*Canadian Mineralogist*
Vol. 28, pp. 141-146 (1990)

# CRYSTAL STRUCTURE OF Ca-RICH BEUSITE FROM THE YELLOWKNIFE PEGMATITE FIELD, NORTHWEST TERRITORIES

MICHAEL A. WISE*, FRANK C. HAWTHORNE AND PETR ČERNÝ
*Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2*

## ABSTRACT

Ca-rich beusite from the Yellowknife pegmatite field is monoclinic, space group $P2_1/c$, $a$ 8.797(3), $b$ 11.758(4), $c$ 6.170(2) Å, $\beta$ 99.31(2)° and $V$ 629.8(3) Å$^3$. The crystal structure was refined by least-squares method to $R$ and $R_w$ indices of 3.3 and 2.6% using 773 observed reflections. The isostructural relationship with graftonite is confirmed. The structure consists of three unique cation sites, $M(1)$, $M(2)$ and $M(3)$, which are 7-, 5- and 6-coordinated, respectively. This coordination scheme represents a new variation of the graftonite structure. Ca preferentially occupies the seven-coordinated site, causing an elongation of the O(1)*b*–O(3)*c* interatomic distance, which results in the lengthening of the *b* dimension relative to Ca-poor beusite.

*Keywords*: beusite, crystal structure, phosphate, pegmatite, Yellowknife, Northwest Territories.

## SOMMAIRE

La béusite riche en Ca qui provient du champ de pegmatites de Yellowknife, Territoires du Nord-Ouest, est monoclinique, groupe spatial $P2_1/c$, $a$ 8.797(3), $b$ 11.758(4), $c$ 6.170(2) Å, $\beta$ 99.31(2)°, $V$ 629.8(3) Å$^3$. Nous avons affiné sa structure par la méthode des moindres carrés jusqu'aux résidus $R$ et $R_w$ de 3.3 et de 2.6% en utilisant 773 réflexions observées. La relation isostructurale avec la graftonite est confirmée. La structure comprend trois sites cationiques uniques, $M(1)$, $M(2)$ et $M(3)$, qui ont une coordinence de 7, 5 et 6, respectivement. Ce schéma de coordinence représente une variation nouvelle de la structure de la graftonite. Le Ca occupe de préférence le site à coordinence 7, ce qui cause un allongement dans la distance O(1)*b*–O(3)*c* et donc dans la période *b* par rapport à celle de la béusite à faible teneur en calcium.

(Traduit par la Rédaction)

*Mots-clés*: béusite, structure cristalline, phosphate, pegmatite, Yellowknife, Territoires du Nord-Ouest.

## INTRODUCTION

Beusite, $(Mn,Fe,Ca)_3(PO_4)_2$, is the manganese end-member of the graftonite–beusite series, first described by Hurlbut & Aristarain (1968) from pegmatites of the San Luis Province, Argentina. There, it occurs interlaminated with lithiophilite. Beusite was later reported from Finland (Lahti 1981), Namibia (Fransolet *et al.* 1986) and Yellowknife (Wise & Černý 1990). X-ray powder-diffraction studies of beusite from the Yellowknife locality showed an anomalously large *b* cell dimension compared to the samples previously reported. Results of an electron-microprobe analysis of the Yellowknife sample revealed a significantly higher Ca content, to which was attributed the increase in *b*. These findings prompted the refinement of the beusite structure, which previously had not been investigated.

Beusite is isostructural with graftonite; both are structurally related to glaserite (Moore 1981). The crystal structure of graftonite of composition $(Fe_{0.60}Mn_{0.27}Ca_{0.13})_3(PO_4)_2$ was first solved by Calvo (1968). His results show three distinct cation sites; $M(1)$, $M(2)$ and $M(3)$, with seven-, five- and five-coordination, respectively. Kostiner & Rea (1974) verified the graftonite structure for synthetic $Fe_3(PO_4)_2$, but found the $M(1)$ site to be six-coordinated. The structure of $(Fe_{0.50}Mn_{0.50})_3(PO_4)_2$, refined by neutron powder-diffraction methods, also was shown to have a six-coordinated $M(1)$ site (Nord & Ericsson 1982a). All three studies agree on the basic structural framework of graftonite despite the ambiguity in the coordination of the $M(1)$ site. In each study, the Fe-rich member of the graftonite–beusite series was investigated. There has been no structure analysis of graftonite-like minerals with Mn > Fe. We report here on the structure of the Ca-rich beusite described by Wise & Černý (1990).

