*The Canadian Mineralogist*
Vol. 49, pp. 1221-1242 (2011)
DOI: 10.3749/canmin.49.5.1221

# THE CRYSTAL STRUCTURE AND CRYSTAL CHEMISTRY OF MANITOBAITE, IDEALLY $(Na_{16}\square)Mn^{2+}_{25}Al_8(PO_4)_{30}$, FROM CROSS LAKE, MANITOBA

KIMBERLY T. TAIT‡, T. SCOTT ERCIT¶, YASSIR A. ABDU, PETR ČERNÝ AND FRANK C. HAWTHORNE§

*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*

## ABSTRACT

The crystal structures of green (brown) variants of manitobaite, ideally $(Na_{16}\square)Mn^{2+}_{25}Al_8(PO_4)_{30}$, monoclinic, *Pc*, Z = 2: green: *a* 13.4517(7), *b* 12.5266(7), *c* 26.6765(13) Å, β 101.582(1)°, *V* 4403.6(7) Å$^3$, $D_{calc.}$ 3.642 g/cm$^3$; brown: 13.4499(6), *b* 12.5046(5), *c* 26.6148(11) Å, β 101.221(1)°, *V* 4390.7(5)(3) Å$^3$, $D_{calc.}$ 3.621 g/cm$^3$, from pegmatite #22 at Cross Lake, Manitoba, Canada, have been solved by direct methods and refined to $R_1$ = 5.0 (6.0)% for 22,580 (25,613) unique ($F_o > 4\sigma F$) reflections collected on a Bruker single-crystal *P*4 diffractometer equipped with a 4K CCD detector and Mo*K*α X-radiation. Chemical analysis by electron microprobe plus $Fe^{3+}$ determination by Mössbauer spectroscopy gave: green: $P_2O_5$ 44.19, $Al_2O_3$ 6.91, $Fe_2O_3$ 1.73, FeO 6.23, MnO 27.57, ZnO 0.54, MgO 0.73, CaO 1.71, $Na_2O$ 9.97, sum 99.58 wt%; brown: $P_2O_5$ 44.42, $Al_2O_3$ 6.96, $Fe_2O_3$ 3.54, FeO 4.66, MnO 27.86, ZnO 0.53, MgO 0.81, CaO 1.59, $Na_2O$ 8.94, sum 99.32 wt%. The resulting empirical formulae are as follows: green: $Na_{15.55}Ca_{1.47}Mg_{0.88}Fe^{2+}_{4.19}Mn^{2+}_{18.78}Zn_{0.32}Al_{6.54}Fe^{3+}_{1.05}P_{30.08}O_{120}$; brown: $Na_{13.90}Ca_{1.37}Mg_{0.97}Fe^{2+}_{3.12}Mn^{2+}_{18.92}Zn_{0.31}Al_{6.58}Fe^{3+}_{2.09}P_{30.15}O_{120}$. The general formula of manitobaite is $(Na_{16}\square)(Mn^{2+},Fe^{2+},Mg,Zn,Ca)_{25}(Al,Fe^{3+})_8(PO_4)_{30}$, and the end-member formula is $(Na_{16}\square)Mn^{2+}_{25}Al_8(PO_4)_{30}$. There are 80 cation sites and 120 anion sites in the structure. There are 30 tetrahedrally coordinated sites occupied by P, 33 octahedrally coordinated sites occupied by $Mn^{2+}$, $Fe^{2+}$, Al, $Fe^{3+}$ plus minor Mg and Zn, and 17 sites occupied predominantly by Na with coordination numbers from [5] to [8]. Manitobaite is an ordered superstructure of the alluaudite structure. In particular, there are eight octahedrally coordinated sites occupied predominantly by Al, emphasizing the key role of Al in producing superstructures in these minerals.

*Keywords*: manitobaite, crystal structure, electron-microprobe analysis, phosphate, alluaudite group, Cross Lake, Manitoba.

## SOMMAIRE

Nous avons résolu les structures cristallines de deux variantes de manitobaïte, l'une verte, l'autre brune, de formule idéale $(Na_{16}\square)Mn^{2+}_{25}Al_8(PO_4)_{30}$, monoclinique, *Pc*, Z = 2: verte: *a* 13.4517(7), *b* 12.5266(7), *c* 26.6765(13) Å, β 101.582(1)°, *V* 4403.6(7) Å$^3$, $D_{calc.}$ 3.642 g/cm$^3$; brune: 13.4499(6), *b* 12.5046(5), *c* 26.6148(11) Å, β 101.221(1)°, *V* 4390.7(5)(3) Å$^3$, $D_{calc.}$ 3.621 g/cm$^3$, les deux provenant de la pegmatite #22 au lac Cross, Manitoba, Canada, par méthodes directes, et nous les avons affiné jusqu'à un résidu $R_1$ de 5.0 (6.0)% pour 22,580 (25,613) réflexions uniques ($F_o > 4\sigma F$) prélevées avec un diffractomètre Bruker *P*4 pour monocristaux muni d'un détecteur 4K CCD et avec rayonnement Mo*K*α. Des analyses chimiques avec une microsonde électronique en plus de déterminations du $Fe^{3+}$ par spectroscopie de Mössbauer ont donné: verte: $P_2O_5$ 44.19, $Al_2O_3$ 6.91, $Fe_2O_3$ 1.73, FeO 6.23, MnO 27.57, ZnO 0.54, MgO 0.73, CaO 1.71, $Na_2O$ 9.97, total 99.58% (poids); brune: $P_2O_5$ 44.42, $Al_2O_3$ 6.96, $Fe_2O_3$ 3.54, FeO 4.66, MnO 27.86, ZnO 0.53, MgO 0.81, CaO 1.59, $Na_2O$ 8.94, total 99.32%. Les formules empiriques qui en résultent sont: verte: $Na_{15.55}Ca_{1.47}Mg_{0.88}Fe^{2+}_{4.19}Mn^{2+}_{18.78}Zn_{0.32}Al_{6.54}Fe^{3+}_{1.05}P_{30.08}O_{120}$; brune: $Na_{13.90}Ca_{1.37}Mg_{0.97}Fe^{2+}_{3.12}Mn^{2+}_{18.92}Zn_{0.31}Al_{6.58}Fe^{3+}_{2.09}P_{30.15}O_{120}$. La formule générale de la manitobaïte est $(Na_{16}\square)(Mn^{2+},Fe^{2+},Mg,Zn,Ca)_{25}(Al,Fe^{3+})_8(PO_4)_{30}$, et la formule du pôle est $(Na_{16}\square)Mn^{2+}_{25}Al_8(PO_4)_{30}$. Il y a 80 sites cationiques et 120 sites anioniques dans la structure. Il y a 30 sites à coordinence tétraédrique à occupation par le P, 33 site à coordinence octaédrique à occupation par $Mn^{2+}$, $Fe^{2+}$, Al, $Fe^{3+}$, avec Mg et Zn comme occupants mineurs, et 17 sites remplis surtout par Na en coordinence de [5] à [8]. La manitobaïte est une surstructure ordonnée de l'alluaudite. En particulier, il y a huit sites à coordinence octaédrique remplis surtout par Al, ce qui souligne le rôle primordial des cations Al dans la production de surstructures dans ces minéraux.

(Traduit par la Rédaction)

*Mots-clés*: manitobaïte, structure cristalline, analyse avec microsonde électronique, phosphate, groupe de l'alluaudite, lac Cross, Manitoba.

‡ Currently at: Department of Natural History, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario M5S 2C6, Canada.
¶ Currently at: Canadian Museum of Nature, P.O. Box 3443, Station "D", Ottawa, Ontario K1P 6P4, Canada.
§ *E-mail address*: frank_hawthorne@umanitoba.ca

## Introduction

Manitobaite, ideally $(Na_{16}\square)Mn^{2+}{}_{25}Al_8(PO_4)_{30}$, is a phosphate mineral from Cross Lake, Manitoba, Canada (Ercit *et al*. 2010). It occurs as large (up to 2 cm across) crystals or cleavage masses intergrown with other phosphate minerals in a phosphate pod in the intermediate and core zones of a granitic pegmatite on the southeastern shoreline of a small unnamed island in Cross Lake, about 5 km north–northwest of the Cross Lake settlement. Manitobaite is a primary mineral in the large (~10 cm) phosphate nodule. Associated minerals are fluorapatite, chlorapatite, bobfergusonite, eosphorite, dickinsonite, fillowite, triploidite, goyazite, perloffite, beusite and triplite plus quartz, K-feldspar, muscovite, schorl, beryl, spessartine, gahnite and (Nb,Ta, Sn) oxides. The color of manitobaite varies from bright green to honey brown; Ercit *et al*. (2010) showed that this difference in color correlates with differences in $Fe^{3+}$ content. The unit-cell dimensions and chemical composition indicate that manitobaite is an ordered superstructure of the alluaudite atomic arrangement, with a cell volume five times that of alluaudite (Ercit *et al*. 2010). Here, we describe the crystal structure of manitobaite and discuss its crystal-chemical relations with the other structure types of the alluaudite group *sensu lato*: alluaudite, rosemaryite and bobfergusonite.

## X-Ray Data Collection and Structure Solution-Refinement

X-ray-diffraction data for green (brown) crystals of manitobaite from the type specimen were collected with Mo*K*α radiation on a Bruker *P*4 diffractometer equipped with an APEX 4K CCD detector. The intensities of 75,109 (134,888) reflections were collected to 60° 2θ at 24°C using 45 (30) s per 0.2° frame for $-18 < h < 18$, $-17 < k < 17$, $-37 < l < 37$. An empirical absorption correction (SADABS, Sheldrick 2008) was applied, and the data were corrected for Lorentz, polarization and background effects. The refined unit-cell parameters (Table 1) were obtained from 6349 (7776) reflections with $I > 10\ \sigma I$. The structures were solved in the space group $P2_1/c$ by direct methods. Because of the large number of cation sites, each site was assigned a single scattering species (Hawthorne *et al*. 1995): (1) the *P* sites were considered as fully occupied by P, as indicated by the unit formulae (see below, Table 5), the observed <*P*–O> distances (see below, Table 3) and the resulting equivalent isotropic-displacement parameters (Table 2), and the occupancies of these sites were considered as fixed in the refinement; (2) the octahedrally coordinated sites were assigned scattering species in accord with the unit formulae and the preliminary observed scattering and the mean bond-lengths; (3) the *Na* sites were assigned as such based on the unit formulae, the preliminary observed scattering and coordination numbers greater than [6]. Refinement converged for both crystals, but there were problems with site splitting and unlikely coordinations. Several datasets were collected over a period of several years, but refinement in $P2_1/c$ always converged to $R_1$ indices between 8 and 11%. The structures were solved again in space group *Pc*, and the resulting refined models had no site splitting, although convergence was slow owing to correlation resulting from pseudosymmetry. In the final models, we considered the sites occupied predominantly by transition metals as anisotropic, and the remainder of the sites in the structures as isotropic. The Flack parameter converged to ~0.5 for both structures, indicating the presence of pervasive twinning, and a twin correction was introduced into the refinement. The twin fractions converged to ~0.5 for both green and brown crystals. Final refinement converged to $R_1$ indices of 0.050 (0.060) for 22,580 (25,613) reflections for 977 variable parameters with the SHELXTL version 5.1 system of programs (Bruker AXS 1997). The maximum and minimum residual densities in the final difference-Fourier maps are +2.0 and –1.6 eÅ$^{-3}$ (green) and +2.4 and –1.3 eÅ$^{-3}$ (brown), respectively. Refined extinction coefficients were not significantly different from zero, and hence this parameter was fixed at zero. Details of

TABLE 1. MISCELLANEOUS INFORMATION FOR MANITOBAITE

| | Green | Brown | | Green | Brown |
|---|---|---|---|---|---|
| *a* (Å) | 13.4517(7) | 13.4499(6) | Crystal size (μm) | 60 × 100 × 120 | 80 × 120 × 140 |
| *b* | 12.5266(7) | 12.5046(5) | Radiation | Mo*K*α | |
| *c* | 26.6765(13) | 26.6148(11) | Total no. of I | 75,109 | 134,888 |
| β (°) | 101.582(1) | 101.221(1) | No. in Ewald sphere | 40,049 | 49,615 |
| *V* (Å$^3$) | 4403.6(7) | 4390.7(5) | No. of $\|F\|$ | 22,580 | 25,615 |
| Space group | *Pc* | *Pc* | No. of $\|F_o\| > 4\sigma$ | 19,964 | 23,451 |
| *Z* | 2 | 2 | *R* (obs) % | 5.03 | 5.98 |
| | | | *wR* (obs) % | 14.07 | 15.59 |
| | | | GooF | 1.022 | 1.069 |
| | | | Parameters refined | 977 | 977 |

$R = \Sigma(|F_o|B|F_c|) / \Sigma|F_o|$; $wR = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma F_o^{2}]^2$, $w = 1 / \sigma^2 F^*\ [1 - \exp(-2.5\{\sin\theta/\lambda\}^2)]$.

TABLE 2A. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN GREEN MANITOBAITE

| | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| *Mn*(1) | 0.27507(7) | 0.48754(8) | 0.53463(4) | 0.0090(5) | 0.0096(5) | 0.0142(5) | 0.0008(4) | 0.0014(4) | -0.0008(3) | 0.0111(3) |
| *Mn*(2) | 0.08521(8) | 0.51473(8) | 0.23568(4) | 0.0144(5) | 0.0092(5) | 0.0056(4) | 0.0009(4) | 0.0018(3) | -0.0009(4) | 0.0098(3) |
| *Mn*(3) | 0.38701(7) | 0.01272(8) | 0.43005(4) | 0.0101(5) | 0.0059(5) | 0.0095(5) | 0.0007(3) | 0.0008(3) | 0.0014(3) | 0.0086(3) |
| *Mn*(4) | 1.04125(9) | 0.25301(10) | -0.20979(5) | 0.0186(6) | 0.0128(5) | 0.0319(7) | -0.0010(4) | 0.0111(5) | -0.0008(4) | 0.0203(4) |
| *Mn*(5) | 0.22275(7) | 0.24635(8) | 0.57565(4) | 0.0030(4) | 0.0043(5) | 0.0222(6) | 0.0007(4) | 0.0064(4) | -0.0008(3) | 0.0093(3) |
| *Mn*(6) | 0.87662(8) | 0.48637(8) | -0.06323(4) | 0.0084(5) | 0.0115(5) | 0.0091(5) | 0.0005(4) | 0.0014(3) | -0.0000(4) | 0.0097(3) |
| *Mn*(7) | 0.43438(9) | 0.24765(9) | 0.38375(5) | 0.0103(5) | 0.0051(5) | 0.0182(5) | -0.0027(3) | 0.0078(4) | -0.0017(3) | 0.0105(3) |
| *Mn*(8) | 0.82869(9) | 0.25261(10) | -0.01776(5) | 0.0100(5) | 0.0105(5) | 0.0236(6) | -0.0005(4) | 0.0059(4) | -0.0000(3) | 0.0144(3) |
| *Mn*(9) | 0.17913(8) | -0.01368(8) | 0.13076(4) | 0.0115(5) | 0.0097(5) | 0.0095(4) | -0.0017(4) | 0.0012(3) | 0.0013(4) | 0.0104(3) |
| *Mn*(10) | -0.0113(7) | -0.01214(8) | 0.33218(4) | 0.0101(5) | 0.0094(5) | 0.0040(4) | -0.0009(3) | 0.0020(3) | -0.0017(3) | 0.0077(3) |
| *Fe*(1) | 0.19871(7) | 0.39896(8) | 0.34672(4) | 0.0072(5) | 0.0054(5) | 0.0053(4) | 0.0013(3) | 0.0019(3) | 0.0012(3) | 0.0059(3) |
| *Fe*(2) | 0.59775(7) | 0.39878(8) | -0.05414(4) | 0.0086(5) | 0.0056(5) | 0.0096(5) | 0.0001(3) | 0.0010(3) | -0.0003(3) | 0.0081(3) |
| *Fe*(3) | 0.99429(7) | 0.60248(8) | 0.04841(4) | 0.0082(5) | 0.0080(5) | 0.0085(5) | -0.0017(3) | 0.0001(3) | 0.0032(3) | 0.00845(3) |
| *Fe*(4) | 0.49414(7) | 0.09107(9) | 0.04032(4) | 0.0095(5) | 0.0158(5) | 0.0070(5) | -0.0001(3) | -0.0008(3) | -0.0009(3) | 0.0111(3) |
| *Fe*(5) | 0.77060(7) | 0.40985(8) | 0.32664(4) | 0.0085(5) | 0.0060(5) | 0.0094(5) | 0.0010(3) | 0.0038(3) | -0.0001(3) | 0.0077(3) |
| *Fe*(6) | 1.06581(8) | 1.10090(8) | 0.02103(4) | 0.0116(5) | 0.0098(5) | 0.0113(5) | -0.0018(4) | 0.0010(3) | -0.0018(3) | 0.0111(3) |
| *Fe*(7) | 1.26967(7) | 0.10208(8) | -0.18088(4) | 0.0096(5) | 0.0086(5) | 0.0102(5) | -0.0012(3) | 0.0020(3) | 0.0027(3) | 0.0095(3) |
| *Fe*(8) | 0.66696(7) | -0.10120(8) | -0.07847(4) | 0.0099(5) | 0.0095(5) | 0.0083(5) | 0.0025(3) | 0.0026(3) | -0.0002(3) | 0.0091(3) |
| *X*(1) | 0.17085(9) | 0.58558(9) | 0.42249(4) | 0.0098(5) | 0.0069(5) | 0.0095(5) | -0.0015(4) | 0.0029(4) | -0.0009(4) | 0.0086(3) |
| *X*(2) | 0.09331(8) | 0.08534(9) | 0.44465(4) | 0.0073(5) | 0.0087(5) | 0.0071(5) | -0.0016(4) | -0.0011(3) | -0.0014(4) | 0.0081(3) |
| *M*(1) | 0.40036(8) | 0.39500(8) | 0.14503(4) | 0.0156(5) | 0.0122(5) | 0.0133(5) | 0.0010(4) | 0.0015(4) | -0.0020(4) | 0.0139(3) |
| *M*(2) | 0.86433(7) | 0.10538(8) | 0.22203(3) | 0.0043(4) | 0.0095(5) | 0.0031(4) | -0.0020(3) | 0.0016(3) | 0.0011(3) | 0.0055(3) |
| *Y*(1) | 0.63196(14) | 0.25018(14) | 0.18278(9) | 0.0128(3) | 0.0110(3) | 0.0431(5) | -0.0070(3) | 0.0142(3) | -0.0037(2) | 0.0211(2) |
| *Z*(1) | 0.48574(8) | 0.48313(9) | 0.33333(4) | 0.0089(5) | 0.0071(5) | 0.0125(5) | 0.0030(4) | 0.0007(4) | -0.0004(4) | 0.0097(3) |
| *Z*(2) | 0.77802(9) | 0.01716(9) | 0.03361(4) | 0.0169(6) | 0.0135(6) | 0.0085(5) | -0.0009(4) | 0.0026(4) | -0.0006(4) | 0.0130(4) |

