *et al.* 1992). The pegmatite intrudes metagreywacke, and is 40 m long and up to 6.7 m wide in outcrop (Ercit *et al.* 1986a), and consists of a wall zone of saccharoidal albite and quartz with minor garnet, schorl, muscovite and K-feldspar, an outer intermediate zone of the same assemblage plus columbite–tantalite, microlite, apatite and beryl, an inner intermediate zone of coarse K-feldspar and muscovite, and a quartz core. Manitobaite occurs in both the inner intermediate zone and the core zone. In the inner intermediate zone, it is the most common phosphate mineral and typically forms anhedral homogeneous crystals (Fig. 1a) up to ~4 cm across. These large grains are cross-cut by fractures and narrow veins of Mn-rich apatite. Manitobaite also occurs in pods of primary phosphates, where it is associated with other phosphates such as eosphorite, Mn-rich apatite and minor dickinsonite, fillowite and triploidite (Fig. 1b). Manitobaite is a minor phosphate in the core zone, where it occurs as a fine-grained constituent of phosphate pods at the margin between the pod and the silicate host. The associated minerals are as follows: interior-wall zone: phosphates: fluorapatite, chlorapatite, bobfergusonite, eosphorite, dickinsonite, triploidite, goyazite, perloffite, beusite,
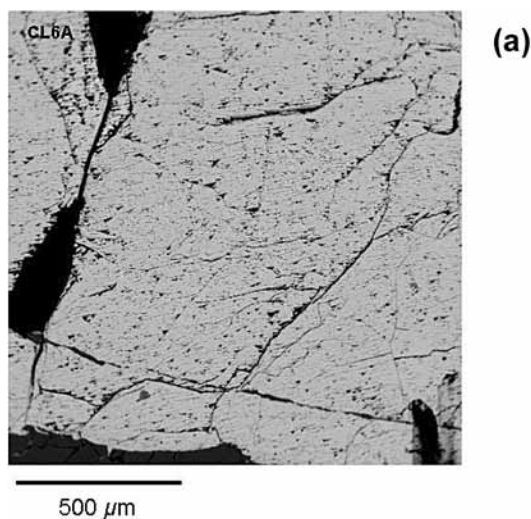
FIG. 1a. Back-scattered electron image of homogeneous manitobaite from the inner wall zone.
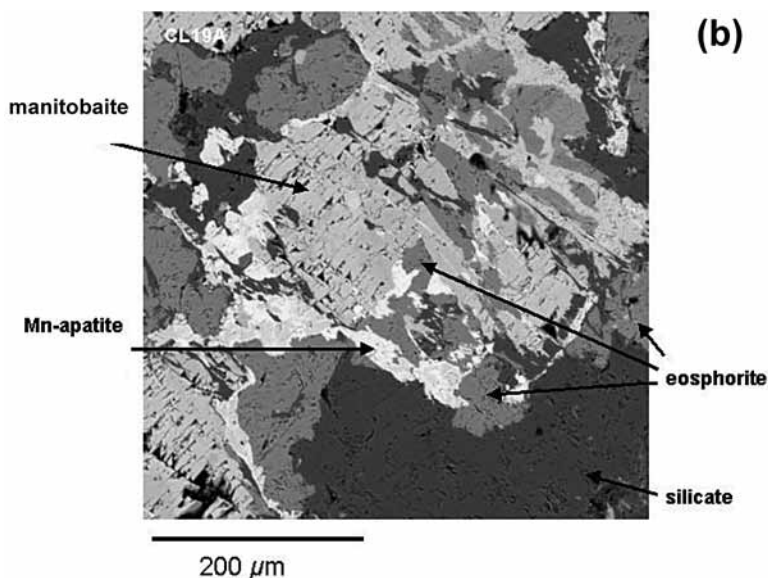

FIG. 1b. Back-scattered electron image of manitobaite associated with eosphorite, Mn-rich apatite and silicate minerals.

triplite, plus quartz, K-feldspar, muscovite, schorl, beryl, spessartine, gahnite and (Nb,Ta,Sn) oxides; core zone: phosphates: fluorapatite, chlorapatite, triploidite, eosphorite, dickinsonite, fillowite, plus quartz, K-feldspar, muscovite, schorl, beryl, gahnite and (Nb,Ta,Sn) oxides.

PHYSICAL PROPERTIES

Manitobaite is opaque in large (up to 4 cm) crystals, and transparent to translucent in small (<1 mm) grains. Large crystals show flat cleavage surfaces that have a mottled appearance in which the color varies from green to brown, and small transparent fragments vary in color from bright green to brown. The streak varies from colorless to very pale green or very pale greenish brown, and the luster is vitreous to resinous. Manitobaite does not fluoresce under ultraviolet light. The cleavage is perfect on {010}, there is no parting, the tenacity is brittle, and the fracture is hackly. The density was measured with a Berman balance as 3.621(6) g cm^{-3}, and the calculated value is 3.628 g cm^{-3}.

