

The crystal structure of hōgbomite-8H

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Abstract

Hōgbomite-8H from Central Australia has hexagonal symmetry, $P6_3mc$ with unit-cell parameters of $a = 5.734(3)\text{Å}$ and $c = 18.389(8)\text{Å}$. Its unit-cell composition, as determined from microprobe analysis (combined with information from the structure determination), is $\text{Al}_{14.61}\text{Fe}_{2.84}^{2+}\text{Fe}_{1.44}^{3+}\text{Mg}_{1.40}\text{Ti}_{1.00}\text{Zn}_{0.60}(\text{Ga},\text{Mn},\text{Na})_{0.11}\text{O}_{30}(\text{OH})_2$. The correct structural model was predicted with the aid of geometric principles previously derived from a structure determination for the related mineral, nigerite-24R. The structure was refined to an R value of 0.032 ($R_w = 0.031$) for 1425 observed reflections, with $F \geq 6\sigma(F)$, collected using $\text{MoK}\alpha$ radiation. The model is based on a closest-packed anion framework with an 8-layer mixed stacking sequence along c given by ABCABACB, *i.e.* (ccchccch), and with cations ordered into 6 tetrahedral and 16 octahedral sites per unit cell. The structure may be described as a 1:1 intergrowth of a spinel-like structure with composition $2(\text{Fe},\text{Zn},\text{Mg})_2^{[4]}\text{Al}_4^{[6]}\text{O}_8$ and a nolanite-like structure with composition $2(\text{Mg},\text{Al},\text{Fe})^{[4]}(\text{Al},\text{Fe},\text{Ti})_4^{[6]}\text{O}_7(\text{OH})$.

Introduction

The minerals hōgbomite, nigerite, and taaffeite form a series of polytypes that have similar X-ray diffraction patterns and that have been considered to have closely related structures, based on various stacking sequences of closest-packed oxygen layers with interstitial cations on octahedral and tetrahedral sites (McKie, 1963). Their diffraction patterns have in common a spinel-like subcell grouping of strong reflections, as well as extra reflections that can be indexed using hexagonal (H) or rhombohedral (R) lattices, with hexagonal cell dimensions $a_h \approx 5.7\text{Å}$, $c_h \approx 2.3 \times n\text{Å}$. Using Peacor's (1967) nomenclature, the various polytypes are then designated as $n\text{H}$ or $n\text{R}$, where n is the number of closest-packed oxygen layers.

We recently reported the structure determination for a 24-layer rhombohedral nigerite polytype, nigerite-24R, from which the geometric principles relating the structures of various polytypes were established (Grey and Gatehouse, 1979). These principles were used to predict the structures of some simple polytypes such as nigerite-6H, hōgbomite-8H, and taaffeite-8H. We subsequently com-

pleted a structure refinement for hōgbomite-8H that confirmed the model predicted, and the results of that refinement are the subject of this paper.

Experimental

A sample of zincian hōgbomite from the Strangways Range, Central Australia (Wilson, 1977), was kindly supplied by Ian M. Threadgold. It was in the form of a hexagonal column, rounded at the edges, so that it closely approximated a cylinder 0.25 mm in diameter and 0.19 mm long. Precession photographs showed that it was predominantly an 8H polytype with a few weak reflections from a 10H polytype. The large crystal was broken, and a fragment measuring $0.17 \times 0.14 \times 0.13$ mm was found for which the precession photographs showed reflections only from an 8H polytype. The only systematic absence observed was $(hh2\bar{h}l)$, $l = 2n + 1$, consistent with space groups $P6_3mc$, $P\bar{6}2c$, or $P6_3/mmc$.

For the collection of intensity data, the crystal fragment was remounted on a Philips PW1100 4-circle automatic diffractometer in an arbitrary orientation. Lattice parameters were obtained from