| | *x* | *y* | *z* | $U_{eq}$ | | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| *Al*(1) | 0.79378(12) | 0.40085(13) | -0.24963(6) | 0.0091(5) | *Al*(5) | 0.37517(12) | 0.59176(13) | 0.22079(6) | 0.0053(5) |
| *Al*(2) | 0.69337(14) | 0.08254(16) | -0.15735(8) | 0.0111(6) | *Al*(6) | 0.96963(10) | 0.41774(11) | 0.12540(5) | 0.0028(4) |
| *Al*(3) | 0.57167(13) | 0.41841(14) | 0.52499(7) | 0.0034(5) | *Al*(7) | -0.11089(13) | -0.09417(14) | 0.14659(7) | 0.0158(5) |
| *Al*(4) | 0.47177(11) | -0.09752(12) | 0.11731(6) | 0.0038(5) | *Al*(8) | 0.29588(11) | 0.08395(12) | 0.24195(6) | 0.0127(4) |
| *P*(1) | 0.40209(11) | 0.13488(11) | 0.14892(6) | 0.0030(3) | *P*(16) | 0.56239(12) | 0.15909(13) | 0.51283(6) | 0.0065(3) |
| *P*(2) | 0.70153(12) | 0.34258(12) | -0.14612(6) | 0.0066(3) | *P*(17) | 0.90474(11) | 0.35027(12) | -0.33908(6) | 0.0066(3) |
| *P*(3) | 0.30164(11) | 0.34793(13) | 0.25316(6) | 0.0091(3) | *P*(18) | 0.36003(12) | 0.15004(13) | 0.70594(6) | 0.0094(3) |
| *P*(4) | 0.60162(11) | 0.13727(13) | -0.05494(6) | 0.0063(3) | *P*(19) | 0.17276(12) | -0.14959(14) | 0.41438(6) | 0.0099(3) |
| *P*(5) | 0.09175(11) | 0.35266(13) | 0.45270(6) | 0.0063(3) | *P*(20) | 0.45212(13) | 0.35515(13) | 0.61159(6) | 0.0100(3) |
| *P*(6) | 0.38732(11) | 0.46137(12) | 0.43812(6) | 0.0062(3) | *P*(21) | 0.81270(11) | 0.14356(11) | -0.24362(6) | 0.0040(3) |
| *P*(7) | 0.20519(12) | 0.13444(12) | 0.34885(6) | 0.0062(3) | *P*(22) | 0.28217(11) | 0.03770(13) | 0.53366(6) | 0.0079(3) |
| *P*(8) | 1.05946(12) | 0.36547(13) | 0.01903(7) | 0.0082(3) | *P*(23) | -0.03645(12) | 0.15884(13) | 0.11323(6) | 0.0108(3) |
| *P*(9) | 1.26781(12) | 0.36553(13) | -0.18399(6) | 0.0070(3) | *P*(24) | 0.99742(12) | 0.86386(13) | 0.05301(6) | 0.0087(3) |
| *P*(10) | 0.18424(12) | 0.53436(12) | 0.13790(6) | 0.0073(3) | *P*(25) | 0.66298(12) | 0.36209(13) | 0.42220(6) | 0.0078(3) |
| *P*(11) | -0.01674(11) | 0.53784(13) | 0.33383(6) | 0.0071(3) | *P*(26) | 0.07951(12) | -0.03460(12) | 0.22874(6) | 0.0066(3) |
| *P*(12) | 0.49305(12) | 0.35253(13) | 0.05063(6) | 0.0075(3) | *P*(27) | 0.48318(11) | 0.03183(13) | 0.32755(6) | 0.0059(3) |
| *P*(13) | 0.86212(14) | 0.36354(14) | 0.21862(7) | 0.0127(3) | *P*(28) | 0.77030(12) | 0.14964(12) | 0.31600(6) | 0.0069(3) |
| *P*(14) | 0.78071(11) | 0.46791(13) | 0.03942(6) | 0.0081(3) | *P*(29) | 0.87667(12) | 0.03750(13) | -0.07163(6) | 0.0080(3) |
| *P*(15) | 0.58616(13) | 0.47773(13) | 0.23731(7) | 0.0112(3) | *P*(30) | 0.67915(12) | 0.02383(11) | 0.12999(6) | 0.0048(3) |
| *Na*(1) | 0.58711(15) | 0.01517(15) | 0.22905(8) | 0.0053(5) | *Na*(10) | 0.1266(2) | 0.7510(2) | 0.17767(9) | 0.0123(5) |
| *Na*(2) | 0.67265(16) | 0.48283(16) | 0.13788(8) | 0.0104(6) | *Na*(11) | 0.9843(2) | 0.2745(3) | 0.33739(13) | 0.0163(10) |
| *Na*(3) | 0.77833(3) | 0.7265(3) | 0.04229(12) | 0.0243(11) | *Na*(12) | 0.4874(3) | 0.2275(3) | -0.17186(13) | 0.0256(11) |
| *Na*(4) | 0.27998(3) | 0.2288(3) | 0.03146(14) | 0.0289(11) | *Na*(13) | 1.0844(3) | 0.2286(3) | 0.23757(14) | 0.0212(9) |
| *Na*(5) | 0.18229(3) | 0.2689(3) | 0.13214(15) | 0.0279(10) | *Na*(14) | 0.72405(19) | 0.2534(2) | 0.07897(10) | 0.0170(7) |
| *Na*(6) | 0.88288(3) | 0.7743(3) | -0.06103(13) | 0.0238(10) | *Na*(15) | 0.9333(2) | 0.2464(2) | -0.11579(10) | 0.0157(8) |
| *Na*(7) | 0.32117(19) | 0.2532(2) | 0.47428(9) | 0.0123(7) | *Na*(16A) | 0.5869(6) | 0.2584(6) | -0.2831(3) | 0.027(2) |
| *Na*(8) | 0.52955(19) | 0.2480(2) | 0.27670(10) | 0.0125(7) | *Na*(16B) | 0.6768(5) | 0.2455(6) | 0.6541(3) | 0.037(2) |
| *Na*(9) | 0.3820(3) | -0.2751(3) | 0.42969(12) | 0.0183(10) | | | | | |
| O(1) | 0.2157(3) | -0.0369(4) | 0.55875(17) | 0.0091(8) | O(61) | 0.7335(4) | 0.3806(4) | 0.00169(18) | 0.0145(9) |
| O(2) | 0.3082(3) | 0.5281(3) | 0.45960(15) | 0.0046(7) | O(62) | 0.3376(3) | 0.1147(4) | 0.57543(17) | 0.0102(8) |
| O(3) | 0.5526(3) | 0.2423(3) | -0.07616(16) | 0.0081(8) | O(63) | 0.4549(4) | 0.2504(4) | 0.02053(18) | 0.0125(9) |
| O(4) | 1.1420(4) | 0.4256(4) | -0.00312(18) | 0.0156(9) | O(64) | 0.8187(3) | 0.1026(4) | -0.11683(17) | 0.0109(8) |
| O(5) | 0.2672(4) | -0.0947(4) | 0.39937(19) | 0.0142(9) | O(65) | 0.8467(4) | 0.5405(4) | 0.01414(19) | 0.0141(9) |

TABLE 2A (cont'd). COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN GREEN MANITOBAITE

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O(6) | 1.0307(4) | 0.4315(4) | 0.06254(19) | 0.0170(10) | O(66) | 0.0164(3) | 0.0390(4) | 0.25565(16) | 0.0072(8) |
| O(7) | 0.5675(3) | 0.3456(4) | 0.37889(16) | 0.0092(8) | O(67) | 0.8090(4) | 0.2509(4) | 0.34555(18) | 0.0133(9) |
| O(8) | 1.3126(3) | 0.2593(4) | -0.16320(17) | 0.0112(8) | O(68) | 0.5727(4) | 0.3234(4) | 0.09851(18) | 0.0163(9) |
| O(9) | 1.1037(3) | 0.2593(4) | 0.03920(17) | 0.0100(8) | O(69) | 0.2475(4) | 0.4604(4) | 0.11107(18) | 0.0137(9) |
| O(10) | 0.9626(3) | 0.3513(3) | -0.02450(15) | 0.0065(8) | O(70) | 0.4522(4) | 0.5346(4) | 0.41105(19) | 0.0149(9) |
| O(11) | 0.0575(4) | 0.0976(4) | 0.10099(19) | 0.0156(10) | O(71) | 0.65983(3) | 0.5557(4) | 0.21891(18) | 0.0131(9) |
| O(12) | 0.1041(4) | 0.4660(4) | 0.15834(17) | 0.0120(9) | O(72) | -0.0751(4) | 0.6144(4) | 0.29081(18) | 0.0157(9) |
| O(13) | 0.9486(3) | 0.7598(4) | 0.03040(17) | 0.0106(8) | O(73) | 0.3315(4) | 0.0832(4) | 0.74857(17) | 0.0130(9) |
| O(14) | 0.6578(3) | 0.0992(4) | 0.50275(17) | 0.0105(8) | O(74) | 0.3450(3) | 0.4189(3) | 0.21420(15) | 0.0134(8) |
| O(15) | 1.1671(3) | 0.3473(3) | -0.22442(15) | 0.0032(7) | O(75) | 0.4315(4) | 0.4180(4) | 0.65766(16) | 0.0097(8) |
| O(16) | 1.3448(3) | 0.4172(4) | -0.21388(16) | 0.0129(8) | O(76) | 0.7170(3) | 0.1038(3) | 0.17244(16) | 0.0090(8) |
| O(17) | 0.7442(3) | 0.4056(4) | -0.18626(18) | 0.0121(9) | O(77) | 0.2364(3) | 0.0675(3) | 0.30558(16) | 0.0068(8) |
| O(18) | 0.3527(3) | 0.3466(3) | 0.57063(15) | 0.0050(7) | O(78) | 0.0455(3) | 0.6191(4) | 0.36917(17) | 0.0141(8) |
| O(19) | 0.5321(3) | 0.4158(3) | 0.58863(15) | 0.0068(8) | O(79) | 0.5492(4) | 0.4019(4) | 0.19203(18) | 0.0189(10) |
| O(20) | 0.7002(3) | 0.5388(4) | 0.05777(17) | 0.0117(8) | O(80) | 0.9105(4) | 0.2659(4) | 0.24579(19) | 0.0170(9) |
| O(21) | 1.2443(4) | 0.4358(4) | -0.14177(18) | 0.0139(9) | O(81) | 0.1299(3) | 0.4240(4) | 0.41313(17) | 0.0127(8) |
| O(22) | 0.4782(3) | 0.1618(4) | 0.46357(16) | 0.0085(8) | O(82) | 0.2208(4) | 0.1147(4) | 0.49404(18) | 0.0180(9) |
| O(23) | 0.1347(4) | 0.6220(4) | 0.10101(19) | 0.0160(9) | O(83) | 0.5201(3) | 0.0974(3) | 0.55388(16) | 0.0071(8) |
| O(24) | 0.7861(4) | 0.3333(4) | -0.09712(18) | 0.0133(9) | O(84) | 0.2665(3) | 0.1623(3) | 0.66292(15) | 0.0071(8) |
| O(25) | 0.7441(3) | 0.4243(4) | 0.40206(17) | 0.0135(9) | O(85) | -0.0766(3) | 0.1028(3) | 0.15428(16) | 0.0186(9) |
| O(26) | 0.9338(3) | 0.4226(4) | -0.38092(16) | 0.0107(8) | O(86) | 0.1288(3) | -0.1220(4) | 0.26605(16) | 0.0077(8) |
| O(27) | 0.2078(4) | -0.2567(4) | 0.43725(19) | 0.0128(9) | O(87) | 0.0468(4) | 0.4610(4) | 0.30830(18) | 0.0112(9) |
| O(28) | 0.4160(3) | -0.0399(3) | 0.35359(16) | 0.0057(8) | O(88) | 0.4382(3) | 0.0581(3) | 0.11045(14) | 0.0037(7) |
| O(29) | 0.6307(3) | 0.4298(4) | 0.46454(17) | 0.0109(8) | O(89) | 0.3506(4) | -0.0275(4) | 0.50570(18) | 0.0124(9) |
| O(30) | 0.8378(4) | 0.4021(4) | 0.08442(18) | 0.0148(9) | O(90) | 0.1575(3) | 0.0324(4) | 0.20642(17) | 0.0097(8) |
| O(31) | 0.3977(4) | 0.2575(4) | 0.72980(18) | 0.0137(9) | O(91) | 0.7082(4) | 0.2569(4) | 0.44322(19) | 0.0159(10) |
| O(32) | 0.5981(3) | 0.2696(3) | 0.53140(15) | 0.0069(8) | O(92) | -0.1212(3) | 0.1644(4) | 0.06483(17) | 0.0113(9) |
| O(33) | 0.9434(4) | 0.4199(4) | 0.19349(18) | 0.0152(9) | O(93) | 0.7692(4) | 0.2541(4) | -0.26036(18) | 0.0134(9) |
| O(34) | 0.1758(4) | 0.3383(4) | 0.50052(17) | 0.0132(9) | O(94) | 0.4276(4) | 0.0946(4) | 0.28069(18) | 0.0133(9) |
| O(35) | 0.0574(4) | 0.2412(4) | 0.4292(2) | 0.0179(10) | O(95) | 0.5407(3) | 0.4294(3) | 0.01605(15) | 0.0055(7) |
| O(36) | 0.8353(4) | 0.0808(4) | -0.28988(18) | 0.0135(9) | O(96) | 0.5218(3) | 0.0714(3) | -0.03358(15) | 0.0055(7) |
| O(37) | 0.3520(3) | 0.2357(3) | 0.12195(17) | 0.0090(8) | O(97) | 0.5284(3) | 0.1185(4) | 0.36695(16) | 0.0096(8) |
| O(38) | 0.1340(3) | -0.0858(4) | 0.45503(17) | 0.0131(9) | O(98) | -0.0001(3) | 0.4054(3) | 0.46792(17) | 0.0081(8) |
| O(39) | 0.0852(3) | -0.1569(4) | 0.36618(16) | 0.0097(8) | O(99) | 0.4027(3) | 0.4079(4) | 0.06671(17) | 0.0096(8) |
| O(40) | 0.8293(4) | 0.4406(4) | 0.25769(19) | 0.0185(10) | O(100) | 1.0979(4) | 0.8463(4) | 0.09005(19) | 0.0180(10) |
| O(41) | 0.3866(4) | 0.3306(4) | 0.30186(18) | 0.0152(9) | O(101) | 0.6967(4) | 0.1581(4) | -0.01362(17) | 0.0129(9) |
| O(42) | 0.6666(3) | 0.2286(4) | -0.16624(17) | 0.0130(9) | O(102) | 0.7318(3) | 0.0802(4) | -0.22270(17) | 0.0116(9) |
| O(43) | 0.7689(3) | 0.3374(4) | 0.17650(17) | 0.0107(8) | O(103) | 0.9531(4) | -0.0296(4) | -0.0935(2) | 0.0181(10) |
| O(44) | 0.8135(3) | -0.0357(4) | -0.04471(17) | 0.0093(8) | O(104) | 0.6349(3) | 0.0694(4) | -0.09713(16) | 0.0077(8) |
| O(45) | 0.4445(3) | 0.0971(3) | 0.68327(15) | 0.0084(8) | O(105) | 0.6104(3) | 0.4017(4) | -0.13406(17) | 0.0114(9) |
| O(46) | 0.5009(3) | 0.5439(4) | 0.25249(17) | 0.0112(9) | O(106) | 0.3183(3) | 0.0772(4) | 0.17134(17) | 0.0112(9) |
| O(47) | 0.1578(4) | 0.2407(4) | 0.32789(18) | 0.0115(8) | O(107) | 0.1241(3) | 0.0736(4) | 0.36999(17) | 0.0117(9) |
| O(48) | -0.0884(3) | 0.4744(4) | 0.36085(16) | 0.0075(8) | O(108) | 0.9177(3) | 0.9237(4) | 0.07648(17) | 0.0139(9) |
| O(49) | 0.8645(3) | 0.0941(4) | 0.30139(17) | 0.0110(9) | O(109) | 0.6867(3) | 0.1697(4) | 0.26900(17) | 0.0122(9) |
| O(50) | 0.6288(4) | 0.4081(4) | 0.28293(19) | 0.0189(10) | O(110) | 0.9147(4) | 0.1551(4) | -0.20436(18) | 0.0138(9) |
| O(51) | 0.3378(3) | 0.3751(4) | 0.39965(18) | 0.0132(9) | O(111) | 0.2092(3) | 0.4018(4) | 0.26655(17) | 0.0084(8) |
| O(52) | 0.6046(3) | -0.0526(3) | 0.14860(16) | 0.0077(8) | O(112) | 0.4951(4) | 0.1667(4) | 0.18886(17) | 0.0138(9) |
| O(53) | 0.4929(3) | 0.2449(3) | 0.62732(16) | 0.0091(8) | O(113) | 0.3019(3) | 0.1509(4) | 0.38952(17) | 0.0116(9) |
| O(54) | 0.4478(3) | 0.3950(4) | 0.48267(17) | 0.0113(8) | O(114) | 0.8158(3) | 0.4044(4) | -0.32021(17) | 0.0129(9) |
| O(55) | 0.0192(3) | -0.0952(4) | 0.18236(17) | 0.0109(8) | O(115) | 1.0183(3) | 0.9366(4) | 0.00970(17) | 0.0118(9) |
| O(56) | 0.7273(4) | 0.0740(4) | 0.35189(19) | 0.0165(10) | O(116) | 0.5602(3) | -0.0384(3) | 0.30651(16) | 0.0065(7) |
| O(57) | 0.9993(4) | 0.3346(4) | -0.29549(18) | 0.0156(9) | O(117) | 0.6384(3) | 0.0874(4) | 0.08163(17) | 0.0131(9) |
| O(58) | 0.0016(3) | 0.2712(4) | 0.13359(17) | 0.0173(9) | O(118) | 0.8662(4) | 0.2417(4) | -0.3630(2) | 0.0181(10) |
| O(59) | 0.2438(4) | 0.5963(4) | 0.1838(2) | 0.0180(10) | O(119) | 0.7632(4) | -0.0443(4) | 0.11237(19) | 0.0169(10) |
| O(60) | 0.9263(3) | 0.1256(4) | -0.03436(16) | 0.0101(8) | O(120) | 0.2656(4) | 0.2389(4) | 0.23025(19) | 0.0213(10) |

the data collection and structure refinement are given in Table 1, final atom parameters are given in Table 2, selected interatomic distances in Table 3, and refined site-scattering values and site populations in Table 4. A table of structure factors and a cif file may be obtained from the Depository of Unpublished Data, on the MAC website [document Manitobaite CM49_1221].

## Chemical Composition

Both green and brown crystals of manitobaite used for the collection of the X-ray intensity data were subsequently mounted in epoxy, ground, polished, and analyzed using a Cameca SX–100 electron microprobe. Preliminary analysis was done using energy-dispersion

TABLE 2B. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN BROWN MANITOBAITE

| | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| *Mn*(1) | 0.27529(1) | 0.48839(2) | 0.53518(1) | 0.00980(8) | 0.01328(8) | 0.01084(8) | 0.00029(7) | 0.00330(7) | -0.00104(7) | 0.01113(5) |
| *Mn*(2) | 0.08466(1) | 0.51101(2) | 0.23588(1) | 0.00533(7) | 0.00499(8) | 0.00107(7) | -0.00087(6) | 0.00140(6) | -0.00011(6) | 0.00369(4) |
| *Mn*(3) | 0.38849(1) | 0.01317(2) | 0.42983(1) | 0.00481(7) | 0.00521(7) | 0.00637(8) | -0.00085(6) | 0.00163(6) | 0.00017(6) | 0.00539(4) |
| *Mn*(4) | 1.03936(2) | 0.25383(2) | -0.21216(1) | 0.01595(10) | 0.01367(10) | 0.02879(12) | -0.00128(9) | 0.00670(9) | -0.00095(9) | 0.01915(6) |
| *Mn*(5) | 0.22374(1) | 0.24721(2) | 0.57739(1) | 0.00467(7) | 0.00353(8) | 0.02546(10) | 0.00149(7) | 0.01037(7) | -0.00087(6) | 0.01022(5) |
| *Mn*(6) | 0.87586(2) | 0.48721(2) | -0.06304(1) | 0.01544(9) | 0.01344(9) | 0.01058(9) | 0.00222(8) | 0.00072(7) | 0.00100(8) | 0.01339(5) |
| *Mn*(7) | 0.43490(1) | 0.24867(2) | 0.38158(1) | 0.00891(9) | 0.00537(8) | 0.02676(11) | -0.00044(8) | 0.00673(8) | 0.00347(7) | 0.01324(6) |
| *Mn*(8) | 0.82974(2) | 0.25278(2) | -0.01663(1) | 0.01060(9) | 0.00878(8) | 0.02342(10) | -0.00223(8) | 0.00548(8) | -0.00442(8) | 0.01397(5) |
| *Mn*(9) | 0.18001(2) | -0.01133(2) | 0.13110(1) | 0.02006(10) | 0.01786(10) | 0.01454(9) | -0.00111(8) | 0.00056(8) | 0.00237(9) | 0.01787(6) |
| *Mn*(10) | -0.01078(2) | -0.01178(2) | 0.33187(1) | 0.00968(8) | 0.00604(8) | 0.00530(8) | -0.00163(7) | 0.00031(7) | -0.00298(7) | 0.00716(5) |
| *Fe*(1) | 0.19853(2) | 0.39835(2) | 0.34668(1) | 0.01055(8) | 0.00785(8) | 0.01027(8) | 0.00096(7) | 0.00443(7) | 0.00015(7) | 0.00923(5) |
| *Fe*(2) | 0.59746(1) | 0.39758(2) | -0.05448(1) | 0.01370(8) | 0.00906(8) | 0.01114(8) | 0.00369(7) | 0.00220(7) | 0.00164(7) | 0.01133(5) |
| *Fe*(3) | 0.99296(1) | 0.60353(2) | 0.04861(1) | 0.00884(8) | 0.00822(8) | 0.00242(7) | 0.00048(6) | -0.00016(6) | -0.00084(7) | 0.00666(4) |
| *Fe*(4) | 0.49437(2) | 0.09127(2) | 0.04105(1) | 0.01047(8) | 0.01141(8) | 0.00978(8) | -0.00172(7) | 0.00012(7) | -0.00159(7) | 0.01080(5) |
| *Fe*(5) | 0.77059(1) | 0.40964(2) | 0.32656(1) | 0.00569(8) | 0.00867(8) | 0.00423(8) | 0.00209(7) | 0.00179(6) | 0.00026(7) | 0.00609(5) |
| *Fe*(6) | 1.06606(1) | 1.10258(2) | 0.02095(1) | 0.00810(8) | 0.00525(8) | 0.00620(8) | -0.00107(7) | -0.00325(7) | -0.00027(7) | 0.00714(5) |
| *Fe*(7) | 1.27039(2) | 0.10331(2) | -0.18101(1) | 0.01118(9) | 0.00626(8) | 0.01427(9) | 0.00035(7) | 0.00170(7) | -0.00039(7) | 0.01067(5) |
| *Fe*(8) | 0.66752(1) | -0.10181(2) | -0.07924(1) | 0.00483(8) | 0.00498(8) | 0.00521(8) | 0.00600(7) | 0.00162(6) | 0.00122(7) | 0.00492(5) |
| *X*(1) | 0.17105(2) | 0.58596(2) | 0.42339(1) | 0.00863(9) | 0.00789(9) | 0.00931(9) | 0.00057(8) | 0.00080(7) | -0.00083(8) | 0.00874(5) |
| *X*(2) | 0.09331(2) | 0.08517(2) | 0.44509(1) | 0.00695(9) | 0.00657(9) | 0.00507(9) | 0.00043(8) | 0.00026(7) | -0.00095(8) | 0.00632(5) |
| *M*(1) | 0.39856(2) | 0.39316(2) | 0.14518(1) | 0.01842(9) | 0.01422(9) | 0.00902(8) | 0.00306(7) | -0.00023(7) | 0.00064(8) | 0.01428(5) |
| *M*(2) | 0.86606(1) | 0.10735(2) | 0.22175(1) | 0.00604(8) | 0.00601(8) | 0.00559(8) | -0.00404(7) | 0.00132(6) | 0.00094(7) | 0.00586(5) |
| *Y*(1) | 0.62967(3) | 0.25097(3) | 0.17730(1) | 0.00856(8) | 0.00898(8) | 0.04212(16) | -0.00124(10) | 0.00423(10) | -0.00099(7) | 0.01998(7) |
| *Z*(1) | 0.48728(2) | 0.48431(2) | 0.33329(1) | 0.00867(8) | 0.00938(9) | 0.00742(8) | 0.00348(7) | 0.00033(7) | -0.00409(7) | 0.00866(5) |
| *Z*(2) | 0.77782(2) | 0.01746(2) | 0.03333(1) | 0.01880(11) | 0.01330(10) | 0.01183(10) | -0.00055(8) | 0.00104(9) | 0.00056(9) | 0.01491(6) |