Optical properties in transmitted light were measured on a Bloss spindle stage in monochromatic Na light (λ = 590 nm), and the program EXCALBR II (Bartelmehs *et al.* 1992) was used to determine optic orientation (Gunter & Twamley 2001). Manitobaite is biaxial negative with α 1.682, β 1.691, γ 1.697, (all ±0.001); X $\wedge$ **a** = 31.7° (in β obtuse), Y ‖ **b**, Z $\wedge$ **c** = 20.2 (in β acute); $2V_{(obs)}$ = 78.1(6), $2V_{(calc)}$ = 77.9°. It is pleochroic X = orange brown, Y = green, Z = greenish brown, with absorption Y ≥ Z > X and dispersion $r > v$, medium.

MÖSSBAUER SPECTROSCOPY

Samples of green and brown manitobaite were separated by hand-picking under a binocular microscope, ground with an agate mortar and pestle, and placed on a Pb ring (2 mm inner diameter) and secured in place with tape. Mössbauer spectra were acquired in transmission geometry at room temperature using a ^{57}Co(Rh) point source, and the spectrometer was calibrated with the room-temperature spectrum of α-Fe. The spectra were analyzed in terms of a Voigt-function-based quadrupole-splitting distribution (Rancourt & Ping 1991) using the RECOIL® software package.

Figure 2 shows the Mössbauer spectra of green (upper) and brown (lower) manitobaite. They were fit to a model having two generalized sites, each with one Gaussian component, due to Fe^{2+} (solid line) and Fe^{3+} (dashed line). The hyperfine parameters are summarized in Table 1. Assuming equal recoil-free fractions for Fe^{2+} and Fe^{3+}, the Fe^{3+}/Fe_{tot} value of green manitobaite is 0.21(3), and that of brown manitobaite is 0.39(2).

INFRARED ABSORPTION SPECTROSCOPY

The infrared powder absorption spectrum of manitobaite was recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000–400 cm^{-1} (Fig. 3). In accord with the absence of OH and H_2O in the structure, there are no bands observed in the 3000–3600 or 1610–1640 cm^{-1} regions. The strong bands at ~1035 cm^{-1} and 570 cm^{-1} may be assigned to $(PO_4)^{3-}$ stretching modes and Mn–O stretching modes, respectively. The bands are extremely broad, in accord with the large number of crystallographically distinct sites in the structure.

CHEMICAL COMPOSITION

Numerous crystals were analyzed with a Cameca SX–100 electron microprobe operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 20 nA, and a beam diameter of 10 μm. The following standards were used for $K\alpha$ lines: apatite (P, Ca), andalusite (Al), fayalite (Fe), spessartine (Mn), gahnite (Zn), forsterite (Mg), albite (Na), with peak-count times of 20 s and background-count times of 10 s. Raw intensities were converted to concentrations using the *PAP* procedure of Pouchou &

Pichoir (1985). The chemical compositions (mean of ten determinations for each) of the green and brown varieties are given in Table 2; note that the Fe_2O_3 and FeO contents were derived from the Fe^{3+} / (Fe^{2+} + Fe^{3+}) values measured by Mössbauer spectroscopy. The empirical formulae of the green and brown varieties of manitobaite were calculated on the basis of 120 anions (all O^{2-}) as determined from their crystal structures, and are also given in Table 2.

CHEMICAL FORMULA

The structure of both green and brown variants has 79 cation sites and 120 anion sites; a summary of the cation sites is given in Table 3. We may write a *structural formula* for the mineral (applicable to both green and brown structures) that identifies the oxyanion, and that contains the correct number of sites:

$$Na_{16}\ Z_2\ M_{23}\ Al_8\ (PO_4)_{30}$$
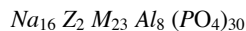
where *Na*: Na, ☐ (vacancy), Ca;

Z: Mn^{2+}, Ca;

M: Mn^{2+}, Fe^{2+}, Ca, Al, Fe^{3+}, Mg, Zn;

Al: Al, Fe^{3+}, Mg, Mn^{2+}, Fe^{2+}.

TABLE 1. MÖSSBAUER PARAMETERS* FOR MANITOBAITE

		CS (mm/s)	QS (mm/s)	Area (%)
Green	Fe^{2+}	1.23	2.15	79(3)
	Fe^{3+}	0.40	0.77	21(3)
Brown	Fe^{2+}	1.20	2.25	61(2)
	Fe^{3+}	0.42	0.66	39(2)

* CS: center shift, QS: quadrupole splitting.