## EXPERIMENTAL

The crystal used in this study was taken from a sample of intergrown beusite and triphylite collected from a pegmatite in the Yellowknife pegmatite field, Northwest Territories (Wise & Černý 1990). The empirical formula for the Yellowknife beusite based on electron-microprobe analytical results is $(Ca_{0.98}Mn_{0.02})(Fe_{0.92}Mn_{0.08})Mn_{1.00}(PO_4)_2$. A fragment of beusite measuring 0.2 × 0.2 × 0.15 mm was mounted on a Nicolet $R3m$ automated four-circle diffractometer for data collection. The setting angles of fifteen automatically aligned intense reflections were used to refine the monoclinically constrained unit-cell dimensions (Table 1).

---

*Present address: Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.

TABLE 1. MISCELLANEOUS CRYSTAL DATA FOR BEUSITE FROM YELLOWKNIFE

| | | |
|---|---|---|
| a | 8.797(3) Å | |
| b | 11.758(4) | |
| c | 6.170(2) | |
| $\beta$ | 99.31(2)° | |
| V | 629.8(3) $Å^3$ | |
| Space Group $P2_1/c$ | | |
| Chemical composition: $Mn_{1.10}Ca_{0.98}Fe_{0.92}P_2O_8$ | | |
| Radiation | MoKα | |
| Monochromator | Graphite | |
| Total \|Fo\| | 927 | |
| No. of \|Fo\|>5σ | 773 | |
| Final R(obs) | 3.3% | $R=\Sigma(\lvert Fo\rvert-\lvert Fc\rvert)/\Sigma\lvert Fo\rvert$ |
| Final $R_w$(obs) | 2.6% | $R_w=[\Sigma w(\lvert Fo\rvert-\lvert Fc\rvert)^2/\Sigma w\lvert Fo\rvert^2]^{½}$, w=1 |

TABLE 2. COMPARISON OF UNIT-CELL DATA FOR BEUSITE AND GRAFTONITE

| Sample No. | a(Å) | b(Å) | c(Å) | β(°) | V($Å^3$) |
|---|---|---|---|---|---|
| 1 | 8.797(3) | 11.758(4) | 6.170(2) | 99.31(2) | 629.8(3) |
| 2 | 8.818(1) | 11.750(1) | 6.175(1) | 99.35(1) | 631.3(1) |
| 3 | 8.78(1) | 11.52(1) | 6.1591) | 99.42(35) | 613.7(1) |
| 4 | 8.788(3) | 11.434(2) | 6.255(1) | 98.98(2) | 620.8(4) |
| 5 | 8.91(1) | 11.58(1) | 6.239(8) | 98.9(1) | 636.0(3) |

1 Beusite single-crystal data (this study), 2 beusite powder data (Wise & Černý 1990),3 beusite [$(Mn_{1.77}Fe_{0.70}Ca_{0.29}Mg_{0.22})(PO_4)_2$] Los Aleros, San Luis, Argentina (Hurlbut & Aristarain 1968), 4 synthetic beusite [$(Mn_3(PO_4)_2$], synthesized at 25 kbar, 600°C, 24 hrs.,(Nord & Annersten 1987),5 graftonite [$(Fe_{0.60}Mn_{0.27}Ca_{0.13})(PO_4)_2$] (Calvo 1968).

Table 2 compares the cell dimensions of the Yellowknife beusite with those of other samples. X-ray powder-diffraction data were obtained on a Philips PW 1710 automated diffractometer. Operating conditions were as follows: graphite-monochromatized Cu$K\alpha_1$ radiation (λ 1.54060 Å), operating voltage 40 kV, operating current 40 mA, scanning speed ½° 2$\theta$/min. Powder-diffraction data were calibrated using $SiO_2$ [*a* 4.9145(1), *c* 5.4061(3) Å] as an internal standard, and cell dimensions were calculated using a modified version of the CELREF program of Appleman & Evans (1973). The unit-cell dimensions of the Yellowknife beusite, particularly the *b* dimension, are significantly different from those of the Argentinian and synthetic beusite.

Intensity data for the structure refinement were collected in the $\theta$–2$\theta$ scan mode using 96 steps with a scan range from [2$\theta$(Mo$K\alpha_1$)–1] to [2$\theta$(Mo$K\alpha_2$) + 1]° and a variable scan-rate between 4.0 and 29.3°/minute depending on the intensity of an initial 1-s count at the center of the scan range. Backgrounds were measured for half the scan duration at the beginning and end of each scan. Two standard reflections were monitored every 48 measurements to check for stability and constancy of crystal alignment. A total of 1072 reflections were measured over one asymmetric unit out to a maximum 2$\theta$ of 60°. Ten strong reflections were measured at 10° intervals of $\psi$ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 350°. These data were used to calculate an ellipsoidal empirical absorption-correction. The data also were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. Of the 927 unique reflections, 773 were classified as observed (>5$\sigma$).

Because of the homogeneity of the beusite, an average of 5 determinations of its composition using the electron microprobe (Wise & Černý 1990) led to the formula, given in Table 1, that was used in the structure refinement.