| | *x* | *y* | *z* | $U_{eq}$ | | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| *Al*(1) | 0.79342(3) | 0.40049(3) | -0.25022(1) | 0.01107(6) | *Al*(5) | 0.37424(2) | 0.59111(3) | 0.22120(1) | 0.00431(6) |
| *Al*(2) | 0.69418(3) | 0.08221(3) | -0.15739(1) | 0.01052(7) | *Al*(6) | 0.96999(2) | 0.41537(2) | 0.12547(1) | 0.00488(5) |
| *Al*(3) | 0.57235(3) | 0.41914(3) | 0.52527(1) | 0.00351(7) | *Al*(7) | -0.10993(3) | -0.09204(3) | 0.14656(1) | 0.01560(7) |
| *Al*(4) | 0.47268(2) | -0.09917(2) | 0.11728(1) | 0.00208(5) | *Al*(8) | 0.29549(2) | 0.08434(2) | 0.24249(1) | 0.01013(5) |
| *P*(1) | 0.40451(2) | 0.13325(2) | 0.14978(1) | 0.00270(5) | *P*(16) | 0.56115(2) | 0.15930(3) | 0.51214(1) | 0.00521(5) |
| *P*(2) | 0.70158(2) | 0.34239(3) | -0.14610(1) | 0.00683(6) | *P*(17) | 0.90598(2) | 0.35024(2) | -0.33862(1) | 0.00485(5) |
| *P*(3) | 0.30326(3) | 0.34825(3) | 0.25489(1) | 0.01117(6) | *P*(18) | 0.35949(3) | 0.15185(3) | 0.70616(1) | 0.00834(6) |
| *P*(4) | 0.60296(2) | 0.13651(2) | -0.05385(1) | 0.00400(5) | *P*(19) | 0.17135(2) | -0.14968(3) | 0.41413(1) | 0.00700(6) |
| *P*(5) | 0.09267(2) | 0.35153(3) | 0.45333(1) | 0.00817(6) | *P*(20) | 0.45191(3) | 0.35655(3) | 0.61179(1) | 0.00828(6) |
| *P*(6) | 0.38566(2) | 0.46182(3) | 0.43817(1) | 0.00596(5) | *P*(21) | 0.81359(2) | 0.14265(2) | -0.24401(1) | 0.00365(5) |
| *P*(7) | 0.20642(3) | 0.13427(3) | 0.35023(1) | 0.00983(6) | *P*(22) | 0.28070(3) | 0.03746(3) | 0.53300(1) | 0.01142(7) |
| *P*(8) | 1.05772(2) | 0.36556(2) | 0.01926(1) | 0.00412(5) | *P*(23) | -0.03808(2) | 0.15713(3) | 0.11294(1) | 0.00717(6) |
| *P*(9) | 1.26631(2) | 0.36545(2) | -0.18397(1) | 0.00297(5) | *P*(24) | 0.99974(3) | 0.86526(3) | 0.05282(1) | 0.01038(6) |
| *P*(10) | 0.18281(2) | 0.53312(2) | 0.13784(1) | 0.00137(5) | *P*(25) | 0.66273(3) | 0.36195(3) | 0.42251(1) | 0.00906(6) |
| *P*(11) | -0.01870(2) | 0.53721(2) | 0.33417(1) | 0.00215(5) | *P*(26) | 0.07963(3) | -0.03521(3) | 0.22843(1) | 0.01205(7) |
| *P*(12) | 0.49317(2) | 0.35141(2) | 0.05120(1) | 0.00500(5) | *P*(27) | 0.48299(3) | 0.03191(3) | 0.32811(1) | 0.00939(6) |
| *P*(13) | 0.86100(3) | 0.36353(3) | 0.21831(1) | 0.01234(7) | *P*(28) | 0.77105(3) | 0.15108(3) | 0.31577(1) | 0.00953(6) |
| *P*(14) | 0.78064(2) | 0.46884(2) | 0.03980(1) | 0.00417(5) | *P*(29) | 0.87654(2) | 0.03654(3) | -0.07156(1) | 0.00686(6) |
| *P*(15) | 0.58530(2) | 0.47681(3) | 0.23691(1) | 0.00742(6) | *P*(30) | 0.67863(3) | 0.02137(3) | 0.12956(1) | 0.00855(6) |
| *Na*(1) | 0.59115(3) | 0.01595(3) | 0.22921(1) | 0.00749(7) | *Na*(10) | 0.12781(7) | 0.74978(7) | 0.17951(3) | 0.01491(10) |
| *Na*(2) | 0.67392(4) | 0.48572(4) | 0.13790(2) | 0.01596(9) | *Na*(11) | 0.98501(6) | 0.27302(7) | 0.33573(3) | 0.02071(18) |
| *Na*(3) | 0.77758(7) | 0.72828(7) | 0.04320(3) | 0.02469(18) | *Na*(12) | 0.48787(7) | 0.22765(7) | -0.17178(3) | 0.02836(19) |
| *Na*(4) | 0.27766(6) | 0.23226(6) | 0.03604(3) | 0.02821(16) | *Na*(13) | 1.08484(8) | 0.22981(9) | 0.23605(4) | 0.0242(2) |
| *Na*(5) | 0.17900(10) | 0.26727(10) | 0.13857(5) | 0.0327(3) | *Na*(14) | 0.72461(6) | 0.25403(7) | 0.07985(3) | 0.01986(17) |
| *Na*(6) | 0.88371(5) | 0.77215(6) | -0.06119(3) | 0.02042(14) | *Na*(15) | 0.93188(5) | 0.24718(6) | -0.11657(3) | 0.01751(15) |
| *Na*(7) | 0.32368(4) | 0.25332(4) | 0.47543(2) | 0.01254(11) | *Na*(16A) | 0.59083(16) | 0.25046(17) | -0.28804(8) | 0.0245(4) |
| *Na*(8) | 0.53007(5) | 0.24815(5) | 0.27562(3) | 0.01437(13) | *Na*(16B) | 0.67976(15) | 0.24262(16) | 0.64754(8) | 0.0495(5) |
| *Na*(9) | 0.38295(6) | -0.27238(7) | 0.43047(3) | 0.02453(18) | | | | | |
| O(1) | 0.21674(7) | -0.03608(7) | 0.55823(3) | 0.00800(17) | O(61) | 0.73557(8) | 0.38117(8) | 0.00046(4) | 0.01432(19) |
| O(2) | 0.30747(7) | 0.52669(7) | 0.45980(3) | 0.00884(17) | O(62) | 0.33624(7) | 0.11596(8) | 0.57466(4) | 0.01071(18) |
| O(3) | 0.55305(7) | 0.24152(7) | -0.07716(3) | 0.00662(16) | O(63) | 0.45508(8) | 0.24769(9) | 0.02116(4) | 0.0178(2) |
| O(4) | 1.13792(8) | 0.42569(8) | -0.00332(4) | 0.0157(2) | O(64) | 0.81893(7) | 0.10055(7) | -0.11790(4) | 0.00770(17) |
| O(5) | 0.26556(8) | -0.09814(9) | 0.39878(4) | 0.0161(2) | O(65) | 0.84668(7) | 0.54479(8) | 0.01315(4) | 0.01240(19) |
| O(6) | 1.02764(8) | 0.43360(8) | 0.06233(4) | 0.01349(19) | O(66) | 0.01658(7) | 0.03671(8) | 0.25543(4) | 0.01057(18) |

TABLE 2B (cont'd). COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN BROWN MANITOBAITE

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O(7) | 0.56643(6) | 0.34517(7) | 0.37922(3) | 0.00524(16) | O(67) | 0.80800(8) | 0.25312(8) | 0.34477(4) | 0.01258(19) |
| O(8) | 1.30991(8) | 0.26048(8) | -0.16335(4) | 0.01285(19) | O(68) | 0.57329(8) | 0.32516(8) | 0.09826(4) | 0.0152(2) |
| O(9) | 1.10025(7) | 0.25998(8) | 0.03795(4) | 0.01167(18) | O(69) | 0.24755(7) | 0.45956(7) | 0.11058(4) | 0.00754(17) |
| O(10) | 0.96005(6) | 0.35101(7) | -0.02412(3) | 0.00439(15) | O(70) | 0.44955(7) | 0.53859(8) | 0.41109(4) | 0.01040(18) |
| O(11) | 0.05505(7) | 0.09923(8) | 0.10029(4) | 0.01215(19) | O(71) | 0.65900(7) | 0.55698(8) | 0.21859(4) | 0.00892(17) |
| O(12) | 0.10441(7) | 0.46673(7) | 0.15967(3) | 0.00723(16) | O(72) | -0.07492(8) | 0.61498(8) | 0.29190(4) | 0.0135(2) |
| O(13) | 0.95140(7) | 0.75988(8) | 0.02974(4) | 0.01015(18) | O(73) | 0.33097(7) | 0.08621(8) | 0.74854(4) | 0.01115(18) |
| O(14) | 0.65420(7) | 0.10117(8) | 0.50142(4) | 0.01293(19) | O(74) | 0.34429(8) | 0.42177(8) | 0.21548(4) | 0.0146(2) |
| O(15) | 1.16566(7) | 0.34821(7) | -0.22387(3) | 0.00663(16) | O(75) | 0.42731(8) | 0.41867(8) | 0.65698(4) | 0.01288(19) |
| O(16) | 1.34273(8) | 0.41832(8) | -0.21353(4) | 0.0158(2) | O(76) | 0.71743(7) | 0.10078(8) | 0.17361(4) | 0.00970(17) |
| O(17) | 0.74498(7) | 0.40956(7) | -0.18626(3) | 0.00833(17) | O(77) | 0.23472(7) | 0.06822(7) | 0.30574(4) | 0.00835(17) |
| O(18) | 0.35094(6) | 0.34781(6) | 0.57111(3) | 0.00242(14) | O(78) | 0.04399(8) | 0.61567(8) | 0.37223(4) | 0.01322(19) |
| O(19) | 0.52839(7) | 0.41795(7) | 0.58836(4) | 0.00889(17) | O(79) | 0.54787(9) | 0.39828(10) | 0.19414(5) | 0.0222(2) |
| O(20) | 0.69992(7) | 0.53628(8) | 0.05839(4) | 0.01143(18) | O(80) | 0.90513(9) | 0.26569(9) | 0.24341(4) | 0.0202(2) |
| O(21) | 1.24399(7) | 0.43814(8) | -0.14169(4) | 0.01137(18) | O(81) | 0.13094(8) | 0.42505(8) | 0.41315(4) | 0.01287(19) |
| O(22) | 0.47675(7) | 0.16285(8) | 0.46343(4) | 0.01086(18) | O(82) | 0.22005(8) | 0.11377(9) | 0.49369(4) | 0.0182(2) |
| O(23) | 0.13444(8) | 0.62318(8) | 0.10132(4) | 0.0145(2) | O(83) | 0.52108(7) | 0.09972(8) | 0.55400(4) | 0.00873(17) |
| O(24) | 0.78532(7) | 0.33406(8) | -0.09730(4) | 0.01150(19) | O(84) | 0.26508(7) | 0.16070(8) | 0.66199(4) | 0.00867(17) |
| O(25) | 0.74106(8) | 0.42447(9) | 0.40152(4) | 0.0167(2) | O(85) | -0.08032(8) | 0.09769(8) | 0.15288(4) | 0.0139(2) |
| O(26) | 0.93476(7) | 0.42518(7) | -0.38113(3) | 0.00639(16) | O(86) | 0.12953(7) | -0.12225(7) | 0.26584(4) | 0.00674(16) |
| O(27) | 0.20255(8) | -0.25660(8) | 0.43799(4) | 0.01348(19) | O(87) | 0.04835(7) | 0.45882(8) | 0.30885(4) | 0.00978(18) |
| O(28) | 0.41603(7) | -0.03911(7) | 0.35302(3) | 0.00676(16) | O(88) | 0.43619(6) | 0.05660(7) | 0.10980(3) | 0.00436(15) |
| O(29) | 0.62840(8) | 0.42879(8) | 0.46387(4) | 0.01291(19) | O(89) | 0.35092(7) | -0.02842(8) | 0.50509(4) | 0.00869(17) |
| O(30) | 0.83757(8) | 0.40431(8) | 0.08445(4) | 0.0160(2) | O(90) | 0.16076(7) | 0.03474(8) | 0.20832(4) | 0.01193(19) |
| O(31) | 0.39359(8) | 0.25942(8) | 0.72939(4) | 0.0148(2) | O(91) | 0.70690(9) | 0.25683(9) | 0.44061(4) | 0.0194(2) |
| O(32) | 0.59542(7) | 0.26980(7) | 0.53243 | 0.00873(17) | O(92) | -0.12272(7) | 0.16204(8) | 0.06349(4) | 0.01157(19) |
| O(33) | 0.94045(8) | 0.41976(8) | 0.19318(4) | 0.0153(2) | O(93) | 0.76983(8) | 0.25342(9) | -0.26072(4) | 0.0152(2) |
| O(34) | 0.17881(7) | 0.33998(8) | 0.50054(4) | 0.01211(18) | O(94) | 0.42531(7) | 0.09673(8) | 0.28182(4) | 0.01164(19) |
| O(35) | 0.05775(8) | 0.23797(9) | 0.43070(4) | 0.0172(2) | O(95) | 0.53982(6) | 0.42982(7) | 0.01535(3) | 0.00229(15) |
| O(36) | 0.83398(7) | 0.07894(7) | -0.29107 | 0.00786(17) | O(96) | 0.52061(6) | 0.07131(7) | -0.03253(3) | 0.00336(15) |
| O(37) | 0.35373(7) | 0.23522(7) | 0.12187(4) | 0.00944(17) | O(97) | 0.52904(7) | 0.11732(8) | 0.36690(4) | 0.00860(17) |
| O(38) | 0.13296(7) | -0.08505(8) | 0.45456(4) | 0.01144(18) | O(98) | -0.00115(7) | 0.40579(7) | 0.46737(3) | 0.00596(16) |
| O(39) | 0.08643(7) | -0.15824(8) | 0.36562(4) | 0.00984(18) | O(99) | 0.39952(7) | 0.40659(7) | 0.06559(3) | 0.00634(16) |
| O(40) | 0.82687(8) | 0.44146(9) | 0.25733(4) | 0.0181(2) | O(100) | 1.09993(8) | 0.84941(8) | 0.09008(4) | 0.01351(19) |
| O(41) | 0.38564(8) | 0.33355(8) | 0.30288(4) | 0.0154(2) | O(101) | 0.69617(9) | 0.15663(9) | -0.01354(4) | 0.0191(2) |
| O(42) | 0.66691(7) | 0.22807(8) | -0.16540(4) | 0.01098(18) | O(102) | 0.73065(7) | 0.07875(7) | -0.22295(3) | 0.00779(17) |
| O(43) | 0.76580(7) | 0.34054(8) | 0.17681(4) | 0.01007(18) | O(103) | 0.95583(7) | -0.03388(8) | -0.09308(4) | 0.01104(18) |
| O(44) | 0.81219(7) | -0.03374(8) | -0.04447(4) | 0.01054(18) | O(104) | 0.63384(7) | 0.06660(7) | -0.09710(3) | 0.00571(16) |
| O(45) | 0.44443(7) | 0.09943(7) | 0.68411 | 0.00792(17) | O(105) | 0.60822(7) | 0.40277(8) | -0.13401(4) | 0.01022(18) |
| O(46) | 0.50033(8) | 0.54248(8) | 0.25414(4) | 0.01367(19) | O(106) | 0.31936(7) | 0.07558(7) | 0.17254(3) | 0.00563(16) |
| O(47) | 0.15971(8) | 0.24161(8) | 0.32926(4) | 0.01223(19) | O(107) | 0.12350(7) | 0.07310(8) | 0.37180(4) | 0.00918(17) |
| O(48) | -0.09081(7) | 0.47377(8) | 0.36042(4) | 0.00991(17) | O(108) | 0.91868(7) | 0.92445(7) | 0.07651(3) | 0.00671(16) |
| O(49) | 0.86311(8) | 0.09522(8) | 0.30078(4) | 0.0157(2) | O(109) | 0.68989(9) | 0.17131(9) | 0.26779(4) | 0.0193(2) |
| O(50) | 0.62893(8) | 0.41009(9) | 0.28331(4) | 0.0185(2) | O(110) | 0.91405(8) | 0.15518(9) | -0.20477(4) | 0.0152(2) |
| O(51) | 0.33591(7) | 0.37573(8) | 0.40039(4) | 0.01245(19) | O(111) | 0.20808(8) | 0.40305(8) | 0.26748(4) | 0.01288(19) |
| O(52) | 0.60487(7) | -0.05228(8) | 0.14905(4) | 0.01168(18) | O(112) | 0.49662(8) | 0.16456(9) | 0.18931(4) | 0.0166(2) |
| O(53) | 0.49222(7) | 0.24690(7) | 0.62693(3) | 0.00701(16) | O(113) | 0.30233(8) | 0.14815(9) | 0.38997(4) | 0.0151(2) |
| O(54) | 0.44568(8) | 0.39669(8) | 0.48218(4) | 0.01333(19) | O(114) | 0.81511(8) | 0.40349(8) | -0.31995(4) | 0.0142(2) |
| O(55) | 0.02075(8) | -0.09473(9) | 0.18161(4) | 0.0162(2) | O(115) | 1.02269(7) | 0.93559(8) | 0.00856(4) | 0.01119(18) |
| O(56) | 0.72680(8) | 0.07864(9) | 0.35170(4) | 0.0183(2) | O(116) | 0.56112(7) | -0.03936(7) | 0.30709(3) | 0.00565(16) |
| O(57) | 0.99830(7) | 0.33464(8) | -0.29590(4) | 0.01162(18) | O(117) | 0.63717(8) | 0.08731(8) | 0.08159(4) | 0.0147(2) |
| O(58) | -0.00538(8) | 0.26714(9) | 0.13345(4) | 0.0171(2) | O(118) | 0.86856(8) | 0.24001(8) | -0.36275(4) | 0.01258(19) |
| O(59) | 0.24299(7) | 0.59459(8) | 0.18395(4) | 0.00918(17) | O(119) | 0.76211(7) | -0.04835(8) | 0.11325(4) | 0.01068(18) |
| O(60) | 0.92641(7) | 0.12551(8) | -0.03418(4) | 0.00932(18) | O(120) | 0.26863(8) | 0.23497(9) | 0.23250(4) | 0.0173(2) |

spectrometry (EDS) to assess the major-element chemical composition of the crystals. Following this procedure, the elements shown to be present were analyzed quantitatively in wavelength-dispersion mode using an operating voltage of 15 kV, a beam current of 20 nA, a beam size of 10 μm, and count times on peak and background of 30 s. The following elements and standards were used for *K*α lines: apatite (P, Ca), andalusite (Al), fayalite (Fe), spessartine (Mn), gahnite (Zn), forsterite (Mg) and albite (Na). The data were corrected using the PAP procedure of Pouchou & Pichoir (1985). For each crystal, 11 points were analyzed, no significant zoning was observed, and the average compositions are given in Table 5, using the results of Mössbauer spectroscopy