TABLE 2. CHEMICAL COMPOSITION OF GREEN AND BROWN VARIETIES OF MANITOBAITE

	Green	Brown		Green	Brown
P_2O_5 wt.%	44.19	44.42	P *apfu*	30.08	30.15
Al_2O_3	6.91	6.96	Al	6.54	6.58
Fe_2O_3*	1.73	3.45	Fe^{3+}	1.05	2.09
FeO*	6.23	4.66	Fe^{2+}	4.19	3.12
MnO	27.57	27.86	Mn^{2+}	18.78	18.92
ZnO	0.54	0.53	Zn	0.32	0.31
MgO	0.73	0.81	Mg	0.88	0.97
CaO	1.71	1.59	Ca	1.47	1.37
Na_2O	9.97	8.94	Na	15.55	13.90
Total	99.58	99.22	O	120	120

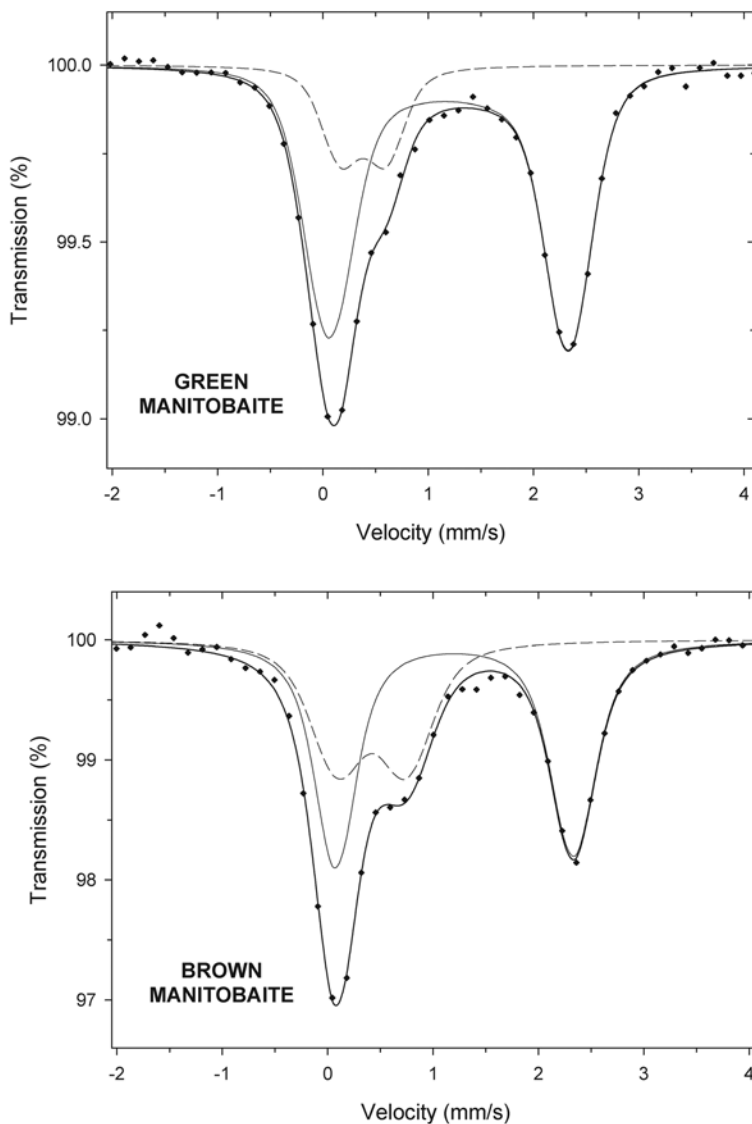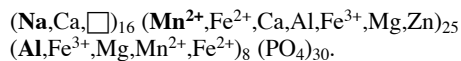* $(FeO)_{tot}$ = 7.79% (green), 7.77% (brown).

FIG. 2.   The Mössbauer spectra of the green and brown varieties of manitobaite.

We may now ask the following pragmatic question: is it useful to specifically identify the Z sites in the formula, as all constituents of the Z sites also occur at the M sites that completely dominate the Z sites in terms of abundance? This means that one cannot identify the occupancy of the Z sites without structure refinement (a non-trivial endeavor, even with access to the necessary instrumentation). Thus we have chosen to merge the Z sites with the M sites in writing the *general formula*, as follows:

$$(\mathbf{Na},Ca,\square)_{16} (\mathbf{Mn^{2+}},Fe^{2+},Ca,Al,Fe^{3+},Mg,Zn)_{25}$$
$$(\mathbf{Al},Fe^{3+},Mg,Mn^{2+},Fe^{2+})_8 (PO_4)_{30}.$$

Now let us consider the end-member formula (Hawthorne 2002): this must be written in terms of the dominant species at each group of sites (the initial species at each group of sites in the above general formula is dominant at that group of sites and is shown in bold font), and the formula must be electronically

neutral: thus we write the end-member formula as Na_{16} Mn^{2+}_{25} Al_8 $(PO_4)_{30}$.