the average of 25 orientation matrices automatically determined at various stages of the data collection, $a = 5.734(3)\text{Å}$, $c = 18.389(8)\text{Å}$. Intensities were collected with $\text{MoK}\alpha$ radiation (0.71069Å) monochromated by a flat graphite crystal ($2\theta_m = 12.0^\circ$), using an ω - 2θ scan technique and a 2θ scan rate of $0.04^\circ \text{sec}^{-1}$. Backgrounds were determined from stationary counts equal to half the scan time at both ends of each dispersion-corrected scan range ($\Delta\theta = 1.50 + 0.3 \tan \theta$). Three non-coplanar reflections measured every two hours showed no significant variation in either intensity or position. A total of 3293 non-systematically absent hkl and $h\bar{k}l$ reflections were collected to a maximum 2θ value of 90° , and the resultant data were corrected for background, Lorentz, and polarization effects with a program written specifically for the PW1100 diffractometer by Hornstra and Stubbe (1972). An absorption correction was applied ($\mu(\text{MoK}\alpha) = 45.6 \text{cm}^{-1}$). The maximum and minimum values of the transmission factors were 0.5869 and 0.4969 respectively. Multiply measured symmetry-equivalent reflections consistent with point group $6mm$ were then averaged to yield a set of 1734 unique structure amplitudes, F . The overall internal consistency factor between averaged intensities was 0.037, but only those 1425 observations with $F \geq 6\sigma(F)$ were included in the subsequent least-squares analysis.

Scattering factor curves for Al, Fe, Mg, Zn, Ti, and O neutral atoms are those of Cromer and Mann (1968). Anomalous dispersion corrections for all atoms are from Cromer and Liberman (1970). All computing was performed on the Monash University Burroughs 6700 and the CSIRO CDC-7600 computers, using the XRAY system of programs (Stewart, 1976) and the SHELX program (Sheldrick, 1976).

Before fragmentation, the original crystal of högbomite was mounted and polished for an electron-microprobe analysis, the results of which are given in Table 1. The derived unit-cell formula, normalized to 30 O + 2 OH, is $\text{Al}_{14.61}\text{Fe}_{2.84}^{2+}\text{Fe}_{1.44}^{3+}\text{Mg}_{1.40}\text{Ti}_{1.00}\text{Zn}_{0.60}\text{Ga}_{0.02}\text{Mn}_{0.03}\text{Na}_{0.06}\text{O}_{30}(\text{OH})_2$, where the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio has been adjusted to give 22 cations per unit cell, consistent with the results of the structure refinement.

Structure determination

The correct model for the structure of högbomite-8H was predicted with the aid of geometric principles established from the structure determination of nigerite-24R. The procedure is outlined below.

First, the stacking sequence of the closest-packed

Table 1. Högbomite-8H: electron-microprobe analyses,* wt. percent

Al	31.00
Fe	18.79
Ti	3.75
Mg	2.68
Zn	3.10
Mn	0.12
Ga	0.13
Na	0.11

*The derived unit-cell composition, normalized to 30 O + 2 OH and with the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio adjusted to give 22 cations per unit cell, is $\text{Al}_{14.61}\text{Fe}_{2.84}^{2+}\text{Fe}_{1.44}^{3+}\text{Mg}_{1.40}\text{Ti}_{1.00}\text{Zn}_{0.60}\text{Ga}_{0.02}\text{Mn}_{0.03}\text{Na}_{0.06}\text{O}_{30}(\text{OH})_2$.

anion layers was established from the c -axis periodicity (value of n), using the tables of Patterson and Kasper (1962). Although in general a relatively large number of stacking sequences is possible for a given n -value and symmetry, they can usually be reduced to only one or two possibilities by applying the restriction that cubic stacking predominate over hexagonal stacking for the högbomite, nigerite, and taaffeite polytypes. For nigerite-24R, for example, this criterion reduced the eight possible stacking sequences to two. In the case of högbomite-8H, only one of the five possible stacking sequences has predominant cubic stacking; it is designated $|(4)|(4)|$ by Patterson and Kasper (1962) and corresponds to the sequence of closest-packed layers . . . ABCA-BACB . . ., *i.e.* (ccchccch . . .), where (c) and (h) are the commonly used symbols for cubic and hexagonal stacking respectively. This is one of the three stacking sequences originally suggested by McKie (1963).

With the ordering of the oxygen layers established, the next step was to determine the ordering of the metal-atom layers between the oxygen layers. Three types of ordered arrangements occur, designated O, T1, and T2, where O and T2 are the all-octahedral and octahedral-tetrahedral cation (111) layers of the spinel structure and T1 is the octahedral-tetrahedral cation (001) layer of the nolite structure (see Fig. 1 in Grey and Gatehouse, 1979). Their sequence is dictated by the oxygen-layer stacking sequence, consistent with the following general principles: O layers must alternate with T1 or T2 layers. T1 layers must occur between cubic- and hexagonal-stacked oxygen layers, *i.e.* c-T1-h. T2 layers must lie between cubic-stacked oxygen layers, *i.e.* c-T2-c. The derived stacking

sequences for the oxygen and metal-atom layers in högbomite-8H are shown in Figure 1.