## STRUCTURE REFINEMENT

Scattering curves for neutral atoms, together with coefficients of anomalous dispersion, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). The SHELXTL system of programs was used for the computational procedures.

Using the atomic positions of Calvo (1968), a least-squares refinement of all atomic positions (fully isotropic) refined to an *R* index of 6.8%. Conversion to anisotropic temperature-factors for all atoms reduced the *R* indices to $R = 3.2$, $R_w = 3.7\%$ for the 773 observed reflections. At this point in the refinement, the *M*-site occupancies were critically exa-

TABLE. 3. ATOMIC POSITIONAL PARAMETERS FOR BEUSITE FROM YELLOWKNIFE

| Atom | x | y | z | *U(equiv.) |
|---|---|---|---|---|
| M(1) | 0.9495(1) | 0.12423(8) | 0.8267(2) | 1.10(3) |
| M(2) | 0.71181(9) | 0.07841(7) | 0.3268(1) | 1.31(2) |
| M(3) | 0.3582(1) | 0.19006(8) | 0.1334(1) | 1.13(2) |
| P(1) | 0.0929(2) | 0.1334(1) | 0.3964(2) | 0.84(4) |
| P(2) | 0.5994(2) | 0.0899(1) | 0.8070(2) | 0.84(3) |
| O(1) | 0.0832(4) | 0.0707(3) | 0.1791(6) | 1.2(1) |
| O(2) | 0.4704(4) | 0.1748(3) | 0.8316(6) | 1.2(1) |
| O(3) | 0.9361(4) | 0.1856(3) | 0.4281(5) | 1.2(1) |
| O(4) | 0.6855(4) | 0.1283(3) | 0.6224(6) | 1.3(1) |
| O(5) | 0.2061(5) | 0.2332(4) | 0.3841(6) | 1.4(1) |
| O(6) | 0.7241(4) | 0.0923(3) | 0.0133(6) | 1.4(1) |
| O(7) | 0.1459(4) | 0.0587(3) | 0.5971(6) | 1.2(1) |
| O(8) | 0.5334(4) | −0.0316(3) | 0.7634(6) | 1.2(1) |

*U(equiv.)=U(equiv.) x $10^2$. Estimated standard deviations are in parentheses.

TABLE 4. ANIOSTROPIC TEMPERATURE-FACTORS FOR BEUSITE FROM YELLOWKNIFE

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| M(1) | 132(6) | 94(5) | 102(5) | −11(4) | 9(4) | −4(4) |
| M(2) | 132(4) | 187(4) | 73(3) | 5(3) | 13(3) | 37(3) |
| M(3) | 124(4) | 125(4) | 89(4) | 3(3) | 13(3) | 25(3) |
| P(1) | 88(6) | 86(6) | 79(6) | 8(5) | 21(5) | −5(5) |
| P(2) | 82(6) | 98(6) | 70(6) | −2(5) | 11(5) | 5(5) |
| O(1) | 156(19) | 113(18) | 93(17) | −12(15) | −1(15) | 16(15) |
| O(2) | 83(17) | 163(18) | 135(17) | 28(14) | 52(13) | 31(14) |
| O(3) | 108(17) | 125(17) | 140(17) | 7(14) | 31(14) | 16(14) |
| O(4) | 139(18) | 141(17) | 106(16) | 3(14) | 14(13) | −25(14) |
| O(5) | 171(20) | 151(21) | 108(19) | −23(16) | 44(16) | −90(18) |
| O(6) | 105(18) | 208(19) | 103(17) | 2(16) | −10(14) | 11(15) |
| O(7) | 122(17) | 139(18) | 102(16) | 30(14) | 13(13) | 36(15) |
| O(8) | 100(18) | 128(19) | 129(17) | −24(15) | 22(15) | 1(14) |

$U_{ij}=U_{ij}$ x $10^4$. Estimated standard deviations are in parentheses.