Relation between the green and brown varieties of manitobaite

Mössbauer spectroscopy shows that one of the principal differences between these two varieties of manitobaite involves a difference in Fe^{3+} content (Table 1, Fig. 2), accompanied by differences in amounts of other cations that maintain electroneutrality in the structure.

The differences in cation content of the two varieties are shown in Table 4. The major differences between the green and brown varieties involves (1) a decrease in the amount of Na and a corresponding increase in the amount of vacancy ($\square$) at the *Na* sites, and (2) an increase in the amount of Fe^{3+} and a decrease in the amount of Fe^{2+} at the (*M, Al*) sites. Hence the principal substitution is as follows:

$$\square + Fe^{3+} \rightarrow Na + Fe^{2+},$$
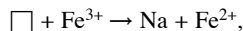
as observed in alluaudite-subgroup minerals (Fransolet *et al.* 2004). The remaining difference in Na is balanced by small increases (<0.30 *apfu*) in Mg, Mn^{2+}, Al and Fe^{3+}. These substitutions do not change the dominant species at any site; the green and brown crystals are the same mineral.

X-RAY POWDER DIFFRACTION

The powder-diffraction pattern of the green variety was recorded on a Philips PW1710 powder diffrac-

TABLE 3. SUMMARY OF THE CATION SITES IN MANITOBAITE

Site	Coordination	Number of sites	Refinement treatment
P	tetrahedral	30	Fixed occupancy
M(1–23), *Al*(1–8)	octahedral	31	Variable occupancy
Z(1–2)	[7]-coordinated	2	Variable occupancy
Na(1–16)	[5–8]-coordinated	16	Variable occupancy

TABLE 4. COMPARISON OF CATION CONTENTS (*apfu*) IN THE
GREEN AND BROWN VARIETIES OF MANITOBAITE

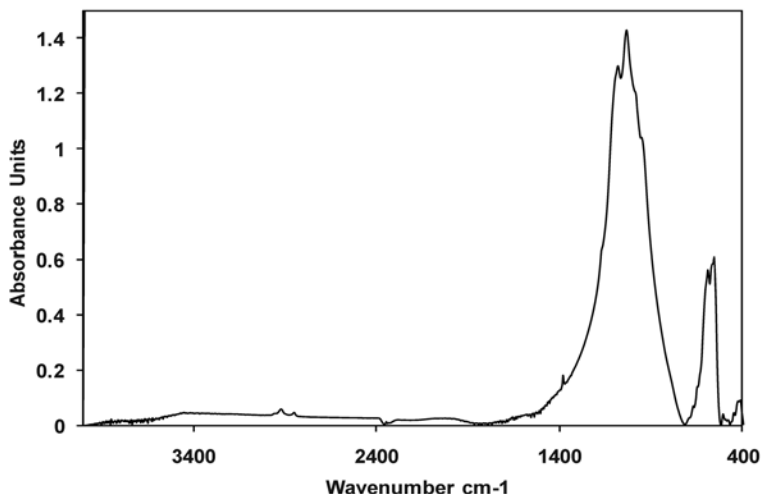|	*Na*			*M + Al + Z*						
Green	$Na_{15.55}$	$Ca_{0.23}$	$\square_{0.23}$	$Ca_{1.24}$	$Mg_{0.88}$	$Fe^{2+}_{4.19}$	$Mn^{2+}_{18.78}$	$Zn_{0.32}$	$Al_{6.54}$	$Fe^{3+}_{1.05}$
Brown	$Na_{13.90}$	$Ca_{0.35}$	$\square_{1.75}$	$Ca_{1.02}$	$Mg_{0.97}$	$Fe^{2+}_{3.12}$	$Mn^{2+}_{18.92}$	$Zn_{0.31}$	$Al_{6.58}$	$Fe^{3+}_{2.09}$
Δ	**1.65**	0.12	**1.52**	0.22	0.09	**1.07**	0.14	0.01	0.04	**1.04**

FIG. 3.   The infrared spectrum of manitobaite.