Structure refinement

With the origin and stacking sequences shown in Figure 1, with aluminum ordered in the octahedral sites of the O and T2 layers (as observed for nigerite-24R), and with a composite scattering curve for the other metal atoms ($M \equiv 0.55\text{Fe} + 0.17\text{Mg} + 0.13\text{Ti} + 0.08\text{Al} + 0.07\text{Zn}$, which is consistent with the amounts of these elements as determined by the electron-microprobe analysis), the refinement was initiated in space group $P6_3mc$. Refinement of all coordinates and isotropic temperature factors resulted in an R value of 0.06. The temperature factors for the M atoms were then assigned the average value of the refined isotropic temperature factors and held fixed while the population parameters for the M sites were refined. The population parameters were then held fixed while the isotropic temperature factors were refined. Finally, all coordinates and isotropic temperature factors, as well as the population parameters for the M sites, were refined together, resulting in convergence at $R = 0.034$ and $R_w = 0.033$. At this stage, conversion to anisotropic temperature factors was made, and the refinement of all U_{ij} values, coordinates, and population parameters for the M sites led to convergence at $R = 0.032$ and $R_w = 0.031$ for the 1425 observed reflections. For all 1734 reflections, $R = 0.042$ and $R_w = 0.036$. In addition, the absolute configuration was checked. With the signs of the coordinates reversed, the R and R_w values increased to 0.059 and 0.054 respectively.

The final atomic coordinates and equivalent isotropic temperature factors are given in Table 2. The anisotropic temperature factors are given in Table 3, and the observed and calculated structure factors are compared in Table 4.¹ The refined values of the population parameters for sites $M(2)$, $M(3)$, $M(6)$, and $M(7)$ in Table 2 were 1.008(3), 0.767(3), 1.037(3), and 0.951(3) respectively. Since the average atomic number of the composite site M was 22.4, the average atomic numbers at the four individual sites were 22.6, 17.2, 23.2, and 21.3 respectively.

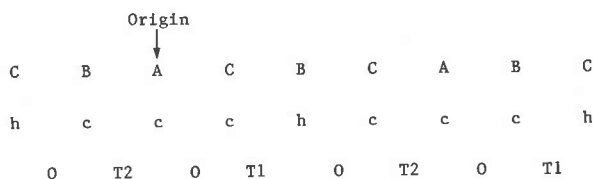


Fig. 1. Stacking sequences for the anion layer (top two lines) and the metal-atom layer (bottom line) in högbomite-8H.

Discussion of the structure

A polyhedral representation of the structure of högbomite-8H is shown in Figure 2. The O, T1, and T2 layers are marked, as are the various metal atoms. A (110) section of the structure is shown in Figure 3, in which all metal atoms and oxygens are labeled according to the site numbers listed in Table 2. This diagram clearly shows the alternating widths of pairs of closest-packed anion layers along [001]. Pairs of anion layers about the O layers are about half an ångström narrower than corresponding pairs about the T layers. The structure may be considered as a 1:1 intergrowth of a spinel-like structure, O-c-T2-c-O, and a nolanite-like structure (Hanson, 1958), O-c-T1-h-O.

Calculated bond lengths and angles for högbomite-8H are given in Table 5. The most striking observation is the large trigonal distortion of the octahedron in the T1 layer, *i.e.* $M(2)\text{-O}_6$. This octahedron shares three of its edges (O(4)-O(4)) with Al(1)-O₆ octahedra in the layer below, and

Table 2. Högbomite-8H: final atomic coordinates and site occupancies

Atom	x	y	z	B_{eq}^*
Al(1)	0.6719(2)	0.8360(1)	0.9427(1)	0.33(2)
$M(2)^\dagger$	0	0	0.7990	0.19(2)
$M(3)$	2/3	1/3	0.8529(1)	0.42(3)
Al(4)	0.0039(2)	0.5019(1)	0.6982(1)	0.19(2)
Al(5)	2/3	1/3	0.5686(1)	0.38(3)
$M(6)$	1/3	2/3	0.5383(1)	0.41(2)
$M(7)$	0	0	0.6059(1)	0.47(2)
O(1)	0	0	0.9974(2)	0.59(9)
O(2)	0.0398(3)	0.5199(2)	0.9994(1)	0.41(6)
O(3)	1/3	2/3	0.8876(2)	0.52(7)
O(4)	0.8462(2)	0.6924(4)	0.8839(1)	0.90(7)
O(5)	2/3	1/3	0.7509(2)	0.72(10)
O(6)	0.6622(4)	0.8311(2)	0.7510(1)	0.59(7)
O(7)	1/3	2/3	0.6452(2)	0.47(7)
O(8)	0.8126(2)	0.6251(4)	0.6342(1)	0.72(8)