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) FOR MANITOBAITE (LEFT: GREEN, RIGHT: BROWN)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Mn*(1)-O(4)g | 2.164(5) | 2.209(1) | *Mn*(2)-O(15)g | 2.205(4) | 2.231(1) | *Mn*(3)-O(5) | 2.132(5) | 2.196(1) |
| *Mn*(1)-O(18) | 2.174(4) | 2.159(1) | *Mn*(2)-O(87) | 2.208(5) | 2.192(1) | *Mn*(3)-O(96)k | 2.153(4) | 2.141(1) |
| *Mn*(1)-O(99)a | 2.193(5) | 2.155(1) | *Mn*(2)-O(12) | 2.214(5) | 2.168(1) | *Mn*(3)-O(89) | 2.228(5) | 2.221(1) |
| *Mn*(1)-O(2) | 2.196(4) | 2.186(1) | *Mn*(2)-O(111) | 2.216(4) | 2.178(1) | *Mn*(3)-O(113) | 2.231(5) | 2.200(1) |
| *Mn*(1)-O(69)a | 2.241(5) | 2.209(1) | *Mn*(2)-O(57)g | 2.281(5) | 2.325(1) | *Mn*(3)-O(28) | 2.251(4) | 2.245(1) |
| *Mn*(1)-O(34) | 2.370(5) | 2.348(1) | *Mn*(2)-O(33)h | 2.336(5) | 2.345(1) | *Mn*(3)-O(22) | 2.314(5) | 2.302(1) |
| <*Mn*(1)-O> | 2.223 | 2.211 | <*Mn*(2)-O> | 2.243 | 2.240 | <*Mn*(3)-O> | 2.218 | 2.217 |
| | | | | | | | | |
| *Mn*(4)-O(110) | 2.127(5) | 2.128(1) | *Mn*(5)-O(100)g | 2.139(5) | 2.137(1) | *Mn*(6)-O(25)b | 2.150(5) | 2.175(1) |
| *Mn*(4)-O(15) | 2.163(4) | 2.141(1) | *Mn*(5)-O(18) | 2.179(4) | 2.156(1) | *Mn*(6)-O(98)c | 2.174(4) | 2.159(1) |
| *Mn*(4)-O(86)l | 2.191(4) | 2.190(1) | *Mn*(5)-O(23)a | 2.214(5) | 2.185(1) | *Mn*(6)-O(10) | 2.188(4) | 2.191(1) |
| *Mn*(4)-O(72)c | 2.284(5) | 2.265(1) | *Mn*(5)-O(62) | 2.260(5) | 2.243(1) | *Mn*(6)-O(48)c | 2.224(4) | 2.224(1) |
| *Mn*(4)-O(39)l | 2.329(5) | 2.367(1) | *Mn*(5)-O(34) | 2.288(5) | 2.327(1) | *Mn*(6)-O(65) | 2.284(5) | 2.257(1) |
| *Mn*(4)-O(57) | 2.464(5) | 2.411(1) | *Mn*(5)-O(84) | 2.515(4) | 2.462(1) | *Mn*(6)-O(24) | 2.353(5) | 2.356(1) |
| <*Mn*(4)-O> | 2.260 | 2.250 | <*Mn*(5)-O> | 2.266 | 2.252 | <*Mn*(6)-O> | 2.229 | 2.227 |
| | | | | | | | | |
| *Mn*(7)-O(97) | 2.155(5) | 2.156(1) | *Mn*(8)-O(101) | 2.155(5) | 2.177(1) | *Mn*(9)-O(1)e | 2.171(5) | 2.175(1) |
| *Mn*(7)-O(51) | 2.154(5) | 2.193(1) | *Mn*(8)-O(60) | 2.165(5) | 2.163(1) | *Mn*(9)-O(90) | 2.174(5) | 2.198(1) |
| *Mn*(7)-O(113) | 2.187(5) | 2.228(1) | *Mn*(8)-O(61) | 2.178(5) | 2.148(1) | *Mn*(9)-O(11) | 2.174(5) | 2.207(1) |
| *Mn*(7)-O(7) | 2.196(5) | 2.153(1) | *Mn*(8)-O(10) | 2.222(4) | 2.181(1) | *Mn*(9)-O(100)m | 2.230(5) | 2.220(1) |
| *Mn*(7)-O(22) | 2.352(4) | 2.395(1) | *Mn*(8)-O(24) | 2.312(5) | 2.345(1) | *Mn*(9)-O(106) | 2.272(5) | 2.260(1) |
| *Mn*(7)-O(41) | 2.388(5) | 2.327(1) | *Mn*(8)-O(92)d | 2.436(5) | 2.390(1) | *Mn*(9)-O(84)e | 2.276(4) | 2.260(1) |
| <*Mn*(7)-O> | 2.239 | 2.242 | <*Mn*(8)-O> | 2.244 | 2.234 | <*Mn*(9)-O> | 2.216 | 2.220 |
| | | | | | | | | |
| *Mn*(10)-O(49)h | 2.165(5) | 2.192(1) | *Fe*(1)-O(47) | 2.091(5) | 2.058(1) | *Fe*(2)-O(3) | 2.101(4) | 2.095(1) |
| *Mn*(10)-O(107) | 2.179(5) | 2.184(1) | *Fe*(1)-O(51) | 2.127(5) | 2.124(1) | *Fe*(2)-O(61) | 2.125(5) | 2.139(1) |
| *Mn*(10)-O(110)f | 2.182(5) | 2.192(1) | *Fe*(1)-O(21)g | 2.163(5) | 2.139(1) | *Fe*(2)-O(70)b | 2.159(5) | 2.174(1) |
| *Mn*(10)-O(103)f | 2.194(5) | 2.206(1) | *Fe*(1)-O(111) | 2.172(4) | 2.137(1) | *Fe*(2)-O(105) | 2.173(5) | 2.151(1) |
| *Mn*(10)-O(66) | 2.241(4) | 2.221(1) | *Fe*(1)-O(81) | 2.180(5) | 2.166(1) | *Fe*(2)-O(95) | 2.196(4) | 2.186(1) |
| *Mn*(10)-O(39) | 2.307(4) | 2.327(1) | *Fe*(1)-O(87) | 2.234(5) | 2.208(1) | *Fe*(2)-O(29)b | 2.228(5) | 2.247(1) |
| <*Mn*(10)-O> | 2.211 | 2.220 | <*Fe*(1)-O> | 2.161 | 2.139 | <*Fe*(2)-O> | 2.164 | 2.165 |
| | | | | | | | | |
| *Fe*(3)-O(13) | 2.092(5) | 2.068(1) | *Fe*(4)-O(117) | 2.031(4) | 2.012(1) | *Fe*(5)-O(50) | 2.026(5) | 2.025(1) |
| *Fe*(3)-O(23)d | 2.129(5) | 2.147(1) | *Fe*(4)-O(96) | 2.093(4) | 2.071(1) | *Fe*(5)-O(67) | 2.094(5) | 2.055(1) |
| *Fe*(3)-O(65) | 2.156(5) | 2.140(1) | *Fe*(4)-O(63) | 2.104(5) | 2.068(1) | *Fe*(5)-O(48)d | 2.095(4) | 2.068(1) |
| *Fe*(3)-O(98)c | 2.166(4) | 2.182(1) | *Fe*(4)-O(89)e | 2.121(5) | 2.130(1) | *Fe*(5)-O(25) | 2.120(5) | 2.117(1) |
| *Fe*(3)-O(6) | 2.213(5) | 2.191(1) | *Fe*(4)-O(88) | 2.191(4) | 2.169(1) | *Fe*(5)-O(40) | 2.177(5) | 2.161(1) |
| *Fe*(3)-O(26)a | 2.221(5) | 2.193(1) | *Fe*(4)-O(83)e | 2.403(4) | 2.430(1) | *Fe*(5)-O(17)a | 2.354(5) | 2.302(1) |
| <*Fe*(3)-O> | 2.163 | 2.153 | <*Fe*(4)-O> | 2.157 | 2.147 | <*Fe*(5)-O> | 2.144 | 2.121 |
| | | | | | | | | |
| *Fe*(6)-O(9)i | 2.081(5) | 2.052(1) | *Fe*(7)-O(8) | 2.079(5) | 2.066(1) | *Fe*(8)-O(91)e | 2.077(5) | 2.051(1) |
| *Fe*(6)-O(38)c | 2.151(5) | 2.145(1) | *Fe*(7)-O(86)l | 2.140(4) | 2.146(1) | *Fe*(8)-O(97)e | 2.134(4) | 2.127(1) |
| *Fe*(6)-O(115) | 2.159(5) | 2.176(1) | *Fe*(7)-O(28)l | 2.144(4) | 2.148(1) | *Fe*(8)-O(44) | 2.159(5) | 2.160(1) |
| *Fe*(6)-O(11)j | 2.159(5) | 2.146(1) | *Fe*(7)-O(5)l | 2.150(5) | 2.138(1) | *Fe*(8)-O(14)e | 2.195(5) | 2.189(1) |
| *Fe*(6)-O(60)l | 2.165(4) | 2.166(1) | *Fe*(7)-O(77)l | 2.186(4) | 2.211(1) | *Fe*(8)-O(56)e | 2.198(5) | 2.161(1) |
| *Fe*(6)-O(1)c | 2.215(5) | 2.236(1) | *Fe*(7)-O(73)t | 2.217(5) | 2.195(1) | *Fe*(8)-O(104) | 2.217(5) | 2.187(1) |
| <*Fe*(6)-O> | 2.155 | 2.153 | <*Fe*(7)-O> | 2.153 | 2.151 | <*Fe*(8)-O> | 2.163 | 2.146 |
| | | | | | | | | |
| *X*(1)-O(78) | 2.020(5) | 2.002(1) | *X*(2)-O(82) | 1.976(5) | 1.962(1) | | | |
| *X*(1)-O(2) | 2.043(4) | 2.040(1) | *X*(2)-O(35) | 2.033(5) | 1.989(1) | | | |
| *X*(1)-O(27)i | 2.056(5) | 2.035(1) | *X*(2)-O(103)f | 2.076(5) | 2.033(1) | | | |
| *X*(1)-O(81) | 2.100(5) | 2.087(1) | *X*(2)-O(107) | 2.119(5) | 2.074(1) | | | |
| *X*(1)-O(4)g | 2.102(5) | 2.089(1) | *X*(2)-O(115)g | 2.193(5) | 2.109(1) | | | |
| *X*(1)-O(21)g | 2.160(5) | 2.171(1) | *X*(2)-O(38) | 2.216(5) | 2.197(1) | | | |
| <*X*(1)-O> | 2.080 | 2.071 | <*X*(2)-O> | 2.102 | 2.060 | | | |
| | | | | | | | | |
| *M*(1)-O(99) | 2.102(5) | 2.127(1) | *M*(2)-O(85)d | 2.116(4) | 2.100(1) | *Y*(1)-O(112) | 2.152(5) | 2.167(1) |
| *M*(1)-O(79) | 2.141(5) | 2.172(1) | *M*(2)-O(49) | 2.121(5) | 2.117(1) | *Y*(1)-O(43) | 2.177(5) | 2.149(1) |
| *M*(1)-O(74) | 2.145(4) | 2.166(1) | *M*(2)-O(76) | 2.150(4) | 2.156(1) | *Y*(1)-O(76) | 2.208(4) | 2.231(1) |
| *M*(1)-O(37) | 2.151(4) | 2.122(1) | *M*(2)-O(80) | 2.161(5) | 2.100(1) | *Y*(1)-O(79) | 2.241(5) | 2.235(1) |
| *M*(1)-O(69) | 2.230(5) | 2.222(1) | *M*(2)-O(66)d | 2.223(4) | 2.231(1) | *Y*(1)-O(68) | 2.410(5) | 2.289(1) |
| *M*(1)-O(75)b | 2.391(5) | 2.395(1) | *M*(2)-O(36)k | 2.375(5) | 2.382(1) | *Y*(1)-O(109) | 2.484(5) | 2.586(1) |
| <*M*(1)-O> | 2.193 | 2.201 | <*M*(2)-O> | 2.191 | 2.181 | <*Y*(1)-O> | 2.279 | 2.276 |
| | | | | | | | | |
| *Z*(1)-O(105)a | 2.250(5) | 2.201(1) | *Z*(2)-O(14)e | 2.210(5) | 2.267(1) | | | |
| *Z*(1)-O(7) | 2.262(4) | 2.269(1) | *Z*(2)-O(119) | 2.284(5) | 2.328(1) | | | |
| *Z*(1)-O(70) | 2.301(5) | 2.327(1) | *Z*(2)-O(108)n | 2.313(5) | 2.327(1) | | | |
| *Z*(1)-O(46) | 2.334(5) | 2.268(1) | *Z*(2)-O(101) | 2.313(5) | 2.293(1) | | | |

TABLE 3 (cont'd). SELECTED INTERATOMIC DISTANCES (Å) FOR MANITOBAITE (LEFT: GREEN, RIGHT: BROWN)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Z*(1)-O(41) | 2.384(5) | 2.376(1) | *Z*(2)-O(44) | 2.331(5) | 2.299(1) | | | |
| *Z*(1)-O(16)g | 2.404(5) | 2.423(1) | *Z*(2)-O(92)d | 2.342(5) | 2.299(1) | | | |
| *Z*(1)-O(50) | 2.726(5) | 2.692(1) | *Z*(2)-O(117) | 2.628(5) | 2.634(1) | | | |
| <*Z*(1)-O> | 2.380 | 2.365 | <*Z*(2)-O> | 2.346 | 2.349 | | | |
| | | | | | | | | |
| *Al*(1)-O(93) | 1.880(5) | 1.878(1) | *Al*(2)-O(64) | 1.828(5) | 1.813(1) | *Al*(3)-O(54) | 1.839(5) | 1.880(1) |
| *Al*(1)-O(72)c | 1.884(5) | 1.912(1) | *Al*(2)-O(42) | 1.871(5) | 1.865(1) | *Al*(3)-O(20)a | 1.853(5) | 1.856(1) |
| *Al*(1)-O(71)b | 1.908(5) | 1.912(1) | *Al*(2)-O(102) | 1.916(5) | 1.903(1) | *Al*(3)-O(19) | 1.879(5) | 1.886(1) |
| *Al*(1)-O(17) | 1.939(5) | 1.941(1) | *Al*(2)-O(104) | 1.933(5) | 1.944(1) | *Al*(3)-O(32) | 1.899(5) | 1.897(1) |
| *Al*(1)-O(114 | 1.965(5) | 1.934(1) | *Al*(2)-O(116)e | 1.936(4) | 1.930(1) | *Al*(3)-O(29) | 1.940(5) | 1.932(1) |
| *Al*(1)-O(40)b | 2.043(5) | 2.028(1) | *Al*(2)-O(56)e | 2.018(5) | 2.063(1) | *Al*(3)-O(95)a | 1.956(4) | 1.945(1) |
| <*Al*(1)-O> | 1.936 | 1.934 | <*Al*(2)-O> | 1.917 | 1.919 | <*Al*(3)-O> | 1.894 | 1.899 |
| | | | | | | | | |
| *Al*(4)-O(45)e | 1.869(5) | 1.890(1) | *Al*(5)-O(46) | 1.833(5) | 1.854(1) | *Al*(6)-O(58)d | 1.889(5) | 1.888(1) |
| *Al*(4)-O(53)e | 1.879(5) | 1.877(1) | *Al*(5)-O(59) | 1.844(5) | 1.849(1) | *Al*(6)-O(30) | 1.898(5) | 1.904(1) |
| *Al*(4)-O(52) | 1.900(4) | 1.907(1) | *Al*(5)-O(16)g | 1.871(5) | 1.870(1) | *Al*(6)-O(33) | 1.919(5) | 1.920(1) |
| *Al*(4)-O(83)e | 1.931(5) | 1.920(1) | *Al*(5)-O(31)b | 1.921(5) | 1.894(1) | *Al*(6)-O(12)d | 1.942(5) | 1.967(1) |
| *Al*(4)-O(62)e | 1.935(5) | 1.972(1) | *Al*(5)-O(75)b | 1.984(5) | 1.980(1) | *Al*(6)-O(6) | 2.017(5) | 1.996(1) |
| *Al*(4)-O(88) | 2.001(4) | 2.009(1) | *Al*(5)-O(74) | 2.204(4) | 2.155(1) | *Al*(6)-O(26)a | 2.056(5) | 2.049(1) |
| <*Al*(4)-O> | 1.919 | 1.929 | <*Al*(5)-O> | 1.943 | 1.934 | <*Al*(6)-O> | 1.953 | 1.954 |
| | | | | | | | | |
| *Al*(7)-O(55) | 1.817(5) | 1.823(1) | *Al*(8)-O(94) | 1.869(5) | 1.859(1) | | | |
| *Al*(7)-O(119)h | 1.864(5) | 1.858(1) | *Al*(8)-O(106) | 1.969(5) | 1.953(1) | | | |
| *Al*(7)-O(118)f | 1.882(5) | 1.882(1) | *Al*(8)-O(120) | 1.995(5) | 1.926(1) | | | |
| *Al*(7)-O(36)f | 1.979(5) | 1.959(1) | *Al*(8)-O(90) | 2.018(5) | 1.963(1) | | | |
| *Al*(7)-O(108)m | 1.996(5) | 1.986(1) | *Al*(8)-O(77) | 2.027(4) | 2.020(1) | | | |
| *Al*(7)-O(85) | 2.511(4) | 2.406(1) | *Al*(8)-O(73)e | 2.147(5) | 2.185(1) | | | |
| <*Al*(7)-O> | 2.008 | 1.986 | <*Al*(8)-O> | 2.004 | 1.984 | | | |
| | | | | | | | | |
| *P*(1)-O(112) | 1.524(5) | 1.512(1) | *P*(2)-O(105) | 1.521(5) | 1.552(1) | *P*(3)-O(111) | 1.519(5) | 1.545(1) |
| *P*(1)-O(37) | 1.539(5) | 1.564(1) | *P*(2)-O(17) | 1.531(5) | 1.559(1) | *P*(3)-O(120) | 1.535(5) | 1.572(1) |
| *P*(1)-O(88) | 1.554(4) | 1.552(1) | *P*(2)-O(24) | 1.555(5) | 1.548(1) | *P*(3)-O(41) | 1.564(5) | 1.530(1) |
| *P*(1)-O(106) | 1.555(5) | 1.571(1) | *P*(2)-O(42) | 1.564(5) | 1.559(1) | *P*(3)-O(74) | 1.566(4) | 1.573(1) |
| <*P*(1)-O> | 1.543 | 1.550 | <*P*(2)-O> | 1.543 | 1.555 | <*P*(3)-O> | 1.546 | 1.555 |
| | | | | | | | | |
| *P*(4)-O(3) | 1.528(5) | 1.548(1) | *P*(5)-O(98) | 1.526(5) | 1.541(1) | *P*(6)-O(54) | 1.542(5) | 1.523(1) |
| *P*(4)-O(101) | 1.534(5) | 1.504(1) | *P*(5)-O(34) | 1.536(5) | 1.541(1) | *P*(6)-O(70) | 1.542(5) | 1.556(1) |
| *P*(4)-O(104) | 1.547(5) | 1.565(1) | *P*(5)-O(81) | 1.547(5) | 1.571(1) | *P*(6)-O(51) | 1.546(5) | 1.535(1) |
| *P*(4)-O(96) | 1.550(4) | 1.568(1) | *P*(5)-O(35) | 1.562(6) | 1.578(1) | *P*(6)-O(2) | 1.551(4) | 1.527(1) |
| <*P*(4)-O> | 1.540 | 1.546 | <*P*(5)-O> | 1.543 | 1.558 | <*P*(6)-O> | 1.545 | 1.535 |
| | | | | | | | | |
| *P*(7)-O(107) | 1.529(5) | 1.552(1) | *P*(8)-O(9) | 1.512(5) | 1.486(1) | *P*(9)-O(21) | 1.512(5) | 1.521(1) |
| *P*(7)-O(113) | 1.531(5) | 1.511(1) | *P*(8)-O(6) | 1.537(5) | 1.543(1) | *P*(9)-O(8) | 1.519(5) | 1.498(1) |
| *P*(7)-O(47) | 1.532(5) | 1.540(1) | *P*(8)-O(4) | 1.553(5) | 1.531(1) | *P*(9)-O(16) | 1.568(5) | 1.558(1) |
| *P*(7)-O(77) | 1.552(4) | 1.551(1) | *P*(8)-O(10) | 1.572(4) | 1.582(1) | *P*(9)-O(15) | 1.570(4) | 1.564(1) |
| <*P*(7)-O> | 1.536 | 1.538 | <*P*(8)-O> | 1.543 | 1.535 | <*P*(9)-O> | 1.542 | 1.535 |
| | | | | | | | | |
| *P*(10)-O(69) | 1.529(5) | 1.542(1) | *P*(11)-O(78) | 1.520(5) | 1.539(1) | *P*(12)-O(99) | 1.533(5) | 1.548(1) |
| *P*(10)-O(23) | 1.535(5) | 1.546(1) | *P*(11)-O(87) | 1.534(5) | 1.570(1) | *P*(12)-O(68) | 1.538(5) | 1.521(1) |
| *P*(10)-O(59) | 1.533(5) | 1.538(1) | *P*(11)-O(48) | 1.536(5) | 1.524(1) | *P*(12)-O(63) | 1.543(5) | 1.557(1) |
| *P*(10)-O(12) | 1.559(5) | 1.542(1) | *P*(11)-O(72) | 1.578(5) | 1.566(1) | *P*(12)-O(95) | 1.557(4) | 1.581(1) |
| <*P*(10)-O> | 1.539 | 1.542 | <*P*(11)-O> | 1.542 | 1.550 | <*P*(12)-O> | 1.543 | 1.552 |
| | | | | | | | | |
| *P*(13)-O(80) | 1.503(5) | 1.463(1) | *P*(14)-O(65) | 1.520(5) | 1.562(1) | *P*(15)-O(50) | 1.513(5) | 1.511(1) |
| *P*(13)-O(43) | 1.541(5) | 1.546(1) | *P*(14)-O(30) | 1.529(5) | 1.515(1) | *P*(15)-O(46) | 1.534(5) | 1.547(1) |
| *P*(13)-O(40) | 1.548(5) | 1.557(1) | *P*(14)-O(61) | 1.535(5) | 1.555(1) | *P*(15)-O(79) | 1.539(5) | 1.513(1) |
| *P*(13)-O(33) | 1.561(5) | 1.537(1) | *P*(14)-O(20) | 1.554(5) | 1.531(1) | *P*(15)-O(71) | 1.540(5) | 1.554(1) |
| <*P*(13)-O> | 1.538 | 1.526 | <*P*(14)-O> | 1.534 | 1.541 | <*P*(15)-O> | 1.532 | 1.531 |
| | | | | | | | | |
| *P*(16)-O(32) | 1.515(4) | 1.522(1) | *P*(17)-O(114) | 1.545(5) | 1.556(1) | *P*(18)-O(73) | 1.522(5) | 1.504(1) |
| *P*(16)-O(83) | 1.539(5) | 1.523(1) | *P*(17)-O(118) | 1.547(5) | 1.562(1) | *P*(18)-O(31) | 1.531(5) | 1.514(1) |
| *P*(16)-O(22) | 1.553(4) | 1.549(1) | *P*(17)-O(26) | 1.548(5) | 1.574(1) | *P*(18)-O(84) | 1.531(4) | 1.558(1) |
| *P*(16)-O(14) | 1.556(5) | 1.522(1) | *P*(17)-O(57) | 1.554(5) | 1.524(1) | *P*(18)-O(45) | 1.540(4) | 1.530(1) |
| <*P*(16)-O> | 1.541 | 1.529 | <*P*(17)-O> | 1.548 | 1.554 | <*P*(18)-O> | 1.531 | 1.526 |