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR MANITOBAITE

$I_{meas.}$	d_{meas} Å	d_{calc} Å	$h\ k\ l$	$I_{meas.}$	d_{meas} Å	d_{calc} Å	$h\ k\ l$
4.3	8.479	8.465	1 0 2	3.8	2.228	2.228	5 3 0
9.2	8.246	8.227	1 1 1	7.2	2.187	2.188	$\bar{5}$ 3 5
7.8	6.384	6.383	$\bar{1}$ 0 4	7.8	2.151	2.151	5 1 5
20.0	6.260	6.258	0 2 0	*B 15.8	2.093	2.097	$\bar{3}$ 1 12
2.8	5.718	5.715	$\bar{2}$ 1 2		2.093	2.093	$\bar{6}$ 2 4
9.7	5.460	5.459	2 0 2		2.093	2.086	0 6 0
3.3	5.299	5.299	$\bar{2}$ 1 3	10.8	2.062	2.063	3 5 3
2.8	4.823	4.821	0 1 5	2.9	2.048	2.047	$\bar{5}$ 1 10
3.5	4.468	4.468	$\bar{1}$ 2 4	3.0	2.005	2.005	0 4 10
4.1	4.264	4.273	$\bar{2}$ 2 3	5.4	1.987	1.986	1 3 11
3.0	4.184	4.186	$\bar{3}$ 1 2	3.0	1.966	1.966	$\bar{3}$ 5 7
4.7	4.118	4.113	2 2 2		1.966	1.965	$\bar{2}$ 6 3
2.1	3.624	3.622	$\bar{3}$ 2 2	5.1	1.948	1.948	2 6 2
46.6	3.494	3.494	3 1 3	8.7	1.935	1.934	5 3 5
	3.494	3.492	$\bar{1}$ 3 4	2.7	1.913	1.913	6 3 1
3.0	3.398	3.396	$\bar{2}$ 3 3		1.913	1.912	$\bar{1}$ 5 9
2.7	3.317	3.314	1 2 6	2.6	1.896	1.895	$\bar{3}$ 3 12
2.5	3.243	3.244	$\bar{4}$ 1 2	2.1	1.878	1.878	2 3 11
2.1	3.205	3.205	0 2 7	5.3	1.865	1.865	2 2 12
2.3	3.127	3.129	0 4 0	7.2	1.815	1.815	5 5 0
26.7	3.078	3.078	$\bar{3}$ 1 7	7.2	1.794	1.794	7 1 2
8.0	3.042	3.041	$\bar{3}$ 3 2		1.794	1.793	$\bar{5}$ 5 5
3.1	2.956	2.956	$\bar{4}$ 2 1	3.5	1.767	1.767	$\bar{4}$ 4 11
17.9	2.924	2.925	$\bar{4}$ 0 6	19.0	1.745	1.746	$\bar{2}$ 6 8
20.5	2.881	2.882	$\bar{1}$ 1 9		1.745	1.745	$\bar{7}$ 3 3
11.2	2.842	2.843	$\bar{2}$ 2 8	3.7	1.722	1.722	$\bar{1}$ 7 4
4.0	2.805	2.804	$\bar{2}$ 1 9	2.0	1.698	1.698	$\bar{4}$ 6 6
17.6	2.758	2.759	$\bar{2}$ 4 3	3.0	1.686	1.687	3 1 13
50.2	2.730	2.729	4 0 4	4.1	1.678	1.678	4 4 9
100.0	2.715	2.715	2 4 2		1.678	1.678	0 2 15
7.7	2.650	2.650	$\bar{4}$ 2 6		1.678	1.677	1 5 11
8.9	2.614	2.612	0 0 10	3.4	1.662	1.662	7 3 2
3.3	2.580	2.579	5 1 0	6.6	1.656	1.657	2 4 12
3.8	2.559	2.558	$\bar{3}$ 4 2	2.9	1.647	1.648	$\bar{7}$ 3 8
20.0	2.524	2.527	$\bar{3}$ 3 7	5.7	1.620	1.621	$\bar{3}$ 5 12
21.5	2.518	2.517	$\bar{5}$ 1 5		1.620	1.619	$\bar{8}$ 2 2
9.2	2.503	2.502	4 2 4	4.4	1.597	1.598	$\bar{5}$ 5 10
2.1	2.434	2.433	$\bar{1}$ 5 2	5.9	1.588	1.588	$\bar{6}$ 0 14
5.2	2.410	2.410	0 2 10	5.4	1.584	1.583	$\bar{7}$ 4 7
3.9	2.330	2.330	$\bar{1}$ 5 4	17.9	1.573	1.573	6 4 6
2.1	2.284	2.284	4 3 4	6.1	1.547	1.548	7 1 7

*B: broad, not used in unit-cell refinement.

tometer; 40 kV, 40 mA; 6–60°2θ, 0.02° step width, 2s/step; Cu radiation (λ Cu$K\alpha_1$ = 1.54059 Å); no internal standard was used. Refinement of the unit-cell parameters gave the following values: a 13.4516(15), b 12.5153(16), c 26.661(3) Å, β 101.579(10)°. The indexed powder pattern for the green variety of manitobaite is given in Table 5. Unit-cell dimensions were also determined on a Bruker single-crystal diffractometer using graphite-monochromated Mo$K\alpha$ X-radiation; the resulting values are close to the values determined by powder diffraction [a 13.4517(7), b 12.5266(7), c 26.6765(13) Å, β 101.582(1)°].