$$*B_{eq} = 1/3(B_{11} + B_{22} + B_{33}).$$

[†]Composite scattering curve for $M \equiv 0.55 \text{ Fe} + 0.17 \text{ Mg} + 0.13 \text{ Ti} + 0.08 \text{ Al} + 0.07 \text{ Zn}$.

¹To obtain a copy of Table 4, order Document AM-82-194 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 3. Högbomite-8H: anisotropic temperature factors* ($10^4/\text{Å}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al(1)	37(2)	37(2)	52(2)	12(4)	5(2)	-5(2)
M(2)	23(1)	23(1)	27(2)	11(1)	0	0
M(3)	54(2)	54(2)	50(3)	27(1)	0	0
Al(4)	22(2)	22(2)	28(2)	6(3)	6(2)	-6(2)
Al(5)	49(3)	49(3)	47(5)	25(1)	0	0
M(6)	53(2)	53(2)	51(2)	26(1)	0	0
M(7)	55(2)	55(2)	72(3)	28(1)	0	0
O(1)	61(7)	61(7)	102(12)	30(4)	0	0
O(2)	44(6)	44(6)	70(5)	12(10)	-5(5)	5(5)
O(3)	83(7)	83(7)	32(8)	42(4)	0	0
O(4)	141(9)	141(9)	58(5)	126(13)	3(5)	-3(5)
O(5)	78(9)	78(9)	116(16)	39(4)	0	0
O(6)	76(7)	76(7)	71(5)	41(11)	-16(5)	16(5)
O(7)	59(7)	59(7)	60(9)	30(4)	0	0
O(8)	96(7)	96(7)	80(6)	61(12)	20(5)	-20(5)

*The temperature factors have the form

$$\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

shares corners with Al(4)-O₆ octahedra in the layer above. The bonds to the oxygens (O(4)) involved in edge-sharing are 0.27 Å longer than the bonds to the oxygens (O(6)) involved in corner-sharing. The angles between the long M(2)-O(4) bonds are reduced to 74.6(1)°, whereas the angles between the short M(2)-O(6) bonds have increased to 100.1(1)°. A similar, though smaller, trigonal distortion occurs in the octahedron in the T1 layer in both nolanite (Hanson, 1958) and nigerite-24R (Grey and Gatehouse, 1979).

The occupied tetrahedral site in the T1 layer is only slightly distorted, with an apical M(3)-O(5) bond identical to the three basal-plane M(3)-O(4) bonds and with values for the O-M(3)-O angles that deviate from the ideal tetrahedral angle by no more than 3°. A final difference Fourier map gave no indication of partial occupancy by metal atoms of the second tetrahedral site in the T1 layer.

The polyhedra associated with the spinel block have only small associated distortions. It is interesting to note that off-center displacements of the tetrahedrally coordinated cations M(6) and M(7) in the T2 layer result in an apical-to-basal M-O bond-length ratio that is less than 1 for M(6)-O₄ (0.994) but greater than 1 for M(7)-O₄ (1.032). At the same time, these tetrahedra are respectively elongated and flattened along *c*. As can be seen from Figures 2 and 3 and Table 2, both M(6)-O₄ and M(7)-O₄ have the same structural and chemical environments in relation to their first-nearest neighbors; the apical

oxygens corner-share to trigonal triads of edge-shared Al-O₆ octahedra, and the basal oxygens corner-share to hexagonal rings of edge-shared Al-O₆ octahedra. However, the second-nearest neighbors are quite different and have a controlling effect on the distortions of the M(6)-O₄ and M(7)-O₄ tetrahedra. Whereas the site opposite M(7) across the intervening trigonal triad Al(1) is occupied by octahedrally coordinated M(2), the corresponding site opposite M(6) is empty. M(2) edge-shares to the three Al-O₆ octahedra of trigonal triad Al(1), resulting in short O(4)-O(4) distances (2.64 Å). The corresponding O(6)-O(6) distances in the other trigonal triad Al(4) associated with M(6), where the site above is empty, are much longer (2.83 Å). Since the shared-edge lengths in both trigonal triads are simi-