TABLE 3 (cont'd). SELECTED INTERATOMIC DISTANCES (Å) FOR MANITOBAITE (LEFT: GREEN, RIGHT: BROWN)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *P*(19)-O(27) | 1.509(5) | 1.504(1) | *P*(20)-O(53) | 1.514(5) | 1.501(1) | *P*(21)-O(93) | 1.534(5) | 1.537(1) |
| *P*(19)-O(38) | 1.521(5) | 1.515(1) | *P*(20)-O(75) | 1.531(5) | 1.521(1) | *P*(21)-O(102) | 1.539(5) | 1.562(1) |
| *P*(19)-O(39) | 1.563(5) | 1.552(1) | *P*(20)-O(19) | 1.541(4) | 1.512(1) | *P*(21)-O(36) | 1.544(5) | 1.553(1) |
| *P*(19)-O(5) | 1.566(5) | 1.546(1) | *P*(20)-O(18) | 1.551(4) | 1.567(1) | *P*(21)-O(110) | 1.557(5) | 1.547(1) |
| <*P*(19)-O> | 1.540 | 1.529 | <*P*(20)-O> | 1.535 | 1.525 | <*P*(21)-O> | 1.543 | 1.550 |
| | | | | | | | | |
| *P*(22)-O(89) | 1.532(5) | 1.548(1) | *P*(23)-O(85) | 1.490(4) | 1.497(1) | *P*(24)-O(100) | 1.521(5) | 1.523(1) |
| *P*(22)-O(1) | 1.536(5) | 1.504(1) | *P*(23)-O(92) | 1.543(5) | 1.565(1) | *P*(24)-O(13) | 1.528(5) | 1.543(1) |
| *P*(22)-O(82) | 1.542(5) | 1.529(1) | *P*(23)-O(58) | 1.557(5) | 1.514(1) | *P*(24)-O(108) | 1.540(5) | 1.550(1) |
| *P*(22)-O(62) | 1.548(5) | 1.558(1) | *P*(23)-O(11) | 1.568(5) | 1.540(1) | *P*(24)-O(115) | 1.540(5) | 1.549(1) |
| <*P*(22)-O> | 1.539 | 1.535 | <*P*(23)-O> | 1.540 | 1.529 | <*P*(24)-O> | 1.532 | 1.541 |
| | | | | | | | | |
| *P*(25)-O(91) | 1.512(5) | 1.484(1) | *P*(26)-O(66) | 1.527(5) | 1.511(1) | *P*(27)-O(28) | 1.536(4) | 1.507(1) |
| *P*(25)-O(25) | 1.524(5) | 1.504(1) | *P*(26)-O(55) | 1.537(5) | 1.533(1) | *P*(27)-O(94) | 1.538(5) | 1.551(1) |
| *P*(25)-O(29) | 1.543(5) | 1.524(1) | *P*(26)-O(86) | 1.538(4) | 1.538(1) | *P*(27)-O(116) | 1.548(5) | 1.562(1) |
| *P*(25)-O(7) | 1.559(4) | 1.571(1) | *P*(26)-O(90) | 1.553(5) | 1.571(1) | *P*(27)-O(97) | 1.548(5) | 1.530(1) |
| <*P*(25)-O> | 1.534 | 1.521 | <*P*(26)-O> | 1.539 | 1.538 | <*P*(27)-O> | 1.542 | 1.538 |
| | | | | | | | | |
| *P*(28)-O(109) | 1.528(5) | 1.531(1) | *P*(29)-O(44) | 1.524(5) | 1.511(1) | *P*(30)-O(117) | 1.522(5) | 1.531(1) |
| *P*(28)-O(67) | 1.529(5) | 1.524(1) | *P*(29)-O(103) | 1.531(6) | 1.574(1) | *P*(30)-O(76) | 1.521(4) | 1.548(1) |
| *P*(28)-O(56) | 1.539(5) | 1.520(1) | *P*(29)-O(64) | 1.532(5) | 1.546(1) | *P*(30)-O(52) | 1.538(5) | 1.517(1) |
| *P*(28)-O(49) | 1.562(5) | 1.540(1) | *P*(29)-O(60) | 1.544(5) | 1.555(1) | *P*(30)-O(119) | 1.562(5) | 1.549(1) |
| <*P*(28)-O> | 1.539 | 1.529 | <*P*(29)-O> | 1.533 | 1.547 | <*P*(30)-O> | 1.536 | 1.536 |
| | | | | | | | | |
| *Na*(1)-O(116) | 2.269(5) | 2.294(1) | *Na*(2)-O(20) | 2.348(5) | 2.300(1) | *Na*(3)-O(32)b | 2.384(5) | 2.411(1) |
| *Na*(1)-O(52) | 2.363(5) | 2.338(1) | *Na*(2)-O(43) | 2.350(5) | 2.323(1) | *Na*(3)-O(13) | 2.411(6) | 2.465(1) |
| *Na*(1)-O(112) | 2.398(5) | 2.382(1) | *Na*(2)-O(71) | 2.384(5) | 2.369(1) | *Na*(3)-O(118)a | 2.597(6) | 2.594(1) |
| *Na*(1)-O(102)k | 2.422(5) | 2.369(1) | *Na*(2)-O(19)b | 2.432(5) | 2.453(1) | *Na*(3)-O(91)b | 2.630(6) | 2.717(1) |
| *Na*(1)-O(109) | 2.471(5) | 2.462(1) | *Na*(2)-O(114)a | 2.468(5) | 2.440(1) | *Na*(3)-O(20) | 2.642(6) | 2.680(1) |
| *Na*(1)-O(45)e | 2.492(5) | 2.549(1) | *Na*(2)-O(68) | 2.517(5) | 2.534(1) | *Na*(3)-O(65) | 2.668(6) | 2.657(1) |
| *Na*(1)-O(76) | 2.762(5) | 2.679(1) | *Na*(2)-O(79) | 2.614(5) | 2.702(1) | *Na*(3)-O(14)b | 2.797(6) | 2.797(1) |
| *Na*(1)-O(94) | 2.946(5) | 3.029(1) | *Na*(2)-O(30) | 3.043(5) | 3.021(1) | <*Na*(3)-O> | 2.590 | 2.617 |
| <*Na*(1)-O> | 2.515 | 2.513 | <*Na*(2)-O> | 2.520 | 2.518 | | | |
| | | | | | | | | |
| *Na*(4)-O(37) | 2.416(6) | 2.315(1) | *Na*(5)-O(37) | 2.390(6) | 2.508(2) | *Na*(6)-O(91)b | 2.407(6) | 2.415(1) |
| *Na*(4)-O(63) | 2.443(6) | 2.501(1) | *Na*(5)-O(58) | 2.438(6) | 2.457(2) | *Na*(6)-O(35)c | 2.421(6) | 2.396(1) |
| *Na*(4)-O(9)h | 2.451(6) | 2.422(1) | *Na*(5)-O(9)h | 2.495(6) | 2.683(2) | *Na*(6)-O(13) | 2.429(6) | 2.419(1) |
| *Na*(4)-O(27)e | 2.530(6) | 2.626(1) | *Na*(5)-O(69) | 2.653(6) | 2.730(2) | *Na*(6)-O(67)b | 2.510(6) | 2.532(1) |
| *Na*(4)-O(1)e | 2.704(6) | 2.688(1) | *Na*(5)-O(120) | 2.659(6) | 2.587(2) | *Na*(6)-O(44)i | 2.625(6) | 2.680(1) |
| *Na*(4)-O(99) | 2.832(6) | 2.749(1) | *Na*(5)-O(11) | 2.749(6) | 2.752(2) | *Na*(6)-O(98)c | 2.766(5) | 2.733(1) |
| *Na*(4)-O(89)e | 2.828(6) | 2.909(1) | *Na*(5)-O(12) | 2.826(6) | 2.786(2) | *Na*(6)-O(103)i | 2.830(6) | 2.805(1) |
| <*Na*(4)-O> | 2.601 | 2.601 | <*Na*(5)-O> | 2.601 | 2.643 | <*Na*(6)-O> | 2.570 | 2.569 |
| | | | | | | | | |
| *Na*(7)-O(82) | 2.324(6) | 2.343(1) | *Na*(8)-O(109) | 2.376(5) | 2.400(1) | *Na*(9)-O(3)k | 2.367(6) | 2.368(1) |
| *Na*(7)-O(54) | 2.440(5) | 2.413(1) | *Na*(8)-O(94) | 2.375(5) | 2.385(1) | *Na*(9)-O(27) | 2.404(6) | 2.481(1) |
| *Na*(7)-O(34) | 2.450(5) | 2.434(1) | *Na*(8)-O(41) | 2.395(6) | 2.447(1) | *Na*(9)-O(63)k | 2.444(6) | 2.440(1) |
| *Na*(7)-O(22) | 2.469(5) | 2.424(1) | *Na*(8)-O(50) | 2.397(6) | 2.409(1) | *Na*(9)-O(8)f | 2.475(6) | 2.504(1) |
| *Na*(7)-O(51) | 2.555(5) | 2.547(1) | *Na*(8)-O(112) | 2.512(5) | 2.484(1) | *Na*(9)-O(70n | 2.647(6) | 2.614(1) |
| *Na*(7)-O(113) | 2.567(5) | 2.594(1) | *Na*(8)-O(97) | 2.906(5) | 2.931(1) | *Na*(9)-O(5) | 2.765(6) | 2.726(1) |
| *Na*(7)-O(18) | 2.778(5) | 2.766(1) | *Na*(8)-O(7) | 2.937(5) | 2.965(1) | *Na*(9)-O(2)n | 2.832(5) | 2.874(1) |
| <*Na*(7)-O> | 2.512 | 2.503 | *Na*(8)-O(79) | 3.021(5) | 2.913(1) | <*Na*(9)-O> | 2.562 | 2.572 |
| | | | <*Na*(8)-O> | 2.615 | 2.617 | | | |
| | | | | | | | | |
| *Na*(10)-O(57)g | 2.256(6) | 2.241(1) | *Na*(11)-O(67) | 2.428(6) | 2.452(1) | *Na*(12)-O(42) | 2.385(6) | 2.381(1) |
| *Na*(10)-O(84)b | 2.275(5) | 2.283(1) | *Na*(11)-O(47)d | 2.435(6) | 2.421(1) | *Na*(12)-O(8)h | 2.441(6) | 2.481(1) |
| *Na*(10)-O(55)i | 2.427(5) | 2.427(1) | *Na*(11)-O(80) | 2.448(6) | 2.485(1) | *Na*(12)-O(3) | 2.534(6) | 2.506(1) |
| *Na*(10)-O(59) | 2.483(6) | 2.472(1) | *Na*(11)-O(35)d | 2.485(6) | 2.564(1) | *Na*(12)-O(116)e | 2.671(6) | 2.654(1) |
| *Na*(10)-O(100)h | 2.584(6) | 2.648(1) | *Na*(11)-O(87)d | 2.652(6) | 2.622(1) | *Na*(12)-O(28)e | 2.677(6) | 2.679(1) |
| *Na*(10)-O(23) | 2.626(6) | 2.630(1) | *Na*(11)-O(48)d | 2.805(5) | 2.835(1) | *Na*(12)-O(31)r | 2.684(6) | 2.718(1) |
| *Na*(10)-O(86)i | 2.839(5) | 2.797(1) | *Na*(11)-O(49) | 2.829(6) | 2.811(1) | *Na*(12)-O(105) | 2.802(6) | 2.792(1) |
| *Na*(10)-O(15)g | 2.840(5) | 2.804(1) | <*Na*(11)-O> | 2.583 | 2.599 | <*Na*(12)-O> | 2.599 | 2.602 |
| <*Na*(10)-O> | 2.541 | 2.538 | | | | | | |

TABLE 3 (cont'd). SELECTED INTERATOMIC DISTANCES (Å) FOR MANITOBAITE (LEFT: GREEN, RIGHT: BROWN)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Na*(13)-O(47)d | 2.418(6) | 2.494(2) | *Na*(14)-O(68) | 2.368(5) | 2.358(1) | *Na*(15)-O(78)c | 2.349(5) | 2.341(1) |
| *Na*(13)-O(80) | 2.438(6) | 2.503(1) | *Na*(14)-O(117) | 2.385(5) | 2.398(1) | *Na*(15)-O(64) | 2.368(5) | 2.377(1) |
| *Na*(13)-O(120)d | 2.487(6) | 2.493(2) | *Na*(14)-O(30) | 2.396(6) | 2.405(1) | *Na*(15)-O(24) | 2.398(6) | 2.392(1) |
| *Na*(13)-O(66)d | 2.625(6) | 2.669(2) | *Na*(14)-O(92)d | 2.457(5) | 2.465(1) | *Na*(15)-O(39)l | 2.461(5) | 2.483(1) |
| *Na*(13)-O(111)d | 2.758(5) | 2.757(2) | *Na*(14)-O(61) | 2.629(6) | 2.671(1) | *Na*(15)-O(110) | 2.592(5) | 2.583(1) |
| *Na*(13)-O(58)d | 2.825(6) | 2.803(2) | *Na*(14)-O(101) | 2.701(5) | 2.727(1) | *Na*(15)-O(60) | 2.665(5) | 2.682(1) |
| *Na*(13)-O(90)d | 2.832(6) | 2.798(2) | *Na*(14)-O(43) | 2.759(5) | 2.753(1) | *Na*(15)-O(10) | 2.725(5) | 2.742(1) |
| <*Na*(13)-O> | 2.626 | 2.645 | <*Na*(14)-O> | 2.528 | 2.540 | *Na*(15)- O(72)c | 3.025(6) | 2.971(1) |
| | | | | | | <*Na*(15)-O> | 2.573 | 2.571 |
| *Na*(16A)-O(93) | 2.406(9) | 2.376(2) | *Na*(16B)-O(93)p | 2.373(8) | 2.509(2) | | | |
| *Na*(16A)-O(53)r | 2.475(9) | 2.390(2) | *Na*(16B)-O(53) | 2.432(8) | 2.475(2) | | | |
| *Na*(16A)-O(71)b | 2.523(9) | 2.570(2) | *Na*(16B)-O(52)k | 2.598(8) | 2.588(2) | | | |
| *Na*(16A)-O(31)r | 2.635(9) | 2.783(2) | *Na*(16B)-O(118)p | 2.677(9) | 2.607(2) | | | |
| *Na*(16A)-O(45)r | 2.805(8) | 2.725(3) | *Na*(16B)-O(114)p | 2.723(8) | 2.738(2) | | | |
| *Na*(16A)-O(46)b | 2.968(9) | 3.159(2) | *Na*(16B)-O(119)k | 3.075(9) | 2.890(2) | | | |
| *Na*(16A)-O(52)b | 3.194(9) | 3.017(2) | <*Na*(16B)-O> | 2.646 | 2.635 | | | |
| <*Na*(16A)-O> | 2.715 | 2.717 | | | | | | |

a: x, –y + 1, z + ½ ; b: x, –y + 1, z – ½ ; c: x + 1, –y + 1, z – ½ ; d: x + 1, y, z; e: x, –y, z – ½ ; f: x – 1, –y, z + ½ ; g: x – 1, –y + 1, z + ½ ; h: x – 1, y, z; i: x, y + 1, z; j: x + 1, y + 1, z; k: x, –y, z + ½ ; l: x + 1, –y, z – ½ ; m: x – 1, y – 1, z; n: x, y – 1, z; o: x – 1, y, z + 1; p: x, y, z + 1; q: x + 1, –y, z + ½ ; r: x, y, z – 1; s: x – 1, –y, z – 1/2; t: x + 1, y, z – 1.

(Ercit *et al*. 2010) to assign $Fe^{2+}$ and $Fe^{3+}$. The unit formulae were calculated on the basis of 60 anions, and the results are also presented in Table 5.

## Assignment of Site Populations

There are thirty tetrahedrally coordinated sites, labeled *P*. The <*P*–O> distances range from 1.521 to 1.558 Å, well within the range 1.51–1.56 Å and close to the grand <P–O> distance of 1.537 Å reported for phosphate minerals by Huminicki & Hawthorne (2002). The stereochemistry, site scattering and observed <*P*–O> distances indicate that these sites are completely occupied by $P^{5+}$.

Site populations were assigned to the other cation sites on the basis of the refined site-scattering values (Table 6), mean bond-lengths (Table 4) and unit formulae (Table 5). The number of cation sites involved (80, with 50 finally considered as variable in the refinement) makes this process somewhat unwieldy, and we used a slightly different procedure than normal to approach this issue. Figure 1 shows the variation in refined site-scattering value for each site as a function of mean bond-length at that site for the green and brown varieties of manitobaite. The data fall predominantly into three principal groups, identified by the dashed-line boundaries in Figure 1; also shown are four smaller groups [enclosed by dotted lines and labeled *X*, *Y*, *Z* and *Na*(1,2)] transitional between these principal groups, and ideal distances for analogous <*M*–O> polyhedra (M = Al, $Fe^{3+}$, $Fe^{2+}$, $Mn^{2+}$, Ca and Na) calculated by summing the appropriate radii of Shannon (1976). The dominant cation(s) at each group of sites obviously corresponds to those cations with ideal distances that lie within the dashed-line boundaries of each of the three principal groups. The groups of sites were initially named *Al*, *M* (= *Mn*, *Fe*, *X*, *Y*, *Z*) and *Na*. Detailed examination of the stereochemistry (see below) shows strong $Mn^{2+}$–$Fe^{2+}$ order, and later we relabeled these sites as *Mn*, *Fe*, *M* and *X*, *Y*, *Z*. Normally, we are not in favor of naming sites in minerals with extensive solid-solution using element symbols for obvious reasons; however, in the present case, there are so many sites that an indicative labeling scheme helps mentally keep track of site-population issues.

Let us compare the refined scattering (derived by SREF: Site-scattering REFinement) with the analogous effective scattering from the constituents of the unit formulae (Table 5) for the principal groups of sites. Table 6 lists the values (in *epfu*: electrons per formula unit, Hawthorne *et al*. 1995) used in the following discussion. The values for the groups of *Al*, *M* (≡ *Fe* + *Mn*) and *Z* sites are almost identical in the green and brown crystals, and there is significant difference (17.7 *epfu*) only for the *Na* groups. Comparison of the total scattering values for the *Na* groups with the effective scattering values of Na in the unit formula derived from electron-microprobe analysis gives a difference of 6.31 and 6.90 *epfu* for each crystal, despite the fact that the total scattering for the *Na* sites in each crystal is significantly different. There is insufficient Al (Table 5) to fill the *Al* sites, and the total scattering at these groups of sites in each crystal (Table 6) indicates that the additional cation at the *Al* sites is Fe or Mn (or both). On the basis of cation size, we assigned Fe to fill the *Al* sites (we will consider the valence of Fe later). The remaining cations (except Na) were provisionally assigned to the *M* sites: ($Fe^{3+}$ + $Fe^{2+}$ –

$^{Al}$Fe), Mg, Zn, $Mn^{2+}$ and Ca. Comparison of the total refined site-scattering values (for the *M* sites) with the effective scattering values of the cations provisionally assigned to the *M* sites from the unit formula derived from electron-microprobe analysis gives a difference of 11.66 and 14.06 *epfu* in each crystal (Table 6). Note that the deficiency in the effective scattering of Na in each crystal is positive (Table 6) relative to the SREF scattering values, and the deficiency in effective scattering of the *M*-site cations is negative (Table 6), indicating that we need to assign some heavier scattering species to the *Na* sites and some Na to the *M* sites. This will be done in the next section.