CRYSTAL STRUCTURE AND RELATION TO OTHER SPECIES

The crystal structures of the green and brown varieties of manitobaite were determined by direct methods and were refined to R_1 values of 0.05 and 0.06, respectively, and the detailed results will be presented elsewhere. Manitobaite is an ordered superstructure of the alluaudite arrangement (Moore 1971), with a volume five times that of the substructure. The chemical formulae, unit cell and symmetry relations of alluaudite and its related superstructure minerals are shown in Table 6. A comparison of some of the more diagnostic physical properties are given for alluaudite, ferrowyllieite, bobfergusonite and manitobaite in Table 7.

Note that manitobaite is associated with bobfergusonite in the Cross lake pegmatite #22. Manitobaite is chemically similar to bobfergusonite (Ercit *et al.* 1986b), but the two species can be readily distinguished by their respective Na_2O contents: manitobaite (9–10% Na_2O), bobfergusonite (6–7% Na_2O).

TABLE 6. RELATIONS AMONG THE CHARACTERISTIC MINERALS OF THE SUBGROUPS OF THE ALLUAUDITE GROUP

	Alluaudite	Ferrowyllieite	Bobfergusonite	Manitobaite
Chemical formula	$NaMn^{2+}Fe^{3+}{}_2(PO_4)_3$	$Na_2Fe^{2+}{}_2Al(PO_4)_3$	$Na_2Mn^{2+}{}_5Fe^{3+}Al(PO_4)_6$	$Na_{16}Mn^{2+}{}_{25}Al_8(PO_4)_{30}$
a (Å)	12.004	11.868	12.776	13.452
b	12.533	12.382	12.488	12.527
c	6.404	6.354	11.035	26.677
β (°)	114.4	114.52	97.21	101.58
V (Å³)	877.4	849.5	1746.7	4403.9
Z	4	4	4	2
Space group	C2/c	P2₁/n	P2₁/n	Pc
N *	1	1	2	5
References	(1)	(2)	(3)	(4)

* N ≈ $V_{mineral}$ / $V_{alluaudite}$. References: (1) Moore (1971), (2) Moore & Molin-Case (1974), Moore & Ito (1979), (3) Ercit *et al.* (1986a), (4) this work.

TABLE 7. PHYSICAL PROPERTIES OF CHARACTERISTIC MINERALS
OF THE SUBGROUPS OF THE ALLUAUDITE GROUP

	Alluaudite				Ferrowyllieite				Bobfergusonite				Manitobaite				
Color	yellow to brownish yellow				bottle green to pale greenish grey				green-brown to red-brown				green to brown				
α	1.782				1.685				1.694				1.682				
β	1.802				1.688				1.698				1.691				
γ	1.835				1.692				1.715				1.697				
$2V$ (°)	79				90				46				78				
d (Å)	I_{obs}	h	k	l	d (Å)	I_{obs}	h	k	l	d (Å)	I_{obs}	h	k	l	d (Å)	I_{obs}	h k l
6.267	75	0	2	0	6.150	60	0	2	0	3.054	100	$\bar{4}$	1	1	6.260	20	0 2 0
5.466	40	2	0	0	3.449	50	3	1	0	2.869	66	4	1	1	3.494	47	3 1 3, $\bar{1}$ 3 4
3.499	40	3	1	0	2.693	100	4	0	0	2.712	49	0	4	2	3.078	27	$\bar{3}$ 1 7
2.733	54	4	0	0	2.674	100	2	4	0	2.508	53	0	2	4	2.730	50	4 0 4
2.718	100	2	4	0	2.498	50	$\bar{1}$	3	2	2.082	67	0	6	0	2.715	100	2 4 2

REFERENCES

ANDERSON, A.J. (1984): *The Geochemistry, Mineralogy and Petrology of the Cross Lake Pegmatite Field, Central Manitoba*. M.Sc. thesis, University of Manitoba, Winnipeg, Manitoba.

ANTENUCCI, D., FRANSOLET, A.-M., MIEHE, G. & TARTE, P. (1995): Synthèse et cristallochimie de NaCaCdMg₂(PO₄)₃, phosphate nouveau à structure alluaudite sans cation trivalent. *Eur. J. Mineral.* **7**, 175-181.

ANTENUCCI, D., MIEHE, G., TARTE, P., SCHMAHL, W.W. & FRANSOLET, A.-M. (1993): Combined X-ray Rietveld, infrared and Raman study of a new synthetic variety of alluaudite, NaCdIn₂(PO₄)₃. *Eur. J. Mineral.* **5**, 207-213.

AUERNHAMMER, M.N., EFFENBERGER, H., HENTSCHEL, G., REINECKE, T. & TILLMANNS, E. (1993): Nickenichite, a new arsenate from the Eifel, Germany. *Mineral. Petrol.* **48**, 153-166.

BARTELMEHS, K.L., BLOSS, F.D., DOWNS, R.T. & BIRCH, J.B. (1992): Excalibr II. *Z. Kristallogr.* **199**, 185-196.