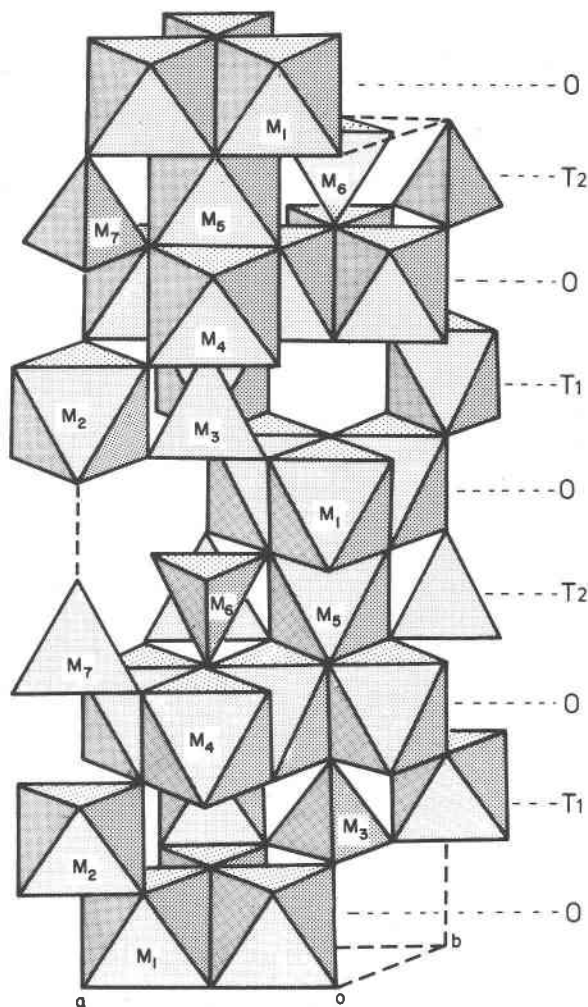


Fig. 2. Polyhedral representation of the structure of högbomite-8H.

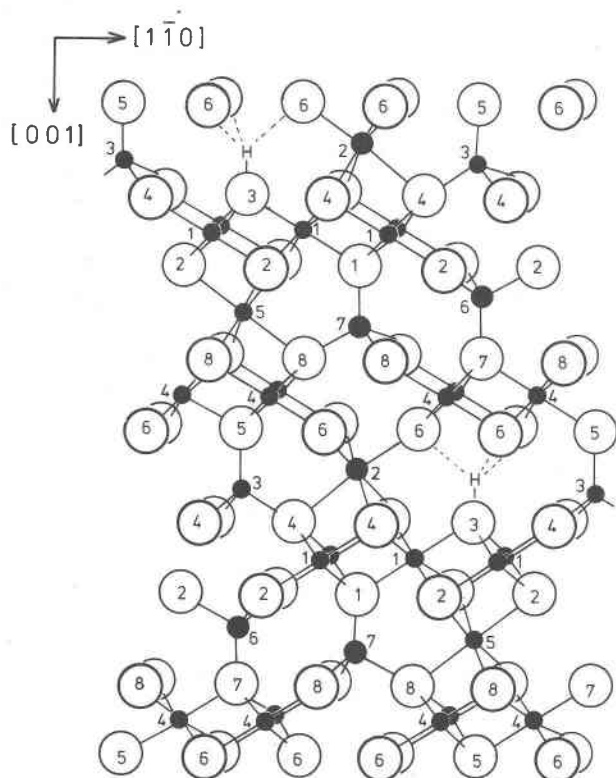


Fig. 3. Ball-and-spoke representation of a (110) section of the structure of högbomite-8H. The numbers beside the anions and cations correspond to the labels given in Table 2.

lar $O(4)-O(1) = 2.58\text{\AA}$ and $O(6)-O(7) = 2.54\text{\AA}$, this results in the empty tetrahedron enclosed by trigonal triad Al(1) having a longer apical-to-basal distance along c (2.08\AA) than that of the empty tetrahedron enclosed by trigonal triad Al(4) (1.95\AA). To compensate, the $M(7)-O_4$ tetrahedron flattens and the $M(6)-O_4$ tetrahedron elongates along c . The off-center displacements of $M(6)$ towards, and $M(7)$ away from, the apical oxygen is presumably in response to these tetrahedral deformations. As can be seen from Table 5, there is a related inverse correlation of the apical-to-basal bond-length ratio with the $O_{\text{basal}}-M-O_{\text{apical}}$ angle, *i.e.* the higher bond ratio is associated with the smaller $O_{\text{basal}}-M-O_{\text{apical}}$ angle. This kind of correlation is commonly observed for tetrahedra involving large cations, and it has been well documented by Griffen and Ribbe (1979).