TABLE 5. SELECTED INTERATOMIC BOND-LENGTHS (Å) FOR BEUSITE FROM YELLOWKNIFE

| | | | | | |
|---|---|---|---|---|---|
| M(1)-O(1)a | 2.383(3) | M(2)-O(3) | 2.339(3) | M(3)-O(1) | 2.850(4) |
| O(1)b | 2.310(4) | O(4) | 1.965(4) | O(2)g | 2.251(4) |
| O(3) | 2.547(4) | O(6) | 1.961(4) | O(2)h | 2.146(3) |
| O(3)c | 2.330(4) | O(7)f | 2.049(4) | O(5) | 2.261(4) |
| O(4) | 2.458(4) | O(8)f | 2.208(4) | O(5)i | 2.075(4) |
| O(6)d | 2.478(4) | | | O(8)f | 2.142(4) |
| O(7)e | 2.525(4) | | | | |
| <M(1)-O> | 2.433 | <M(2)-O> | 2.104 | <M(3)-O> | 2.286 |
| P(1)-O(1) | 1.520(4) | P(2)-O(2) | 1.537(4) | | |
| O(3)j | 1.551(4) | O(4) | 1.534(4) | | |
| O(5) | 1.549(4) | O(6)d | 1.540(3) | | |
| O(7) | 1.528(4) | O(8) | 1.549(4) | | |
| <P(1)-O> | 1.537 | <P(2)-O> | 1.540 | | |
| M1 | | M2 | | M3 | |
| O(1)a-O(1)b | 2.957(5) | O(3)-O(4) | 2.758(5) | O(1)-O(5) | 2.444(5) |
| O(1)a-O(3)c | 3.410(5) | O(3)-O(6) | 3.112(5) | O(1)-O(5)i | 3.230(6) |
| O(1)a-O(6)d | 3.171(5) | O(3)-O(7)f | 2.960(5) | O(1)-O(8)f | 3.366(5) |
| O(1)a-O(7)e | 3.722(5) | O(4)-O(6) | 3.851(5) | O(2)g-O(2)h | 3.556(5) |
| O(1)b-O(3) | 3.888(5) | O(4)-O(7)f | 3.086(5) | O(2)g-O(5)i | 2.631(5) |
| O(1)b-O(4) | 3.211(5) | O(4)-O(8)f | 3.030(5) | O(2)g-O(8)f | 3.017(5) |
| O(3)-O(3)c | 3.437(3) | O(6)-O(7)f | 3.058(5) | O(2)h-O(5) | 2.632(6) |
| O(3)-O(4) | 2.758(5) | O(6)-O(8)f | 2.923(5) | O(2)h-O(5)i | 3.380(6) |
| O(3)-O(7)e | 2.469(5) | | | O(2)h-O(8)f | 3.502(6) |
| O(4)-O(6)d | 2.418(5) | | | O(5)-O(5)i | 3.110(1) |
| | | | | O(5)-O(8)f | 3.518(6) |
| <O-O>M(1) | 3.144 | <O-O>M(2) | 3.097 | <O-O>M(3) | 2.866 |
| P1 | | P2 | | | |
| O(1)-O(3)j | 2.550(5) | O(2)-O(4) | 2.517(5) | | |
| O(1)-O(5) | 2.444(5) | O(2)-O(6)d | 2.523(5) | | |
| O(1)-O(7) | 2.552(5) | O(2)-O(8) | 2.539(5) | | |
| O(3)j-O(5) | 2.497(6) | O(4)-O(6)d | 2.418(5) | | |
| O(3)j-O(7) | 2.469(5) | O(4)-O(8) | 2.541(5) | | |
| O(5)-O(7) | 2.538(5) | O(6)d-O(8) | 2.545(5) | | |
| <O-O>P(1) | 2.508 | <O-O>P(2) | 2.514 | | |

TABLE 6. SELECTED BOND ANGLES (°) FOR BEUSITE FROM YELLOWKNIFE

| | | | |
|---|---|---|---|
| M1 | | M2 | |
| O(1)a-M(1)-O(1)b | 78.1(1) | O(3)-M(2)-O(4) | 79.2(1) |
| O(1)a-M(1)-O(3)c | 92.7(1) | O(3)-M(2)-O(6) | 92.3(1) |
| O(1)a-M(1)-O(6)d | 81.4(1) | O(3)-M(2)-O(7)f | 84.6(1) |
| O(1)a-M(1)-O(7)e | 98.6(1) | O(4)-M(2)-O(7)f | 100.5(1) |
| O(1)b-M(1)-O(3) | 106.3(1) | O(4)-M(2)-O(8)f | 92.9(1) |
| O(1)b-M(1)-O(4) | 84.6(1) | O(6)-M(2)-O(7)f | 99.4(1) |
| O(3)-M(1)-O(3)c | 89.5(1) | O(6)-M(2)-O(8)f | 88.8(1) |
| O(3)-M(1)-O(4) | 66.8(1) | | |
| O(3)-M(1)-O(7)e | 58.3(1) | <O-M(2)-O> | 91.1 |
| O(3)c-M(1)-O(4) | 92.0(1) | | |
| O(4)-M(1)-O(6)d | 58.7(1) | P1 | |
| O(4)-M(1)-O(7)e | 113.2(1) | | |
| <O-M(1)-O> | 85.0 | O(1)-P(1)-O(3)j | 112.3(2) |
| | | O(1)-P(1)-O(5) | 105.6(2) |
| M3 | | O(1)-P(1)-O(7) | 113.7(2) |
| | | O(3)j-P(1)-O(5) | 107.3(2) |
| O(1)-M(3)-O(5) | 55.7(1) | O(3)j-P(1)-O(7) | 106.6(2) |
| O(1)-M(3)-O(5)i | 80.3(1) | O(5)-P(1)-O(7) | 111.1(2) |
| O(1)-M(3)-O(8)f | 83.5(1) | | |
| O(2)g-M(3)-O(2)h | 107.9(1) | <O-P(1)-O> | 109.4 |
| O(2)g-M(3)-O(5)i | 74.8(1) | | |
| O(2)g-M(3)-O(8)f | 86.7(1) | P2 | |
| O(2)h-M(3)-O(5) | 73.3(1) | | |
| O(2)h-M(3)-O(5)i | 106.4(1) | O(2)-P(2)-O(4) | 110.1(2) |
| O(2)h-M(3)-O(8)f | 109.5(1) | O(2)-P(2)-O(6)d | 110.2(2) |
| O(5)-M(3)-O(5)i | 91.6(1) | O(2)-P(2)-O(8) | 110.7(2) |
| O(5)-M(3)-O(8)f | 106.2(2) | O(4)-P(2)-O(6)d | 103.7(2) |
| | | O(4)-P(2)-O(8) | 111.0(2) |
| <O-M(3)-O> | 88.7 | O(6)-P(2)-O(8) | 110.9(2) |
| | | <O-P(2)-O> | 109.4 |