CORKERY, M.T., DAVIS, D.W. & LENTON, P.G. (1992): Geochronological constraints on the development of the Cross Lake greenstone belt, northwest Superior Province, Manitoba. *Can. J. Earth Sci.* **29**, 2171-2185.

DAMOUR, A.A. (1848): Sur un nouveau phosphate de fer, de manganese et de soude, l'alluaudite, trouve dans le département de la Haute Vienne. *Annales des Mines, sér. 4*, **13**, 341-350.

ERCIT, T.S. (1993): Caryinite revisited. *Mineral. Mag.* **57**, 721-727.

ERCIT, T.S., ANDERSON, A.J., ČERNÝ, P. & HAWTHORNE, F.C. (1986a): Bobfergusonite, a new primary phosphate mineral from Cross Lake, Manitoba. *Can. Mineral.* **24**, 599-604.

ERCIT, T.S., HAWTHORNE, F.C. & ČERNÝ, P. (1986b): The crystal structure of bobfergusonite. *Can. Mineral.* **24**, 605-614.

FILATOV, S.K., VERGASOVA, L.P., GORSKAYA, M.G., KRIVOVICHEV, S.V., BURNS, P.C & ANANIEV V.V. (2001): Bradaczekite, NaCu₄(AsO₄)₃, a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *Can. Mineral.* **39**, 1115-1119.

FRANSOLET, A-M., HATERT, F. & FONTAN, F. (2004): Petrographic evidence of primary hagendorfite in an unusual assemblage of phosphate minerals, Kibingo granitic pegmatite, Rwanda. *Can. Mineral.* **42**, 697-704.

GUNTER, M.E. & TWAMLEY, B. (2001): A new method to determine the optical orientation of biaxial minerals: a mathematical approach. *Can. Mineral.* **39**, 1701-1711.

HATERT, F. (2008): Crystal chemistry of the divalent cation in alluaudite-type phosphates: a structural and infrared spectral study of the Na₁.₅(Mn₁₋ₓM²⁺ₓ)₁.₅Fe₁.₅(PO₄)₃ solid solutions ($x = 0$ to 1, M^{2+} = Cd²⁺, Zn²⁺). *J. Solid State Chem.* **181**, 1258-1272.

HATERT, F., FRANSOLET, A.-M. & MARESCH, W.V. (2006a): The stability of primary alluaudites in granitic pegmatites: an experimental investigation of the $Na_2(Mn_{2\pm2x}Fe_{1+2x})(PO_4)_3$ system. *Contrib. Mineral. Petrol.* **152**, 399-419.

HATERT, F., HERMANN, R.P., FRANSOLET, A.-M., LONG, G.J. & GRANDJEAN, F. (2006b): A structural, infrared and Mössbauer spectral study of rosemaryite, $NaMnFe^{3+}Al(PO_4)_3$. *Eur. J. Mineral.* **18**, 775-785.

HATERT, F., HERMANN, R.P., LONG, G.J., FRANSOLET, A.-M. & GRANDJEAN, F. (2003): An X-ray, Rietveld, infrared and Mössbauer spectral study of the $NaMn(Fe_{1-x}In_x)_2(PO_4)_3$ alluaudite-type solid solution. *Am. Mineral.* **88**, 211-222.

HATERT, F., KELLER, P., LISSNER, F., ANTENUCCI, D. & FRANSOLET, A.-M. (2000): First experimental evidence of alluaudite-like phosphates with high Li content; the $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$ series ($x = 0$ to 1). *Eur. J. Mineral.* **12**, 847-857.

HATERT, F., LEFÈVRE, P., FRANSOLET, A.-M., SPIRLET, M.-R., REBBOUH, L., FONTAN, F. & KELLER, P. (2005): Ferrorosemaryite, $NaFe^{2+}Fe^{3+}Al(PO_4)_3$, a new phosphate mineral from the Rubindi pegmatite, Rwanda. *Eur. J. Mineral.* **17**, 749-759.

HAWTHORNE, F.C. (2002): The use of end-member charge-arrangements in defining new mineral species and heterovalent substitutions in complex minerals. *Can. Mineral.* **40**, 699-710.

KELLER, P. & HESS, H. (1988): Die Kristallstrukturen von O'Danielit, $Na(Zn,Mg)_3H_2(AsO_4)_3$, und Johillerit, $Na(Mg,Zn)_3Cu(AsO_4)_3$. *Neues Jahrb. Mineral., Monatsh.*, 395-404.

KELLER, P., HESS, H. & DUNN, P.J. (1982): Johillerit, Na$(Mg,Zn)_3$ Cu $(AsO_4)_3$, ein neues Mineral aus Tsumeb, Namibia. *Tschermaks Mineral. Petrogr. Mitt.* **29**, 169-175.