Metal-atom ordering

In högbomite-8H, five different metal atoms are present in significant amounts: Ti, Fe (both di- and trivalent), Al, Mg, and Zn. The possibility that more

than two of these atoms can statistically occupy any of the individual M sites precludes a direct determination of the metal-atom ordering by a refinement of site occupancies. In the structure refinement, we used a composite scattering curve for these sites and refined the population parameters. This gives an approximate estimate of the relative number of electrons at each site but does not indicate how the different metal atoms are ordered at the sites. However, reasonable conclusions about the metal-atom ordering can be drawn from known associations in structurally related phases. The ordering of trivalent aluminum cations into octahedral sites Al(1), Al(4), and Al(5) of the O and T2 layers is consistent with that found in many related aluminate structures such as taaffeite (Peng and Wang, 1963), nigerite (Grey and Gatehouse, 1979), and the aluminate spinels gahnite ($ZnAl_2O_4$), hercynite ($FeAl_2O_4$), and spinel ($MgAl_2O_4$) (Hill *et al.*, 1979). This ordering also appears to be justified by the reasonable temperature factors obtained from the refinement (Table 2) and by the mean bond lengths (Table 5). Similarly, by analogy with the aluminate spinels, the tetrahedral sites in the T2 layers should be occupied predominantly by large divalent cations, *e.g.* Mg^{2+} , Fe^{2+} , and Zn^{2+} . The ordering of small cations in the octahedral sites and large cations in the tetrahedral sites of the spinel block in högbomite-8H can be explained qualitatively by simple crystal-chemical arguments based on Pauling's third rule (see, for example, Kamb, 1968). In the T2 layers, the octahedra edge-share to triangular clusters of octahedra in the O layers on both sides, whereas the tetrahedra corner-share to octahedra in both adjacent O layers, and the observed ordering can be understood by the stability it gives the structure by allowing shared edges to shorten.

The ordering of metal atoms in the octahedral and tetrahedral sites of the T1 layers is expected to be quite different from that in the T2 layers because of the different interlayer polyhedral articulations involved. When the T layers occur in a mixed anion-stacking sequence (O-c-T1-h-O), then the octahedra in the T1 layer edge-share to octahedra in only one of the adjacent O layers and corner-share to octahedra in the other O layer. This reduction in the degree of articulation allows larger cations to occupy the octahedral sites, *e.g.* Sn^{4+} in nigerite-24R (Grey and Gatehouse, 1979) and large divalent cations in nolanite-related structures such as $Zn_2Mo_3O_8$ (Ansell and Katz, 1966) and $Co_2Mn_3O_8$ (Riou and Lecerf, 1975).

A mixed anion-stacking sequence also results in quite different interlayer articulations of the two independent tetrahedral sites in the T1 layers, which in turn influences the cation ordering in these sites. One of the tetrahedra joins to octahedra in both of the adjacent O layers by corner-sharing only, as in the T2 layers, whereas the other tetrahedron shares its three basal edges with octahedra in one of the O layers, as in olivine. This part of the structure may be stabilized by shortening of the shared edges if a small cation occupies the second tetrahedral site. This is the case in taaffeite (Peng and Wang, 1963), in which the tetrahedron is occupied by Be^{2+} . In högbomite-8H, as in nigerite-24R, we propose that this site is occupied (at least partially) by hydrogen (see below). In nolanite-related structures, the second tetrahedral site is empty.

With the foregoing concepts in mind, we have considered various models for metal-atom ordering in högbomite-8H, subject to the restrictions imposed by the observed bond lengths (Table 5), the approximate number of electrons per site as determined from the population parameter refinement, the overall unit-cell composition, and the requirement of overall electrical neutrality. One possible model that gives a reasonable compromise fit under the above restrictions is given in Table 6. The model gives good agreement between cation valencies calculated from the observed $M\text{-O}$ bond lengths, using the empirical parameters of Brown and Wu (1976), and the sum of the weighted valencies of the various cations occupying each site. As is shown in Table 6, the unit-cell composition determined from the proposed model closely matches the composition determined from the chemical analysis.