mined. Calvo (1968) suggested that Ca preferentially occupies the *M*(1) site because of its larger size. However, Mössbauer work by Nord & Ericsson (1982b) showed that Ca prefers the *M*(1) and *M*(3) sites in synthetic $(Fe_{1-x}Ca_x)_3(PO_4)_2$, which suggests considerable disorder among cations in the structure. To check for such disorder in beusite, several refinements of the site occupancies were carried out.

In the first model, each site was assumed to be completely filled with only one cation; Ca was assigned to the *M*(1) site, Fe to *M*(2) and Mn to *M*(3). This starting model thus assumed no disorder of cations among the *M* sites. The occupancies were allowed to refine unconstrained. Although the *R* indices of this model converged to the same values as the previous refinement, the model failed to reproduce the microprobe-determined concentrations, as it led to the formula $Ca_{1.00}(Fe_{0.90}Ca_{0.10})(Mn_{0.92}Ca_{0.08})(PO_4)_2$. Subsequent refinements of the unconstrained site-occupancies were attempted with unsuccessful results.

The final model allowed only Ca–Mn disorder at the *M*(1) site and a fixed occupancy of the remaining sites at 1.0 (Fe,Mn). The refined site-occupancies closely approximate the microprobe-determined concentrations. The model refined to final *R* indices of 3.3 and $R_w = 2.6\%$. Final positional parameters are given in Table 3. Anisotropic temperature-factors are given in Table 4, and selected interatomic distances and angles are given in Tables 5 and 6, respectively. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

## DESCRIPTION OF THE STRUCTURE

The structural relationship between graftonite and beusite is confirmed in this study. There are three unique cation positions in the beusite structure: *M*(1), *M*(2) and *M*(3) (Fig. 1). The graftonite structure obviously is quite flexible, as evidenced by changes in polyhedron coordination with changes in bulk composition. As stated earlier, six- and seven-coordinated *M*(1) sites have been reported. In the structure of the Yellowknife sample, the coordination number of the *M*(1) site is ambiguous. Bond-valence sums calculated for a seven-coordinated polyhedron (Table 7) are well within expected values. However, an eight-coordinated polyhedron, which includes a significantly longer *M*–O bond (2.787 Å), gives an equally acceptable bond-valence sum. Agreement between the observed and calculated bond-lengths (2.43 *versus* 2.40 Å) for the seven-coordinated polyhedra is better, and therefore we accept a coordination of seven as appropriate for our structure.

The *M*(1) coordination polyhedron resembles an irregular pentagonal bipyramid. Two bipyramids share an edge along O(1)*a* and O(1)*b* to form *M*(1) pairs or "dimers" (Fig. 2). These "dimers" are corner-shared through O(3) with four similar "dimers" related by a *c*-glide operation. This geometry results in a network of *M*(1) "dimers" that form sheets parallel to the *y*–*z* plane (Fig. 3).

The *M*(2) site is five-coordinated in a distorted square pyramid configuration. Isolated *M*(2) polyhedra share their O(3)–O(4) edge with one of the