TABLE 4A. REFINED SITE-SCATTERING VALUES (*epfu*) AND SITE POPULATIONS (*apfu*) FOR THE GREEN CRYSTAL OF MANITOBAITE

| Site | Site assignments | | | | | | | | | SREF | | Mean bond-length (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C.N. | □ | Na | Ca | $Mn^{2+}$ | $Fe^{2+}$ | Al | $Fe^{3+}$ | Mg | | | |
| *Mn*(1) | 6 | | | | 1.00* | | | | | ~24.8 | 25.35(15) | 2.223 |
| *Mn*(2) | 6 | | | | 1.00* | | | | | ~24.8 | 24.53(13) | 2.243 |
| *Mn*(3) | 6 | | | | 1.00* | | | | | ~24.8 | 24.90(13) | 2.218 |
| *Mn*(4) | 6 | | | | 1.00* | | | | | ~24.8 | 25.40(15) | 2.260 |
| *Mn*(5) | 6 | | | | 1.00* | | | | | ~24.8 | 23.90(13) | 2.266 |
| *Mn*(6) | 6 | | | | 1.00* | | | | | ~24.8 | 24.88(13) | 2.229 |
| *Mn*(7) | 6 | | | | 1.00* | | | | | ~24.8 | 23.90(13) | 2.239 |
| *Mn*(8) | 6 | | | | 1.00* | | | | | ~24.8 | 25.18(13) | 2.245 |
| *Mn*(9) | 6 | | | | 1.00* | | | | | ~24.8 | 24.95(13) | 2.216 |
| *Mn*(10) | 6 | | | | 1.00* | | | | | ~24.8 | 24.58(15) | 2.211 |
| *Fe*(1) | 6 | | | | | 1.00** | | | | ~24.8 | 23.58(13) | 2.161 |
| *Fe*(2) | 6 | | | | | 1.00** | | | | ~24.8 | 24.23(13) | 2.164 |
| *Fe*(3) | 6 | | | | | 1.00** | | | | ~24.8 | 24.36(13) | 2.163 |
| *Fe*(4) | 6 | | | | | 1.00** | | | | ~24.8 | 25.09(13) | 2.157 |
| *Fe*(5) | 6 | | | | | 1.00** | | | | ~24.8 | 23.66(13) | 2.144 |
| *Fe*(6) | 6 | | | | | 1.00** | | | | ~24.8 | 25.09(13) | 2.155 |
| *Fe*(7) | 6 | | | | | 1.00** | | | | ~24.8 | 24.75(13) | 2.153 |
| *Fe*(8) | 6 | | | | | 1.00** | | | | ~24.8 | 25.09(13) | 2.163 |
| *X*(1) | 6 | | | | | 0.67 | 0.21 | | 0.12 | ~22.4 | 21.58(13) | 2.080 |
| *X*(2) | 6 | | | | | 0.68 | | | 0.32 | ~23.0 | 21.66(13) | 2.102 |
| *M*(1) | 6 | | | | ~0.5 | ~0.5 | | | | ~24.8 | 25.73(15) | 2.193 |
| *M*(2) | 6 | | | | ~0.5 | ~0.5 | | | | ~24.8 | 23.92(13) | 2.191 |
| *Y*(1) | 6 | | | 0.64 | 0.36 | | | | | 21.80 | 21.83(13) | 2.279 |
| *Z*(1) | 7 | | | 0.28 | 0.72 | | | | | 23.60 | 23.62(16) | 2.380 |
| *Z*(2) | 7 | | | 0.16 | 0.84 | | | | | 24.20 | 24.18(16) | 2.346 |
| *Al*(1) | 6 | | | | | 0.21 | 0.79 | | | 15.60 | 15.78(14) | 1.937 |
| *Al*(2) | 6 | | | | | 0.07 | 0.93 | | | 14.30 | 13.94(14) | 1.917 |
| *Al*(3) | 6 | | | | | 0.01 | 0.99 | | | 13.00 | 13.16(14) | 1.894 |
| *Al*(4) | 6 | | | | | 0.16 | 0.84 | | | 14.95 | 15.08(14) | 1.919 |
| *Al*(5) | 6 | | | | | 0.11 | 0.89 | | 0.05 | 14.25 | 14.44(14) | 1.943 |
| *Al*(6) | 6 | | | | | 0.32 | 0.68 | | | 16.90 | 17.20(14) | 1.954 |
| *Al*(7) | 6 | | | | | 0.29 | 0.71 | | | ~17.7 | 16.82(16) | 2.008 |
| *Al*(8) | 6 | | | | | 0.48 | 0.52 | | | ~19.1 | 19.27(14) | 2.004 |
| *Na*(1) | 8 | | 0.72 | 0.28 | | | | | | 13.52 | 13.52(12) | 2.515 |
| *Na*(2) | 7 | | 0.64 | 0.36 | | | | | | 14.24 | 14.23(12) | 2.445 |
| *Na*(3) | 7 | | 1.00 | | | | | | | 11.00 | 10.86(17) | 2.590 |
| *Na*(4) | 7 | | 1.00 | | | | | | | 11.00 | 11.56(17) | 2.601 |
| *Na*(5) | 7 | | 1.00 | | | | | | | 11.00 | 10.89(14) | 2.601 |
| *Na*(6) | 7 | | 1.00 | | | | | | | 11.00 | 11.21(15) | 2.570 |
| *Na*(7) | 7 | | 1.00 | | | | | | | 11.00 | 10.68(12) | 2.512 |
| *Na*(8) | 7 | 0.07 | 0.93 | | | | | | | 10.23 | 10.10(12) | 2.557 |
| *Na*(9) | 7 | 0.01 | 0.99 | | | | | | | 10.89 | 10.57(15) | 2.562 |
| *Na*(10) | 8 | | 1.00 | | | | | | | 11.00 | 10.55(13) | 2.541 |
| *Na*(11) | 7 | 0.07 | 0.93 | | | | | | | 10.23 | 10.12(15) | 2.583 |
| *Na*(12) | 7 | | 1.00 | | | | | | | 11.00 | 10.62(18) | 2.599 |
| *Na*(13) | 7 | 0.01 | 0.99 | | | | | | | 10.89 | 10.57(14) | 2.626 |
| *Na*(14) | 7 | | 1.00 | | | | | | | 11.00 | 10.66(13) | 2.528 |
| *Na*(15) | 7 | 0.07 | 0.93 | | | | | | | 10.23 | 10.15(13) | 2.508 |
| † *Na*(16A) | 6 | | 0.45 | | | | | | | 4.95 | 4.96(15) | 2.635 |
| † *Na*(16B) | 5 | | 0.55 | | | | | | | 6.05 | 6.02(15) | 2.561 |

* indicates occupancy primarily by $Mn^{2+}$, with small amounts of larger cations (Ca,Na);
** indicates occupancy primarily by $Fe^{2+}$, with small amounts of smaller cations (Mg, $Fe^{3+}$, Al);
† the *Na*(16A) and *Na*(16B) sites are too close for both to be locally occupied.

TABLE 4B. REFINED SITE-SCATTERING VALUES (*epfu*) AND SITE POPULATIONS (*apfu*) FOR THE BROWN CRYSTAL OF MANITOBAITE

| Site | Site assignments | | | | | | | | | SREF | | Mean bond-length (Å) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C.N. | □ | Na | Ca | $Mn^{2+}$ | $Fe^{2+}$ | Al | $Fe^{3+}$ | Mg | | | |
| *Mn*(1) | 6 | | | | 1.00* | | | | | ~24.6 | 26.10 | 2.211 |
| *Mn*(2) | 6 | | | | 1.00* | | | | | ~24.6 | 23.58 | 2.240 |
| *Mn*(3) | 6 | | | | 1.00* | | | | | ~24.6 | 24.93 | 2.218 |
| *Mn*(4) | 6 | | | | 1.00* | | | | | ~24.6 | 24.45 | 2.250 |
| *Mn*(5) | 6 | | | | 1.00* | | | | | ~24.6 | 24.93 | 2.252 |
| *Mn*(6) | 6 | | | | 1.00* | | | | | ~24.6 | 25.38 | 2.227 |
| *Mn*(7) | 6 | | | | 1.00* | | | | | ~24.6 | 24.88 | 2.242 |
| *Mn*(8) | 6 | | | | 1.00* | | | | | ~24.6 | 24.10 | 2.234 |
| *Mn*(9) | 6 | | | | 1.00* | | | | | ~24.6 | 26.45 | 2.220 |
| *Mn*(10) | 6 | | | | 1.00* | | | | | ~24.6 | 24.10 | 2.210 |
| *Fe*(1) | 6 | | | | | 1.00** | | | | ~24.6 | 24.13 | 2.139 |
| *Fe*(2) | 6 | | | | | 1.00** | | | | ~24.6 | 26.31 | 2.165 |
| *Fe*(3) | 6 | | | | | 1.00** | | | | ~24.6 | 24.34 | 2.154 |
| *Fe*(4) | 6 | | | | | 1.00** | | | | ~24.6 | 25.17 | 2.147 |
| *Fe*(5) | 6 | | | | | 1.00** | | | | ~24.6 | 22.98 | 2.121 |
| *Fe*(6) | 6 | | | | | 1.00** | | | | ~24.6 | 24.31 | 2.154 |
| *Fe*(7) | 6 | | | | | 1.00** | | | | ~24.6 | 24.80 | 2.151 |
| *Fe*(8) | 6 | | | | | 1.00** | | | | ~24.6 | 23.04 | 2.146 |
| *X*(1) | 6 | | | | | 0.70 | 0.30 | | | ~23.0 | 21.94 | 2.071 |
| *X*(2) | 6 | | | | | 0.62 | 0.38 | | | ~22.0 | 20.93 | 2.061 |
| *M*(1) | 6 | | | | ~0.50 | ~0.50 | | | | ~24.6 | 26.18 | 2.201 |
| *M*(2) | 6 | | | | ~0.50 | ~0.50 | | | | ~24.6 | 23.45 | 2.181 |
| *Y*(1) | 6 | | | 0.66 | 0.34 | | | | | 21.70 | 21.70 | 2.276 |
| *Z*(1) | 7 | | | 0.16 | 0.84 | | | | | 24.20 | 24.20 | 2.365 |
| *Z*(2) | 7 | | | 0.27 | 0.73 | | | | | 23.65 | 23.66 | 2.350 |
| *Al*(1) | 6 | | | | | | 0.75 | 0.25 | | 16.25 | 16.21 | 1.934 |
| *Al*(2) | 6 | | | | | | 0.90 | 0.10 | | 14.30 | 14.55 | 1.920 |
| *Al*(3) | 6 | | | | | | 1.00 | | | 13.00 | 12.92 | 1.899 |
| *Al*(4) | 6 | | | | | | 0.80 | 0.20 | | 15.60 | 15.44 | 1.929 |
| *Al*(5) | 6 | | | | | | 0.85 | 0.15 | | 14.95 | 14.77 | 1.934 |
| *Al*(6) | 6 | | | | | | 0.65 | 0.35 | | 17.55 | 17.47 | 1.954 |
| *Al*(7) | 6 | | | | | 0.20 | 0.60 | 0.20 | | ~17.9 | 16.76 | 1.986 |
| *Al*(8) | 6 | | | | | 0.15 | 0.55 | 0.30 | | ~18.6 | 18.85 | 1.984 |
| *Na*(1) | 7 | | 0.61 | 0.39 | | | | | | 14.51 | 14.50 | 2.439 |
| *Na*(2) | 7 | | 0.64 | 0.36 | | | | | | 14.24 | 14.25 | 2.446 |
| *Na*(3) | 7 | 0.17 | 0.83 | | | | | | | 9.13 | 8.84 | 2.617 |
| *Na*(4) | 7 | | 1.00 | | | | | | | 11.00 | 10.89 | 2.601 |
| *Na*(5) | 7 | 0.36 | 0.64 | | | | | | | 7.04 | 6.72 | 2.643 |
| *Na*(6) | 7 | | 1.00 | | | | | | | 11.00 | 10.68 | 2.569 |
| *Na*(7) | 7 | | 1.00 | | | | | | | 11.00 | 11.50 | 2.503 |
| *Na*(8) | 8 | 0.10 | 0.90 | | | | | | | 9.90 | 9.55 | 2.617 |
| *Na*(9) | 7 | 0.09 | 0.91 | | | | | | | 10.01 | 9.55 | 2.572 |
| *Na*(10) | 8 | | 1.00 | | | | | | | 11.00 | 10.51 | 2.538 |
| *Na*(11) | 7 | 0.20 | 0.80 | | | | | | | 8.80 | 8.51 | 2.599 |
| *Na*(12) | 7 | 0.10 | 0.90 | | | | | | | 9.90 | 9.50 | 2.602 |
| *Na*(13) | 7 | 0.34 | 0.66 | | | | | | | 7.26 | 6.93 | 2.645 |
| *Na*(14) | 7 | 0.19 | 0.81 | | | | | | | 8.91 | 8.61 | 2.540 |
| *Na*(15) | 8 | 0.08 | 0.92 | | | | | | | 10.12 | 9.76 | 2.571 |
| † *Na*(16A) | 5 | | 0.35 | | | | | | | 3.85 | 3.61 | 2.569 |
| † *Na*(16B) | 6 | [0.12] | 0.53 | | | | | | | 5.83 | 5.67 | 2.635 |

* indicates occupancy primarily by $Mn^{2+}$, with small amounts of larger cations (Ca,Na);
** indicates occupancy primarily by $Fe^{2+}$, with small amounts of smaller cations (Mg, $Fe^{3+}$, Al);
† the *Na*(16A) and *Na*(16B) sites are too close for both to be locally occupied.

*The transitional sites Y(1), Z(1,2) and Na(1,2)*

Above, we argued that a small amount of a heavier scattering species should be assigned to the *Na* sites and a lighter scatterer, Na, should be assigned to the *M* sites. Inspection of Figure 1 indicates that this heavier scattering species should be Ca, and inspection of Table 6 indicates that the assignment of Ca to the *Na* sites and Na to the *M* sites involves net changes in scattering of (6.31 + 11.66)/2 = 8.98 (green) and (6.90 + 14.06)/2 = 10.48 *epfu* (brown). Thus the amounts of Ca assigned to the *Na* sites are 8.98/(20 – 11) = 1.00 *apfu* (green) and 10.48/(20 – 11) = 1.16 *apfu* (brown), respectively. Inspection of Figure 1 and Table 6 shows that only

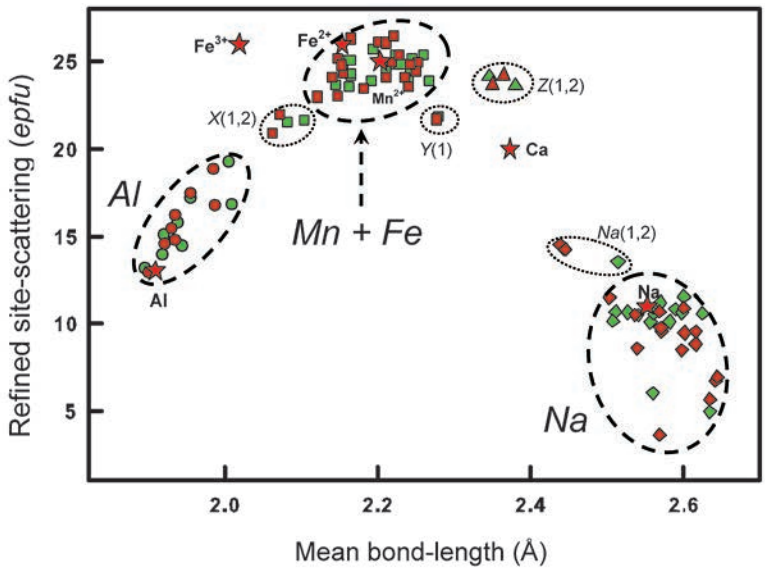


FIG. 1. Variation in refined site-scattering values at the non-tetrahedrally-coordinated cation sites in manitobaite as a function of mean bond-length. Values for green and brown manitobaite are shown by green and brown symbols, respectively. The stars indicate the positions of octahedra occupied by the cations indicated and the mean bond-lengths calculated from the sum of the ionic radii of the constituent ions. *Al* sites: circles; *X*, *Y*, *Fe* and *Mn* sites: squares; *Z* sites: triangles; *Na* sites: diamonds.

TABLE 5. CHEMICAL COMPOSITION AND UNIT FORMULAE OF GREEN AND BROWN MANITOBAITE

| | Green | Brown | | Green | Brown |
|---|---|---|---|---|---|
| $P_2O_5$ wt.% | 44.19 | 44.42 | P | 30.08 | 30.12 |
| $Al_2O_3$ | 6.91 | 6.96 | | | |
| $Fe_2O_3$ | 1.73 | 3.45 | Al | 6.55 | 6.57 |
| FeO | 6.23 | 4.66 | $Fe^{3+}$ | 1.05 | 2.08 |
| MnO | 27.57 | 27.86 | | | |
| ZnO | 0.54 | 0.53 | $Fe^{2+}$ | 4.19 | 3.12 |
| MgO | 0.73 | 0.91 | $Mn^{2+}$ | 18.78 | 18.90 |
| CaO | 1.71 | 1.59 | Zn | 0.32 | 0.31 |
| $Na_2O$ | 9.97 | 8.94 | Mg | 0.88 | 1.09 |
| Total | 99.58 | 99.32 | Ca | 1.47 | 1.36 |
| | | | Na | 15.54 | 13.88 |

TABLE 6. SITE-SCATTERING VALUES (*epfu*) IN MANITOBAITE FOR VARIOUS GROUPS OF SITES BY SREF AND EMPA

| | Green crystal | Brown crystal | Difference |
|---|---|---|---|
| Σ*Al* SREF | 125.69 | 126.97 | -1.28 |
| Σ *M* SREF | 605.94 | 606.04 | -0.10 |
| Σ *Na* SREF | 177.25 | 159.58 | -17.7 |
| Σ *Na* EMPA | 170.94 | 152.68 | 18.26 |
| Δ *Na* (SREF-EMPA) | -6.31 | -6.90 | |
| Σ *M* SREF | 605.94 | 606.04 | -0.10 |
| Σ ($M^{2+}$+$Fe^{3+}$) EMPA | 617.60 | 620.10 | -2.50 |
| Δ | 11.66 | 14.06 | |

the *Na*(1) and *Na*(2) sites have scattering significantly greater than 11 *epfu*, and the refined site-scattering values correspond to 0.28 and 0.36 *apfu* Ca (green) and 0.39 and 0.36 *apfu* Ca (brown). The remaining Ca will be distributed among the other *Na* sites in amounts too small to significantly affect the scattering at these sites.

Assigning Ca to the *Na* sites also entails assigning an equivalent amount of Na to the *M* sites. Inspection of Figure 1 shows that the *Z*(1) and *Z*(2) sites have mean bond-lengths significantly greater than those of the *Fe* and *Mn* sites, and refined site-scattering values slightly less than those at the *Fe* and *Mn* sites. The *Y*(1) site has a refined site-scattering value (21.80 green, 21.70 *epfu*, brown) significantly less than the values at the *Fe* and *Mn* sites (Fig. 1). This indicates that Na should be assigned to the *Y*(1) site, and the Ca should be assigned to the *Z*(1) and *Z*(2) sites in amounts (Table 6) indicated by the refined site-scattering values.

*The Al sites*

The refined site-scattering values (Fig. 2a) and the observed mean bond-lengths (Fig. 2b) show considerable coherence between the green and brown crystals. In both cases, the data lie close to the 1:1 line (shown dashed in Figs. 2a, b). There is a slight excess of scattering (mean value 0.6 e) in five of the eight sites of the brown crystal, and for two of the sites, *Al*(7) and *Al*(8), the mean bond-lengths are approximately 0.02 Å longer in those of the green crystal than of the brown crystal (Fig. 2b). As noted above, the mean bond-lengths (Table 4) at the *Al* sites indicate that they are occupied predominantly by Al, together with smaller amounts of one or more larger heavier cations. Accordingly, Al and Fe were assigned to these sites as indicated by the refined site-scattering values. Intuitively, it seems reasonable to assign $Fe^{3+}$ to the Al sites as the more highly scattering cation because of the similarity of charge and size ($r^{[6]}Al$ = 0.535, $r^{[6]}Fe^{3+}$ = 0.645 Å; Shannon 1976). This produces a linear relation between mean bond-length and constituent-cation radius, but the slope of this relation is ~2.6 in the green crystal (Fig. 2c) and ~2.0 in the brown crystal (Fig. 2d), far from the ideal value of 1.0 for a hard-sphere model. If we assign $Fe^{2+}$ as the more highly scattering species at the *Al* sites, there is a linear relation between mean bond-length and constituent-cation radius, but the slope of this relation is now ~1.0 in both the green and the brown crystals (Figs. 2e, 2f), in accord with the ideal relation for a hard-sphere model. If we assign $Mn^{2+}$ as the more highly scattering species at the *Al* sites, the slope of the relation between mean bond-length and constituent-cation radius is 0.84 in the green crystal and 0.85 in the brown crystal, both significantly less than the ideal relation for a hard-sphere model. Although slopes of this magnitude are known for similar relations in some minerals [*e.g.*, the *M*(2) site in amphiboles, Hawthorne & Oberti 2007], values close to unity are far more common. Thus we assign Al and $Fe^{2+}$ to the *Al* sites in the green crystal in accord with their refined site-scattering values (Table 6). The <*Al*(7)–O> and <*Al*(8)–O> distances in the green crystal are ~0.02 Å longer than the corresponding distances in the brown crystal (Fig. 2b), suggesting that the *Al*(7) and *Al*(8) sites are occupied by some $Fe^{3+}$ in the brown crystal.

*The Fe, Mn, M(1,2) and X(1,2) sites*

There are eight cation species to be assigned to the *Fe, Mn* and transitional sites: Al, $Fe^{3+}$, Mg, Zn, $Fe^{2+}$, $Mn^{2+}$, Ca and Na. Obviously this cannot be done unambiguously, as the refined site-scattering values (Hawthorne *et al.* 1995) can give information only on the occupancy of sites by two scattering species (Hawthorne 1983). However, one may use crystal chemistry and the known chemical formulae of the crystals to assign occupancies consistent with the refined site-scattering values and the observed mean bond-lengths. The refined site-scattering values (Fig. 3a) show much less coherence between the green and brown crystals than those at the *Al* sites. However, the observed mean bond-lengths lie close to the 1:1 line (shown dashed in Fig. 3b). The variation in <*Fe*–O> and <*Mn*–O> distances in each crystal shows significant scatter as a function of refined site-scattering values (Figs. 3c, 3d).