The most unusual feature of the proposed model is the mixing of trivalent aluminum cations with divalent magnesium and iron cations in tetrahedral site $M(3)$. This mixing of large and small cations at the one site seems to be supported by the observed anisotropic temperature factors for the O(4) and O(5) anions forming the tetrahedron. As can be seen from Table 3, the apical O(5) anion has a large r.m.s. displacement along the c -axis and the basal O(4) anions have large r.m.s. displacements in the basal plane, which reflects "breathing" of the tetrahedron to accommodate cations of disparate sizes.

Also given in Table 6 are the calculated valence sums at the anion sites, which are generally close to the value of 2.00 expected for oxygen. Notable exceptions are O(3), which is severely undersatu-

Table 6. Högbomite-8H: electrostatic valence sums

Atom	Site occupancy*	Σs_i (from bond lengths)	Σs_i (from weighted valencies)
Al(1)	Al	2.92	3.00
M(2)	0.5 Ti + 0.35 Fe ³⁺ + 0.15 Fe ²⁺	3.24	3.35
M(3)	0.35 Al + 0.25 Fe ²⁺ + 0.15 Fe ³⁺ + 0.25 Mg	2.41	2.50
Al(4)	0.93 Al + 0.07 Fe	2.94	3.00
Al(5)	Al	3.03	3.00
M(6)	0.6 Fe ²⁺ + 0.2 Mg + 0.15 Zn + 0.05 Al	2.01	2.05
M(7)	0.5 Fe ²⁺ + 0.25 Mg + 0.15 Zn + 0.1 Al	2.09	2.10
O(1)	O	1.93	2.00
O(2)	O	1.97	2.00
O(3)	OH	1.32	1.00
O(4)	O	1.94	2.00
O(5)	O	2.04	2.00
O(6)	O	1.77	2.00
O(7)	O	2.07	2.00
O(8)	O	1.97	2.00

*The calculated unit-cell composition is $\text{Al}_{14.6}\text{Fe}_{4.4}\text{Mg}_{1.4}\text{Ti}_{1.0}\text{Zn}_{0.6}\text{O}_{30}(\text{OH})_2$, as compared with $\text{Al}_{14.61}(\text{Fe},\text{Mn})_{4.31}\text{Mg}_{1.40}\text{Ti}_{1.00}\text{Zn}_{0.60}(\text{Ca},\text{Na})_{0.08}\text{O}_{30}(\text{OH})_2$ from chemical analyses.

rated ($\Sigma s_i = 1.32$), and O(6), which is also considerably undersaturated ($\Sigma s_i = 1.77$). These anions, O(3) + 3 O(6), form the unoccupied tetrahedron in the T1 layer, and a possible explanation for the observed Σs_i values is that this site is partially occupied; *cf.* taaffeite-8H, which has the same oxygen- and cation-layer stacking sequences as högbomite-8H, but which has the second tetrahedral site in the T1 layer fully occupied by the small cation Be^{2+} (Peng and Wang, 1963). In högbomite-8H, the unoccupied site is large enough to accommodate an ion such as Al^{3+} . However, to explain the observed deficiency in Σs_i , a site occupancy of nearly 0.7 is required.

Examination of the final difference Fourier map failed to reveal any significant residual peak that would correspond to partial occupation of the tetrahedral site by a metal ion. An alternative explanation for the valence sum deficiency at O(3) and O(6) is that O(3) is occupied by a hydroxyl group, in which hydrogen bonding of the type O(3)-H . . . O(6) occurs. However, the presence of hydrogen in a structurally reasonable position in the tetrahedral cavity could not be confirmed from the difference Fourier map. The only peak observed, $0.7 \text{ e.}\text{\AA}^{-3}$, was located at (1/3, 2/3, 0.182), which is 1.27\AA from O(3) and 2.05\AA from O(6). This is far too long for an unsymmetrical hydrogen bond and may have resulted from an accumulation of errors. In the absence of a direct confirmation of hydrogen

from the difference Fourier map, we believe that the observed low Σ_s values support the premise that O(3) is occupied by a hydroxyl ion, and we have accordingly normalized the unit-cell composition to 30 O + 2 OH.

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