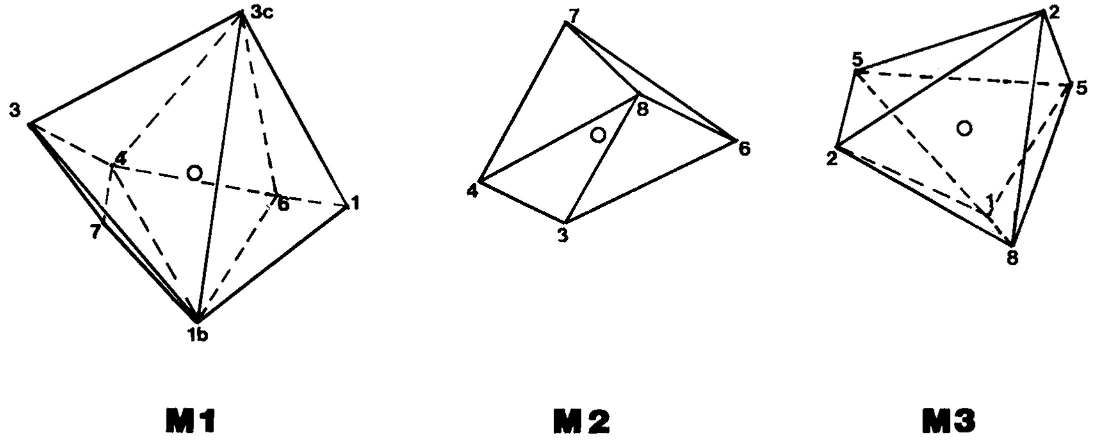

FIG. 1. Sketch of *M*(1), *M*(2) and *M*(3) coordination polyhedra for beusite. Numbers represent oxygen atoms (not shown) for each polyhedron. Open circles represent the cation.

TABLE 7. EMPIRICAL BOND-VALENCE* SUMMATION FOR BEUSITE FROM YELLOWKNIFE

| | M(1) | M(2) | M(3) | P(1) | P(2) | Σ |
|---|---|---|---|---|---|---|
| O(1) | 0.302<br>0.357 | | 0.076 | 1.320 | | 2.055 |
| O(2) | | | 0.284<br>0.371 | | 1.259 | 1.914 |
| O(3) | 0.211<br>0.341 | 0.212 | | 1.211 | | 1.975 |
| O(4) | 0.255 | 0.522 | | | 1.270 | 2.077 |
| O(5) | | | 0.277<br>0.448 | 1.218 | | 1.943 |
| O(6) | 0.244 | 0.559 | | | 1.249 | 2.052 |
| O(7) | 0.221 | 0.439 | | 1.291 | | 1.951 |
| O(8) | | 0.291 | 0.374 | | 1.218 | 1.883 |
| Σ | 1.931 | 2.053 | 1.830 | 5.040 | 4.996 | |

*Bond valences in v.u. calculated from the curves of Brown (1981).

*M*(1) polyhedra, and the O(6) with a similar *M*(1) polyhedron translated one unit-cell along the *z* axis.

Unlike what was found in previous studies, the *M*(3) cation in the Yellowknife beusite is six-coordinated, and the polyhedron resembles a distorted trigonal prism. The *M*(3) polyhedra share edges along O(2) and O(5) to form chains that run parallel to the *z* axis (Fig. 2b). These chains are not linked to the *M*(1) polyhedra, but share the O(8) corner with isolated *M*(2) polyhedra (Fig. 2c).

Two unique P positions exist in beusite; the P is coordinated by four oxygen atoms to form two $PO_4^{3-}$ tetrahedral groups. The two tetrahedra are fairly regular, with average bond-lengths of 1.537 Å for P(1) and 1.540 Å for P(2). Average O-P-O bond angles [109.4° for P(1) and P(2)] agree well with previously reported values for graftonite (Table 8). The *M* cation polyhedra are interconnected by corner-sharing P tetrahedra. The P(1) tetrahedron shares a corner through O(5) with a *M*(3) polyhedron; the remaining three oxygen atoms are corner-

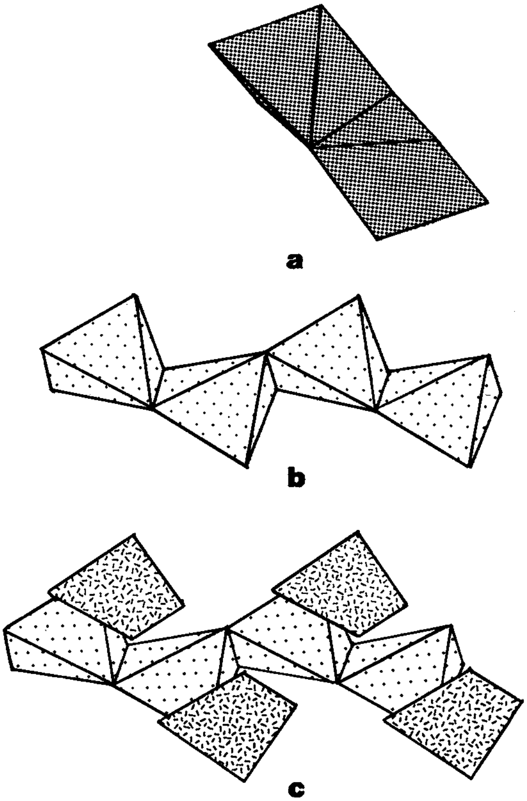

FIG. 2. (a) The *M*(1) dimer with shared edge O(1)*a*–O(1)*b*. (b) The *M*(3) chain with shared O(2)–O(5) edges. (c) The *M*(3) chain with isolated corner-sharing *M*(2) polyhedra.