The *X*(1) and *X*(2) sites stand out in having lower site-scattering values and lower mean distances than the majority of the *Fe* and *Mn* sites (Fig. 1). Thus *X*(1) and *X*(2) must contain smaller cations of lower scattering power than is the case for the majority of the *Fe* and *Mn* sites. First, note that in the assignment of Al to the *Al* sites (Table 6) according to the refined site-scattering values, we did not use all of the Al in the unit formula of each crystal; there are small amounts of Al remaining to be assigned: 0.21 and 1.18 *apfu* in the green and brown crystals, respectively. It seems crystal-chemically most reasonable to assign this Al to the *X*(1) and *X*(2) sites. The grand mean bond-length of the *X*(1) and *X*(2) sites in the green crystal, 2.091 Å, is greater than the corresponding value in the brown crystal, 2.066 Å, in accord with the greater amount of Al available for these sites in the brown crystal. In the green crystal, there is insufficient Al available for the *X*(1) and *X*(2) sites to account for the refined site-scattering values if these sites contain only Al and Fe, indicating that Mg ($Z$ = 12, $^{[6]}r$ = 0.72 Å) must occupy one or more of these sites. For *X*(1) and *X*(2), we may divide the scattering species into two groups: Al* = Al + Mg with Z = 12 and 13, and Fe* = Fe + Zn with Z = 26 and 30, and calculate the amounts of Al* and Fe* at each site: green: *X*(1) = 0.33 Al* + 0.67 Fe*; *X*(2) = 0.32 Al* + 0.68 Fe*; brown: *X*(1) = 0.30 Al* + 0.70 Fe*; *X*(2); 0.38 Al* + 0.62 Fe*. As noted above, there is insufficient Al to account for the scattering of Al* in the green crystal, but there is sufficient Al to account for the scattering of Al* in the brown crystal. As <*X*(1)–O> is 0.022 Å shorter than <*X*(2)–O> in the green crystal, we assign all Al to *X*(1) and make up the balance of Al* in *X*(1) and *X*(2) by Mg. For the brown crystal, there is sufficient Al to account for all Al* at *X*(1) and *X*(2), and we provisionally assign Al* as Al at *X*(1) and *X*(2). The resulting site-populations are as follows: green: *X*(1) = 0.21 Al + 0.12 Mg + 0.67 $Fe^{2+}$; *X*(2) = 0.32 Mg + 0.68 $Fe^{2+}$; brown: *X*(1) = 0.30 Al + 0.70 $Fe^{2+}$; *X*(2); 0.38 Al + 0.62 $Fe^{2+}$. Note that as the <*X*–O> distances for these two sites in each crystal are ~2.08 Å, the majority (if not all) of the Fe* must be divalent. Using an anion radius of 1.367 Å, the resulting calculated (observed) mean bond-lengths are as follows: green: *X*(1): 2.088 (2.080), *X*(2): 2.128 (2.102); brown: *X*(1): 2.071 (2.074), *X*(2): 2.061 (2.054) Å. The agreement between the observed and calculated bond-lengths supports the assigned site-populations; <*X*(2)–O> for the green crystal is 0.026 Å too large, and possibly some Fe at this site is in the trivalent state.

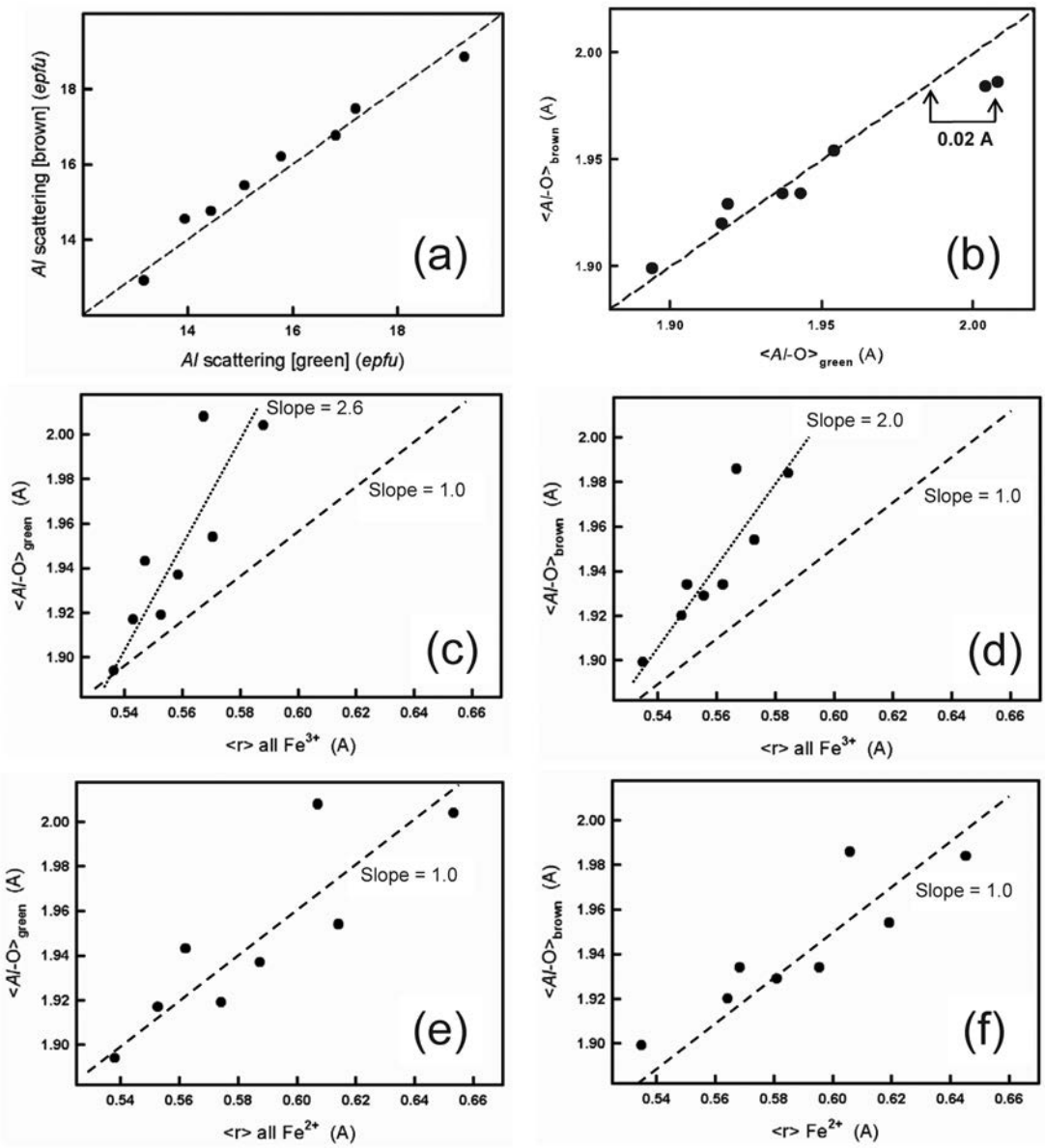


FIG. 2. The stereochemistry of the *Al* sites. (a) Variation in refined site-scattering values of the *Al* sites in brown manitobaite as a function of the refined site-scattering values of the *Al* sites in green manitobaite; the standard deviations are the same size as (or smaller than) the data points, and the broken line shows the 1:1 relation. (b) Variation in <*Al*–O> for brown manitobaite as a function of <*Al*–O> of green manitobaite for the *Al*(1–8) sites; the standard deviations on the bond-lengths are only slightly larger than the size of the data points, and the broken line shows the 1:1 relation; the *Al*(7) and *Al*(8) sites deviate from a linear 1:1 relation by ~0.02 Å. (c) and (d) Variation in <*Al*–O> as a function of <r>, the aggregate radius of the constituent cations with all Fe assigned as $Fe^{3+}$ for green (c) and brown (d) manitobaite. (e) and (f) Variation in <*Al*–O> as a function of <r>, the aggregate radius of the constituent cations with all Fe assigned as $Fe^{2+}$ for green (e) and brown (f) manitobaite.

The remaining *Fe* and *Mn* sites are occupied predominantly by $Mn^{2+}$ with lesser $Fe^{2+}$ and minor amounts of other cations (Al, $Fe^{3+}$, Mg, Zn, Ca and Na). The mean bond-lengths vary in the following ranges: green: 2.144–2.266; brown: 2.121–2.252 Å. Figure 4 shows a histogram of the <*Fe*–O> and <*Mn*–O> distances in both crystals. It is immediately apparent that the distances fall into two groups, with frequency maxima corresponding approximately to the ideal mean bond-distances for [6]-coordinated $Fe^{2+}$ (0.78 + 1.37 = 2.15 Å) and $Mn^{2+}$ (0.83 + 1.37 = 2.20 Å). Furthermore, the individual distributions show a skewed behavior; the skew to high distances for the <$Fe^{2+}$–O> population indicates that the sites forming the tail of the distribution to lower values also contain cations of smaller size (Al, $Fe^{3+}$, Mg, Zn), whereas the skew to low distances for the <$Mn^{2+}$–O> population indicates that the sites forming the tail of the distribution to higher values also contain cations of larger size (Ca, Na). Of course, this behavior does not negate the possibility of joint occupancy of *Fe* or *Mn* sites by $Fe^{2+}$ and $Mn^{2+}$. Indeed, there are some sites lying between the maxima [which we have labeled *M*(1) and *M*(2)] that must contain both $Fe^{2+}$ and $Mn^{2+}$, but this disorder is uncommon in manitobaite; in general, there is strong order involving $Fe^{2+}$ and $Mn^{2+}$. There is no convincing basis on which to assign $Fe^{2+}$, $Fe^{3+}$, Mg and Zn to the smaller *Fe* octahedra. Hence we write their occupancies as Fe* (= $Fe^{2+}$, $Fe^{3+}$, Mg and Zn); similarly, the occupancies of the larger *Mn* octahedra are written as Mn* (= $Mn^{2+}$ + Ca + Na).

*The Na sites*

The unit formulae indicate that the *Na* sites are occupied predominantly by Na (13.9–15.6 *apfu*) with significant vacancy (0.23–1.75 □ *pfu*) and minor Ca

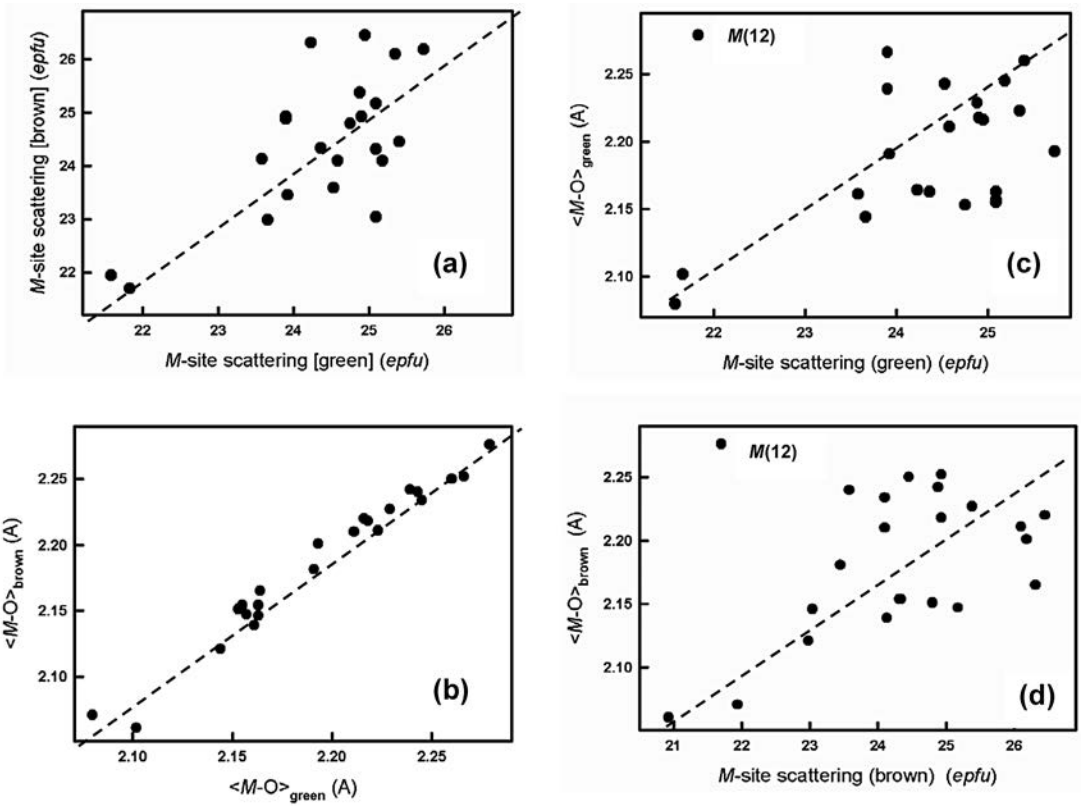


FIG. 3. The stereochemistry of the *M* sites (*M* is the collective designation for the octahedrally coordinated cation sites *Mn*, *Fe*, *Al*, *X*, *Y* and *Z*). (a) Variation in refined site-scattering values of the *M* sites in brown manitobaite as a function of the refined site-scattering values of the *M* sites in green manitobaite; the standard deviations are the same size as the data points, and the broken line shows the 1:1 relation. (b) Variation in <*M*–O> for brown manitobaite as a function of <*M*–O> of green manitobaite for the *M* sites; the standard deviations on the bond-lengths are the same size as the data points, and the broken line shows the 1:1 relation. (c) and (d) Variation in <*M*–O> as a function of the corresponding refined site-scattering values for green (c) and brown (d) manitobaite.

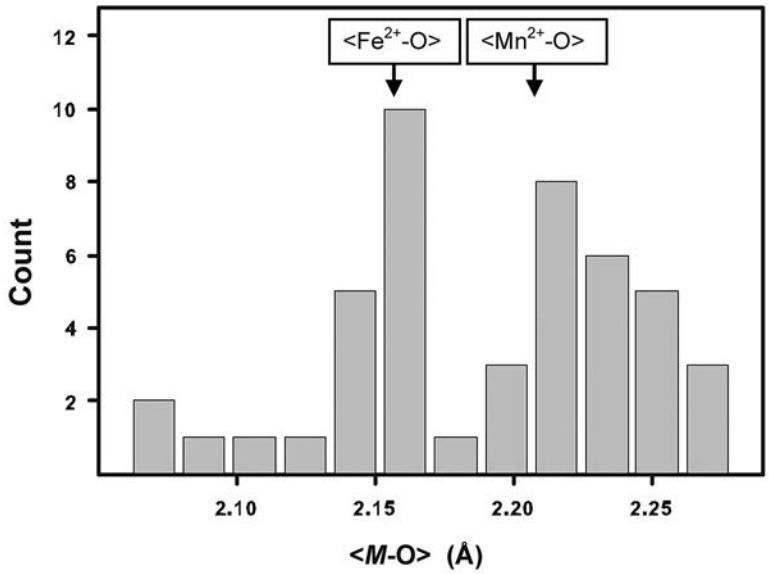


FIG. 4. A histogram of the <*M*–O> distances in green and brown manitobaite, note the bimodal distribution; the ideal <*M*–O> distances for $M = {}^{[6]}Fe^{2+}$ and $^{[6]}Mn^{2+}$ (calculated from the radii of Shannon 1976), are indicated.

(see discussion above). Where the refined site-scattering value is significantly less than 11 *epfu* (the value corresponding to complete occupancy by Na), the site was assigned as Na + □ (vacancy) = 1 *apfu*, and the amount of Na was calculated from the refined site-scattering value (Table 5). The sites *Na*(16A) and *Na*(16B) are separated by ~2.26 Å, and consequently cannot be simultaneously occupied at the local scale; in accord with this constraint, the sites are only partly occupied by Na and the sum of the occupancies is unity in each crystal (Table 6). There are seventeen *Na* sites in manitobaite: *Na*(1–15), *Na*(16A) and *Na*(16B). The occupancies of the *Na*(1–15) and *Na*(16B) sites all exceed 0.5 Na, and their content in the end-member formulae of green and brown manitobaite is thus 16 Na *apfu*. The occupancies of the *Na*(16A) site are less than 0.5 Na, and their content in the end-member formulae of green and brown manitobaite is □ *pfu*. Thus the content of the *Na* sites in the end-member formula of manitobaite is written as ($Na_{16}$□) *apfu*.

The coordination of the *Na*(1) and *Na*(2) sites is not clear merely from inspection of the Na–O distances (Table 4). Consequently, we calculated the bond valences (Brown 1981, Brown & Altermatt 1985) incident at the *Na*(1) and *Na*(2) sites, and at the anion sites involved in long (3.1 > *Na*(1,2)–O > 2.5 Å) distances. The agreement between the sum of the incident bond-valences and the aggregate formal charges of the constituent cations suggests a coordination number of [6] in all cases.

## DESCRIPTION OF THE STRUCTURE

Each polyhedron is labeled by the site which it encloses, *e.g.*, the *M*(1) octahedron. Following the previous descriptions of the structures of alluaudite (Moore 1971), wyllieite (Moore & Molin-Case 1974) and bobfergusonite (Ercit *et al.* 1986a), we may describe manitobaite as an alternation of strongly and weakly bonded layers normal to **b**. The strongly bonded layer (Fig. 5a) consists of staggered chains of octahedra linked by sharing edges. The edges shared by each octahedron are not *trans*, and hence the chains are quite kinked (as is the case in alluaudite, wyllieite and bobfergusonite). The staggered nature of the linkage along the chain means that the layer is quite thick (Fig. 5b). There are two symmetrically distinct strongly bonded layers in the structure of manitobaite, but these are topologically identical (and the second layer is not shown here). The weakly bonded layer consists of two distinct chains of polyhedra that are linked into a sheet by sharing vertices with ($PO_4$) groups. One chain consists of alternating *Mn* and *Na* polyhedra that share edges, and the other consists of *Na* polyhedra that share edges. The latter chain contains the *Na*(16A) and *Na*(16B) sites that are only partly occupied and are sufficiently close that only one of the two sites can be locally occupied. This weakly bonded layer is shown edge-on in Figure 5d and, like the strongly bonded layer, there is another symmetrically distinct but topologically identical layer in the structure.

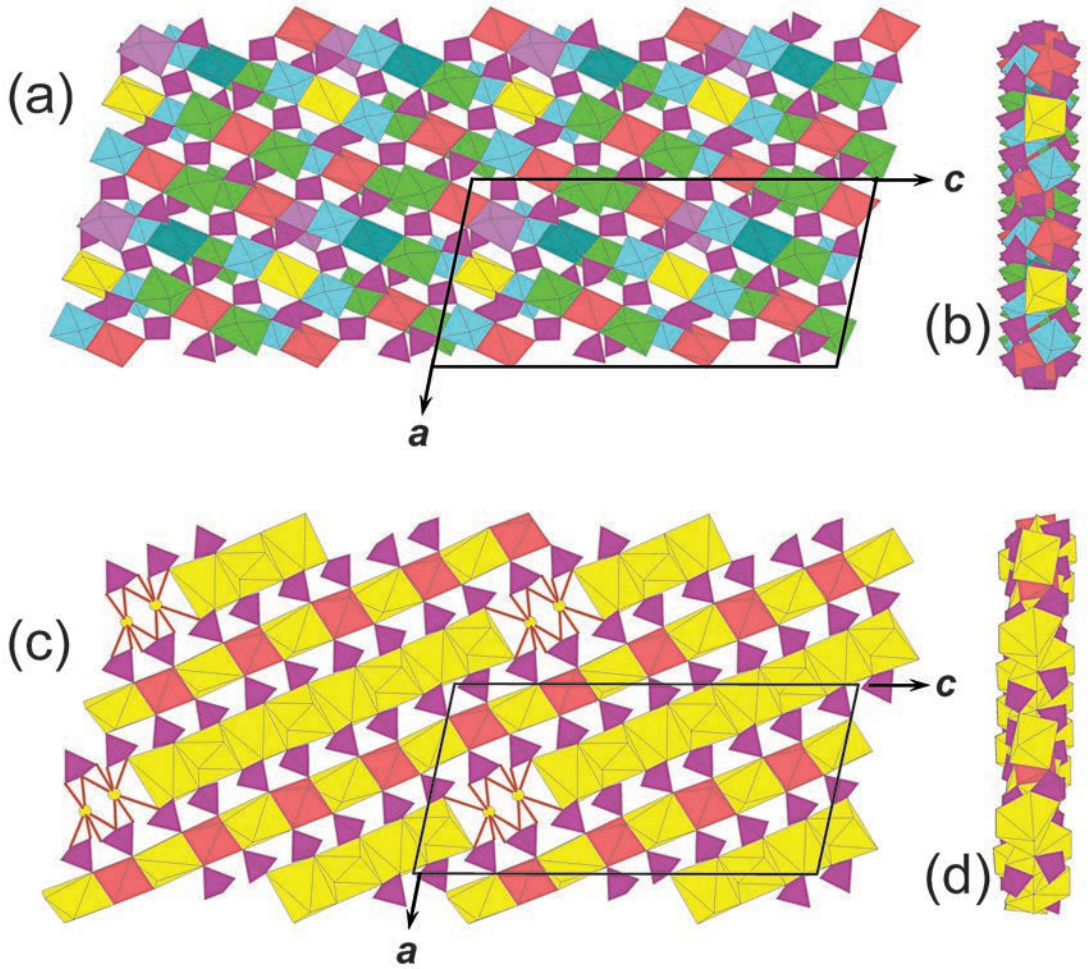


FIG. 5. The crystal structure of manitobaite; (a) the heteropolyhedral *Fe–Mn* layer projected onto (010); (b) the heteropolyhedral *Fe–Mn* layer viewed edge-on down the **c** axis; (c) the heteropolyhedral *Na* layer projected onto (010); (d) the heteropolyhedral *Na* layer viewed edge-on down the **c** axis. Phosphate tetrahedra: pink; *Al* octahedra: pale blue; *Z* polyhedra: grey; *Fe* octahedra: green; *Mn* octahedra: orange-red; *Na* polyhedra: yellow; the partly occupied *Na*(16A) and *Na*(16B) sites are shown as yellow circles with some of the bonds to the coordinating anions shown; the unit cell is shown by thick black lines in (a) and (c).