KELLER, P., HESS, H., DUNN, P.J. & NEWBURY, D. (1981): O'danielite, $NaZn_3H_2(AsO_4)_3$, a new mineral from Tsumeb, Namibia. *Neues Jahrb. Mineral., Monatsh.*, 155-160.

KHORARI, S., RULMONT, A. & TARTE, P. (1997a): Alluaudite-like structure of the arsenate $Na_3In_2(AsO_4)_3$. *J. Solid State Chem.* **134**, 31-37.

KHORARI, S., RULMONT, A. & TARTE, P. (1997b): The arsenates $NaCa_2M^{2+}_2(AsO_4)_3$ (M^{2+} = Mg,Ni,Co): influence of cationic substitutions on the garnet–alluaudite polymorphism. *J. Solid State Chem.* **131**, 290-297.

KHORARI, S., RULMONT, A., TARTE, P., MIEHE, G., ANTENUCCI, D. & GILBERT, B. (1997c): Alluaudite-like structure of the complex arsenate $NaCaCdMg_2(AsO_4)_3$. *J. Solid State Chem.* **131**, 298-304.

LEROUX, F., MAR, A., GUYOMARD, D. & PIFFARD, Y. (1995a): Cation substitution in the alluaudite structure type: synthesis and structure of $AgMn_3(PO_4)(HPO_4)_2$. *J. Solid State Chem.* **117**, 206-212.

LEROUX, F., MAR, A., PAYEN, D., GUYOMARD, D., VERBAERE, A. & PIFFARD, Y. (1995b): Synthesis and structure of $NaMn_3(PO_4)(HPO_4)_2$, an unoxidized variant of the alluaudite structure type. *J. Solid State Chem.* **115**, 240-246.

MOORE, P.B. (1971): Crystal chemistry of the alluaudite structure type: contribution to the paragenesis of pegmatite phosphate giant crystals. *Am. Mineral.* **56**, 1955-1975.

MOORE, P.B. & ITO, J. (1973): Wyllieite, $Na_2Fe^{2+}_2Al(PO_4)_3$, a new species. *Mineral. Rec.* **4**, 131-136.

MOORE, P.B. & ITO, J. (1979): Alluaudites, wyllieites, arrojadites: crystal chemistry and nomenclature. *Mineral. Mag.* **43**, 227-235.

MOORE, P.B. & MOLIN-CASE, J. (1974): Contribution to pegmatite phosphate giant crystal paragenesis. II. The crystal chemistry of wyllieite, $Na_2Fe^{2+}_2Al(PO_4)_3$, a primary phase. *Am. Mineral.* **59**, 280-290.

POUCHOU, J.L. & PICHOIR, F. (1985): "PAP" $\phi(\rho Z)$ procedure for improved quantitative microanalysis. *In* Microbeam Analysis (J.T. Armstrong, ed.). San Francisco Press, San Francisco, California (104-106).

RANCOURT, D.G. & PING, J.Y. (1991): Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy. *Nucl. Instrum. Methods Phys. Res.* **B58**, 85-97.

REDHAMMER, G.J., TIPPELT, G., BERNROIDER, M., LOTTERMOSER, W., AMTHAUER, G. & ROTH, G. (2005): Hagendorfite $(Na,Ca)MnFe_2(PO_4)_3$ from type locality Hagendorf (Bavaria, Germany): crystal structure determination and ^{57}Fe Mössbauer spectroscopy. *Eur. J. Mineral.* **17**, 915-932.

SARP, H. & ČERNÝ, R. (2005): Yazganite, $NaFe^{3+}_2(Mg,Mn)(AsO_4)_3 \bullet H_2O$, a new mineral: its description and crystal structure. *Eur. J. Mineral.* **17**, 367-373.

TAIT, K.T. & HAWTHORNE, F.C. (2003): Refinement of the crystal structure of arseniopleite: confirmation of its status as a valid species. *Can. Mineral.* **41**, 71-77.

TAIT, K.T., HAWTHORNE, F.C., ČERNÝ, P. & GALLISKI, M.A. (2004): Bobfergusonite from the Nancy pegmatite, San Luis Range, Argentina: crystal-structure refinement and chemical composition. *Can. Mineral.* **42**, 705-716.

WARNER, T.E., MILIUS, W. & MAIER, J. (1993): Synthesis and structure of $Cu_{1.35}Fe_3(PO_4)_3$ and $Cu_2Mg_3(PO_4)_3$: new mixed valence compounds of the alluaudite structure type. *J. Solid State Chem.* **106**, 301-309.

YAKUBOVICH, O.V., SIMONOV, M.A., EGOROV-TISMENKO, Y.K. & BELOV, N.V. (1977): The crystal structure of a synthetic variety of alluaudite $Na_2(Fe^{3+}_{0.5}Fe^{2+}_{0.5})_2Fe^{2+}[PO_4]_3$. *Sov. Phys. Dokl.* **22**, 550-552.