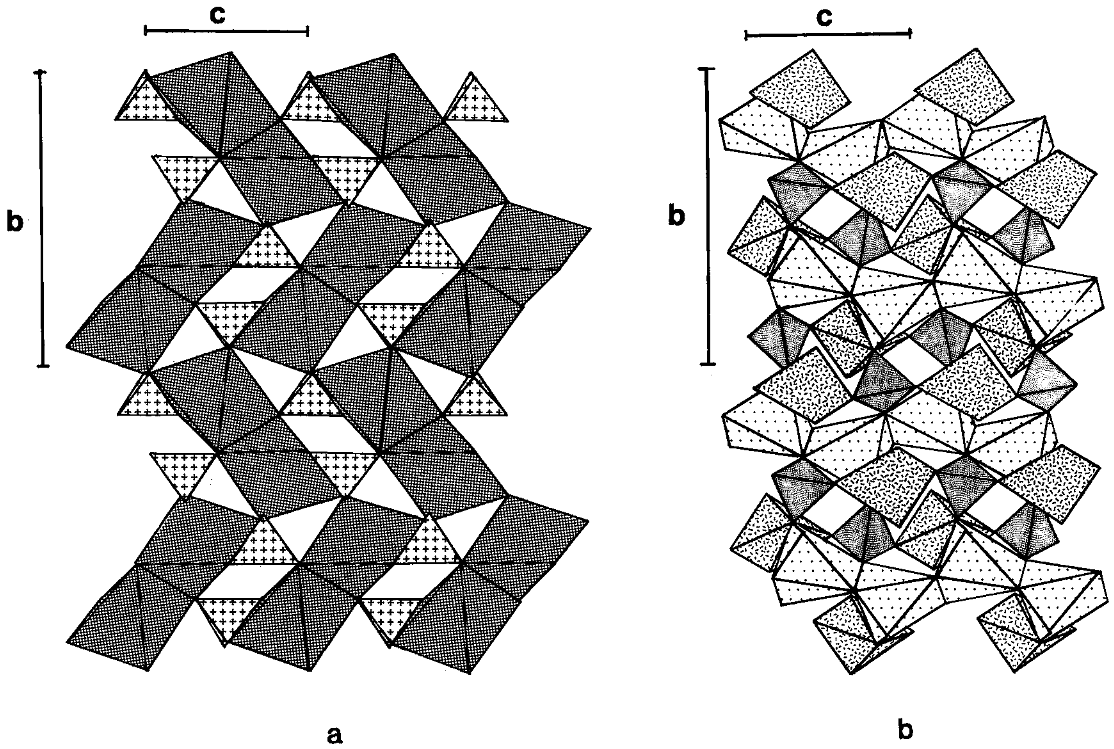

FIG. 3. Projection of the beusite structure down [100]. (a) Note the corner-shared *M*(1) dimers that form a sheet parallel to the *y*–*z* plane. Symbols: dotted pattern *M*(1) site, crosses P(1) site. (b) The *M*(2)–*M*(3) structural network of beusite projected down [100]. Symbols: stippled *M*(2) site, small dots *M*(3) site, densely stippled P(2) site.

linked to the *M*(1) polyhedra. Three corners of the P(2) tetrahedron are linked to three different *M*(2) polyhedra, whereas the remaining oxygen, O(2), is shared with the *M*(3) polyhedron (Fig. 3).

Our structural data compare favorably with those of Calvo (1968). Mean interatomic distances and angles from this and previous studies are summarized in Table 8. Of particular interest are the significantly longer metal–oxygen distances for the *M*(1) site reported by Calvo and also observed here, compared to the *M*(1) sites of synthetic graftonite–beusite of Kostiner & Rea (1974) and Nord & Ericsson (1982a). This difference seems to reflect the preferential occupancy of this site by the larger cations, Ca and, to a lesser extent, Mn. The mean *M*(1) metal–oxygen distances are statistically identical for beusite and Calvo's graftonite, despite the compositional differences between the two minerals.

At first glance, it seems that at least for Mn-dominant specimens, Ca occupies only *M*(1), contrary to the findings of Nord & Ericsson (1982b). However, more structural work, currently in progress, is needed on other members of the graftonite–beusite series in order to adequately characterize the distribution of cations in the series.