A key aspect of the structure of manitobaite is the order of non-tetrahedrally-coordinated cations over the cation sites of the structure. Chains from the sheet of Figure 5a are shown in Figures 6a and 6b, where it is immediately apparent that Na, Al, Ca, Mn and Fe show prominent order within the chains. The character of these chains is better illustrated in the lower parts of Figures 6a,b, which show the staggered nature of the octahedra. In the **b**–**c** projection of each chain, it is apparent that there are two distinct types of octahedra: type 1, the *Na*(1), *Z*(2), *Mn*(10), *Mn*(9), *Mn*(3), *Na*(1)… octahedra that extend along the central axis of the chain, and type-2 dimers of edge-sharing octahedra that are inclined to the central axis of the chain and share edges with the type-1 octahedra. Type-1 octahedra are occupied by Na, $Mn^{2+}$, ($Mn^{2+}$ + Ca) = *Z* and ($Mn^{2+} \approx Fe^{2+}$) = *M*, and type-2 octahedra are occupied by $Fe^{2+}$, Al and ($Mn^{2+} \approx Fe^{2+}$) = *M*.

What is very apparent in manitobaite is the strong difference in order between $Mn^{2+}$ and $Fe^{2+}$. Inspection of Figure 5c shows that the weakly bonded layer is dominated by *Na* (yellow) and *Mn* (red) polyhedra; none of the polyhedra in this layer contain significant $Fe^{2+}$ or Al. As noted above, in the strongly bonded

layers (Figs. 5a, 6), type-1 octahedra are occupied primarily by $Mn^{2+}$ and Na with minor Ca, whereas type-2 octahedra are occupied primarily by $Fe^{2+}$ and Al with minor $Mn^{2+}$ disordered with $Fe^{2+}$ at the *M*(1,2) octahedra.

## Cation Order in the Alluaudite-Supergroup Minerals

The characteristic structure-types of the alluaudite-group minerals are listed in Table 7, together with their chemical formulae, cell dimensions and space groups. The patterns of cation order in the alluaudite, wyllieite and bobfergusonite structures are shown in Figure 7. In the alluaudite structure, compositions commonly vary between two end-member stoichiometries: alluaudite, $\square NaMn^{2+}Fe^{3+}{}_2(PO_4)_3$, and hagendorfite, $NaCaMn^{2+}Fe^{2+}{}_2(PO_4)_3$, where $Mn^{2+}$ occupies the *M*(1) site and both $Fe^{2+}$ and $Fe^{3+}$ occupy the *M*(2) site (Moore 1971, Redhammer *et al.* 2005). In the alluaudite structure, there is one type-1 octahedron, *M*(1), and one type-2 octahedron, *M*(2) (Fig. 7a). The *M*(1) octahedron is occupied by $Mn^{2+}$ or $Fe^{2+}$, depending on composition, and the *M*(2) octahedron is occupied by $Fe^{2+}$ or $Fe^{3+}$, or both.

In the wyllieite structure, compositions may vary between two end-member root stoichiometries: rosemaryite, $\square NaMn^{2+}Fe^{3+}Al(PO_4)_3$, and wyllieite, $NaNaFe^{2+}Fe^{2+}Al(PO_4)_3$. Note that both minerals incorporate significant Al, as indicated by the end-member

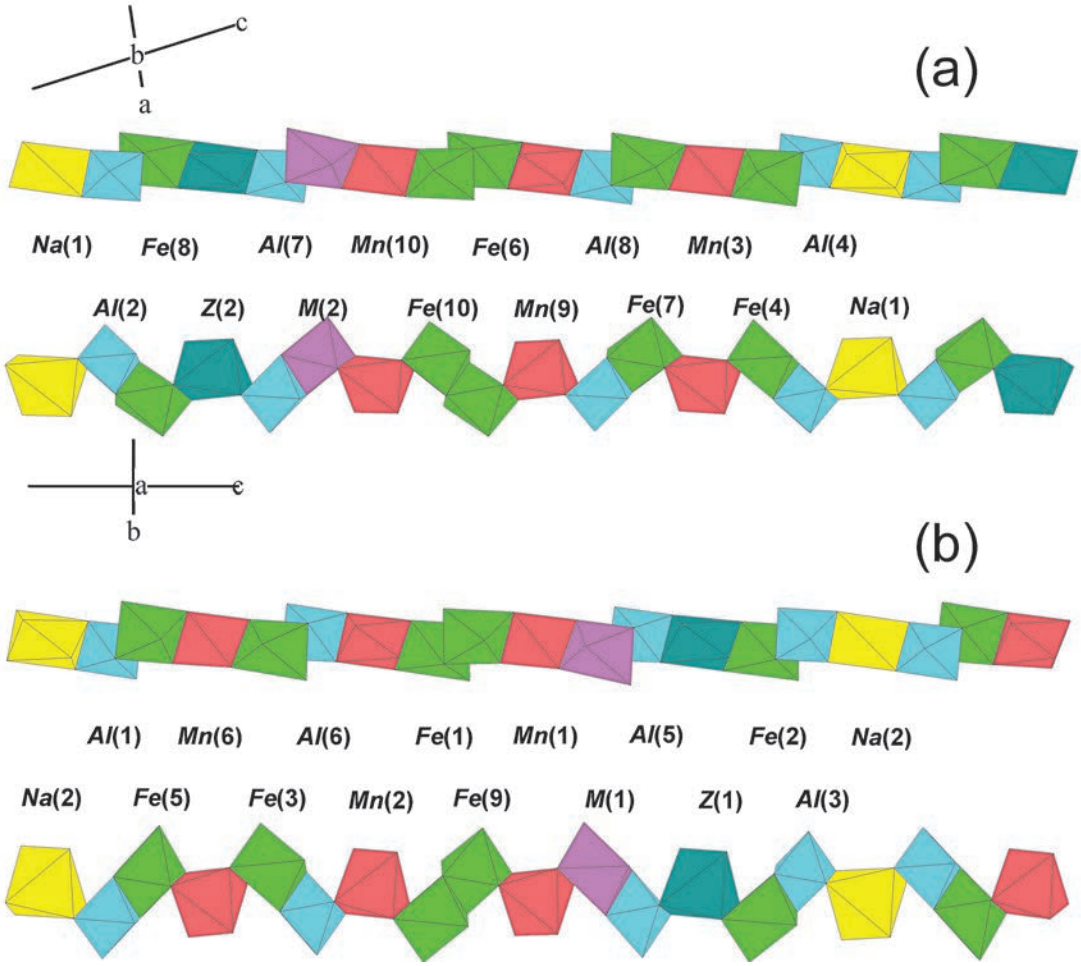


FIG. 6. Two chains of edge-sharing octahedra extracted from the heteropolyhedral sheets (Fig. 5a) in the crystal structure of manitobaite. The upper parts of (a) and (b) are extracted from the sheet shown in Figure 5a, and the lower views show the same chains viewed orthogonal to the sheet, better illustrating the corrugated nature of the chains. The orientations of each chain are the same in (a) and (b).

formulae. There is one type-1 octahedron, *M*(1), and two type-2 octahedra, *M*(2a) and *M*(2b) (Fig. 7b), and $Fe^{2+}$ or $Mn^{2+}$ (or both) occupies the *M*(1) site. There are two end-member patterns of order: in rosemaryite and ferrorosemaryite (Hatert *et al*. 2005, 2006), *M*(2*a*) = Al and *M*(2*b*) = $Fe^{2+}$ (Fig. 7b, top), whereas in ferrowyllieite (Moore & Molin-Case 1974), *M*(2*a*) = $Fe^{2+}$ and *M*(2b) = Al (Fig. 7b, bottom).

In bobfergusonite (Fig. 7c), there are two type-1 octahedra, *M*(1) and *M*(2), and four type-2 octahedra, *M*(3) and *M*(6), and *M*(4) and *M*(5) (Fig. 7c), and $Fe^{2+}$ or $Mn^{2+}$ occupies the *M*(1) and *M*(2) sites. There are two distinct chains of octahedra with different patterns of order over the *M*(4) and *M*(5) sites (upper chain) and the *M*(3) and *M*(6) sites (lower chain): in the *M*(1)–*M*(5)–*M*(4) chain, *M*(5) is occupied by $Fe^{2+}$ + $Fe^{3+}$, and *M*(4) is occupied by $Fe^{2+}$, whereas in the *M*(2)–*M*(3)–*M*(6) chain, *M*(3) is occupied dominantly by $Fe^{2+}$ (with minor $Fe^{3+}$), and *M*(6) is occupied by Al. Again, note the lack of solid solution involving $Fe^{3+}$ and Al.

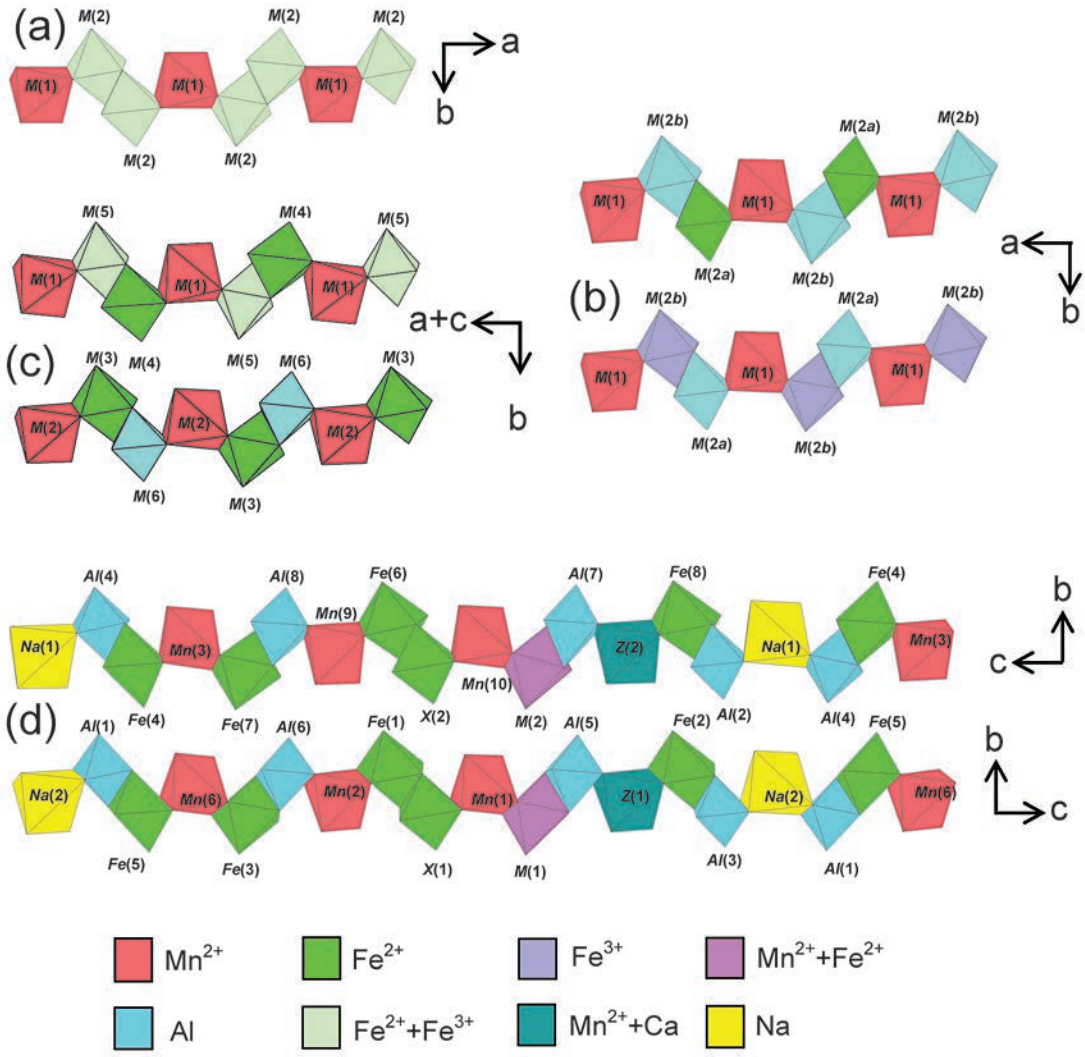


FIG. 7. Ordered chains in the crystal structures of (a) alluaudite [the *M*(1) octahedron may be occupied by $Mn^{2+}$ and $Fe^{2+}$ in this structure type]; (b) rosemaryite (upper) and ferrowyllieite (lower); (c) bobfergusonite (the upper and lower chains are crystallographically distinct and show different patterns of order); (d) manitobaite (as with bobfergusonite, the upper and lower chains are crystallographically distinct, although here they are shown in different orientations to emphasize their pseudosymmetric relation to each other).

TABLE 7. CHARACTERISTIC STRUCTURE-TYPES OF THE ALLUAUDITE-GROUP MINERALS

| | | *a* (Å) | *b* (Å) | *c* (Å) | β (°) | *V* (Å$^3$) | *Z* | Space group | N* | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| Alluaudite | $NaMn^{2+}Fe^{3+}_2(PO_4)_3$ | 12.004 | 12.533 | 6.404 | 114.4 | 877.4 | 4 | *C*2/*c* | 1 | (1) |
| Wyllieite | $Na_2Fe^{2+}_2Al(PO_4)_3$ | 11.868 | 12.382 | 6.354 | 114.52 | 849.5 | 4 | $P2_1/n$ | 1 | (2) |
| Bobfergusonite | $Na_2Mn^{2+}_5Fe^{3+}Al(PO_4)_6$ | 12.776 | 12.488 | 11.035 | 97.21 | 1746.7 | 4 | $P2_1/n$ | 2 | (3) |
| Manitobaite | $Na_{16}Mn^{2+}_{25}Al_8(PO_4)_{30}$ | 13.452 | 12.527 | 26.677 | 101.58 | 4403.9 | 2 | *Pc* | 5 | (4) |

References: (1) Moore (1971); (2) Moore & Ito (1973), Moore & Molin-Case (1974); (3) Ercit *et al.* (1986a, 1986b), Tait *et al.* (2004); (4) Ercit *et al.* (2010). * $N = || V_{Mineral} / V_{Alluaudite} ||$.

In manitobaite (Fig. 7d), there are ten type-1 octahedra, *Na*(1), *Na*(2), *Mn*(1), *Mn*(2), *Mn*(3), *Mn*(6), *Mn*(9), *Mn*(10), *Z*(1) and *Z*(2), and twenty type-2 octahedra, *Al*(1–8), *Fe*(1–8), *X*(1,2) and *M*(1,2). As in bobfergusonite, there are two distinct chains (Fig. 7d, top and bottom), but in manitobaite, the patterns of order are virtually identical in each chain. Type-1 octahedra are occupied by Na (+ minor Ca), $Mn^{2+}$, ($Mn^{2+}$ + $Fe^{2+}$) and ($Mn^{2+}$ + Ca) [*Z*(1,2)]; type-2 octahedra are occupied by $Fe^{2+}$, Al, ($Mn^{2+}$ + $Fe^{2+}$) and ($Fe^{2+}$ + Al). By and large, the dimers of type-2 octahedra consist of one large octahedron and one small octahedron, as is the case also in the wyllieite-type minerals and bobfergusonite, in contrast to alluaudite-type minerals where the symmetry does not allow such (long-range) order.

How does the chain in manitobaite incorporate Na in a type-1 octahedron? Inspection of Figure 7d shows how this is done. The *Na*(1) and *Na*(2) octahedra are each flanked on both sides by Al octahedra, the high-charge Al cations compensating for the low-charge Na cations.

The similarity in order within the two distinct chains in the structure of manitobaite emphasizes the pseudosymmetry present in this structure. However, this is pseudosymmetry and not crystallographic symmetry, as emphasized in the *Experimental* section, and suggests that manitobaite may have crystallized with higher symmetry ($P2_1/c$) and gone through a phase transition on cooling, in accord with the presence of pervasive twinning.

### *Al and $Fe^{3+}$ in alluaudite-group minerals*

The relation between Al and $Fe^{3+}$ in the alluaudite structures *sensu lato* is both interesting and unusual. In most minerals, there is extensive solid-solution between Al and $Fe^{3+}$, but this does not seem to be the case in the alluaudite-group minerals *sensu lato*. A notable feature of the alluaudite structure is that it does not generally incorporate much Al. Thoreau & Bastien (1954) gave a composition of alluaudite from the Buranga pegmatite in Rwanda, and did not list any $Al_2O_3$. Moore (1971) used this information to assign site populations in his structure solution of alluaudite from the same locality. Tait (2002) reported a new refinement of the alluaudite structure from the Buranga pegmatite, and electron-microprobe analysis of the crystal used in that work gave an $Al_2O_3$ content of 2.49 wt%. Analysis of the Buranga alluaudite in thin section gave $Al_2O_3$ contents from 0.32 to 2.57 wt%, with most values exceeding 1.5 wt%. Several alluaudite compositions are listed in the literature, but only one (of alluaudite from Rapid Creek, Yukon, Canada; Robinson *et al.* 1992) gives significant $Al_2O_3$ (2.94 wt%). On the other hand, the alluaudite minerals (*e.g.*, alluaudite, hagendorfite) contain both $Fe^{2+}$ and $Fe^{3+}$ and show a wide range of solid solution involving these two constituents. This lack of solid solution between Al and $Fe^{3+}$, and disorder of $Fe^{2+}$ and $Fe^{3+}$, are in accord with the substitution of Al and $Fe^{2+}$ at the *Al* sites in manitobaite.

Fisher (1965) noted the inverse relation between Na and $Fe^{3+}$ in alluaudite-group minerals, and Fransolet *et al.* (2004) wrote the principal substitution in these minerals as $\square + Fe^{3+} \leftrightarrow Na + Fe^{2+}$. As noted by Ercit *et al.* (2010), this substitution also occurs in manitobaite. However, because of the much larger number of sites (and ensuing disorder) in the structure of manitobaite relative to the other minerals of the alluaudite supergroup, this substitution does not give rise to a new mineral species (as is the case in the alluaudite and wyllieite groups).

## Acknowledgements

We thank Uwe Kolitsch and Stuart Mills for their reviews of this paper, and Associate Editor Frédéric Hatert and Editor Bob (Martin) for their green pens. We thank Mark Cooper for his extensive help with this mineral. The work was supported by a Canada Research Chair in Crystallography and Mineralogy, Research Tools and Equipment, Major Facilities Access and Discovery Grants from the Natural Sciences and Engineering Research Council of Canada and Canada Foundation for Innovation Grants to FCH.

## References


Brown, I.D. (1981): The bond-valence method: an empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II, Vol. 2 (M. O'Keeffe & A. Navrotsky, eds.). Academic Press, New York, N.Y. (1-30).

Brown, I.D. & Altermatt, D. (1985): Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.* **B41**, 244-247.

Bruker AXS (1997): SHELXTL Reference Manual 5.10. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin.

Ercit, T.S., Anderson, A.J., Černý, P. & Hawthorne, F.C. (1986b): Bobfergusonite, a new phosphate mineral from Cross Lake, Manitoba. *Can. Mineral.* **24**, 599-604.

Ercit, T.S., Hawthorne, F.C. & Černý, P. (1986a): The crystal structure of bobfergusonite. *Can. Mineral.* **24**, 605-614.

Ercit, T.S., Tait, K.T., Cooper, M.A., Abdu, Y., Ball, N.A., Anderson, A.J., Černý, P., Hawthorne, F.C. & Galliski, M. (2010): Manitobaite, $Na_{16}Mn^{2+}_{25}Al_8(PO_4)_{30}$, a new phosphate mineral species from Cross Lake, Manitoba, Canada. *Can. Mineral.* **48**, 1455-1463.

Fisher, D.J. (1965): Dickinsonites, fillowites and alluaudites. *Am. Mineral.* **50**, 1647-1669.

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.

Hatert, F., Hermann, R.P., Fransolet, A.-M., Long, G.J. & Grandjean, F. (2006): A structural, infrared and Mössbauer spectral study of rosemaryite, $NaMnFe^{3+}Al(PO_4)_3$. *Eur. J. Mineral.* **18**, 775-785.

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. (1983): Quantitative characterization of site-occupancies in minerals. *Am. Mineral.* **68**, 287-306.

Hawthorne, F.C. & Oberti, R. (2007): Amphiboles: crystal chemistry. *In* Amphiboles: Crystal Chemistry, Occurrence and Health Issues (F.C. Hawthorne, R. Oberti, G. Della Ventura & A. Mottana, eds.). *Rev. Mineral. Geochem.* **67**, 1-54.

Hawthorne, F.C., Ungaretti, L. & Oberti, R. (1995): Site populations in minerals: terminology and presentation of results of crystal-structure refinement. *Can. Mineral.* **33**, 907-911.

Huminicki, D.M.C. & Hawthorne, F.C. (2002): The crystal chemistry of the phosphate minerals. *In* Phosphates: Geochemical, Geobiological, and Materials Importance (M.J. Kohn, J. Rakovan & J.M. Hughes, eds.). *Rev. Mineral. Geochem.* **48**, 123-253.

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. & 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).

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.

Robinson, G.W., Van Velthuizen, J., Ansell, H.G. & Sturman, B.D. (1992): Mineralogy of the Rapid Creek and Big Fish River area, Yukon Territory. *Mineral. Rec.* **23**, 1-47.

Shannon, R.D. (1976): Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751-767.

Sheldrick, G.M. (2008): A short history of SHELX. *Acta Crystallogr.* **A64**, 112-122.

Tait, K.T. (2002): *The Crystal Chemistry of the Alluaudite-Group Minerals*. M.Sc. thesis, University of Manitoba, Winnipeg, Manitoba.

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.

Thoreau, J. & Bastien, G. (1954): Les phosphates des pegmatites du Ruanda occidental. *Bull. Acad. Roy. Belg., Classe Sciences* **25**, 1595-1603.


*Received June 9, 2011, revised manuscript accepted November 5, 2011.*