TABLE 8. MEAN INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR GRAFTONITE AND BEUSITE

| | (1) | (2) | (3) | (4) |
|---|---|---|---|---|
| M(1)-O | 2.231(4) | 2.37(7) | 2.43(2) | 2.433(4) |
| M(2)-O | 2.134(4) | 2.00(5) | 2.14(2) | 2.104(4) |
| M(3)-O | 2.101(4) | 2.03(9) | 2.16(2) | 2.287(4) |
| P(1) | 1.534(4) | 1.61(6) | 1.55(2) | 1.536(4) |
| P(2) | 1.535(4) | 1.62(6) | 1.55(2) | 1.540(4) |
| O-P(1)-O | 109.5(2) | 109(1) | 110(1) | 109.4(2) |
| O-P(2)-O | 109.4(2) | 109(2) | 110(1) | 109.4(2) |

Bulk composition and source: 1 $Fe_3(PO_4)_2$ (Kostiner & Rea 1974), 2 $(Fe_{0.50}Mn_{0.50})_3(PO_4)_2$ (Nord & Ericsson 1982), 3 $(Fe_{0.60}Mn_{0.27}Ca_{0.13})_3(PO_4)_2$ (Calvo 1968), 4 this study.

Close examination of the *M*(1) site interatomic distances shows a plausible explanation for the larger *b* dimension in the Yellowknife beusite. The *M*(1) pentagonal bipyramid contains five oxygen atoms [O(1), O(3), O(4), O(6) and O(7)] that nearly lie in an equatorial plane. The O(1)*b* and O(3)*c* oxygen atoms are apical, and nearly parallel the *y* axis. In Calvo's graftonite, the *M*(1)–O(1′) and *M*(1)–O(3′) bond distances are 2.228 and 2.246 Å, respectively. In comparison, the analogous bond-distances for beusite [*M*(1)–O(1)*b* and *M*(1)–O(3)*c*] are 2.310 and 2.330 Å, respectively. Thus, the axial bond-distances in the Yellowknife beusite are significantly longer than in Calvo's graftonite. This longer distance, a consequence of occupancy of *M*(1) by a larger cation, distends the *M*(1) polyhedra along *y* axis, thereby resulting in the larger *b* dimension.

## ACKNOWLEDGEMENTS

Our study was supported by the Natural Sciences and Engineering Research Council through Operating Grants to F.C. Hawthorne and P. Černý. The beusite sample used in this study was collected during a regional study of the Yellowknife pegmatite field, that was financially supported by the Tantalum Mining Corporation of Canada Ltd. and the Geology Division, Indian and Northern Affairs of Canada, Yellowknife. We also thank R.F. Martin, E.E. Foord and two anonymous referees for critical reviews of the manuscript.

## REFERENCES

APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Job 9214: Indexing and least-squares refinement of powder diffraction data. *U.S. Geol. Surv., Comput. Contrib.* **20** (NTIS Doc. **PB2-16188**).

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

CALVO, C. (1968): The crystal structure of graftonite. *Am. Mineral.* **53**, 742-750.

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X-rays. *J. Chem. Phys.* **53**, 1891-1898.

______ & MANN, J.B. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

FRANSOLET, A.-M., KELLER, P. & FONTAN, F. (1986): The phosphate mineral associations of the Tsaobismund pegmatite, Namibia. *Contrib. Mineral. Petrol.* **92**, 502-517.

HURLBUT, C.S., JR. & ARISTARAIN, L.F. (1968): Beusite, a new mineral from Argentina, and the graftonite–beusite series. *Am. Mineral.* **53**, 1799-1814.

KOSTINER, E. & REA, J.R. (1974): Crystal structure of ferrous phosphate, $Fe_3(PO_4)_2$. *Inorg. Chem.* **13**, 2876-2880.

LAHTI, S.I. (1981): On the granitic pegmatites of the Eräjärvi area in Orivesi, southern Finland. *Geol. Surv. Finland Bull.* **314.**

MOORE, B.P. (1981): Complex crystal structures related to glaserite, $K_3Na(SO_4)_2$: evidence for very dense packings among oxysalts. *Bull. Minéral.* **104**, 536-547.

NORD, A.G. & ANNERSTEN, H. (1987): A high-pressure phase of manganese(II) orthophosphate, $Mn_3(PO_4)O_2$. *Acta Chem. Scand.*, **A41**, 56-58.

______ & ERICSSON, T. (1982a): The cation distribution in synthetic $(Fe,Mn)_3(PO_4)_2$ graftonite-type solid solutions. *Am. Mineral.* **67**, 826-832.

______ & ______ (1982b): Cation distributions in $(Fe_{1-z}Me_z)_3(PO_4)_2$ graftonite-type solid solutions determined by Mössbauer spectroscopy. *Z. Kristallogr.* **161**, 209-224.

WISE, M.A. & ČERNÝ, P. (1990): Beusite–triphylite intergrowths from the Yellowknife pegmatite field, Northwest Territories. *Can. Mineral.* **28**, 133-139.

*Received November 3, 1988, revised manuscript accepted August 31, 1989.*