The crystal structure of nigerite-24R

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Abstract

A 24R nigerite polytype was discovered in tin-bearing skarns at Mt. Garnet in northern Queensland. Its space group is $R\bar{3}m$, with rhombohedral lattice parameters $a_{rh} = 18.826(10)$A, $\alpha_{rh} = 17.508(3)°$. The corresponding hexagonal lattice parameters are $a_{hex} = 5.730(3)$, $c_{hex} = 55.60(3)$A. Its formula, determined from microprobe analysis (combined with information from the structure determination) is $Al_{14.69}Sn_{2.01}Fe_{2.76}Zn_{1.42}Ca_{0.28}Mn_{0.06}Si_{0.21}O_{30}(OH)_2$. The correct structural model was obtained using crystallochemical reasoning based on structural principles established from an analysis of the related structures of spinel, nolanite, and others. The structure was refined to an R value of 0.044 for 448 symmetry-independent reflections with $F^2 \geq 3\sigma[F^2]$, collected using MoKα radiation. The model is based on a close packed anion framework (oxygens and hydroxyls) with a 24-layer mixed stacking sequence along c_{hex} given by ACBABCABCBACABCABACBCABC...(cchcccch...) and with an alternation of three types of metal atom layers in the sequence (...$OT_1OT_1OT_2OT_2$...), where O and T_2 represent the all-octahedral and the mixed octahedral–tetrahedral (111) metal atom layers found in spinel (with composition M_3O_4), and T_1 represents the mixed octahedral–tetrahedral metal atom layer found in nolanite, $Zn_2Mo_3O_8$, $Co_2Mn_3O_8$, etc. (with composition M_2O_4, and one less tetrahedral metal per unit-cell layer than the T_2 type). The interlayer articulation of the various polyhedra is controlled by the oxygen stacking sequence and is such that tetrahedra share only corners with octahedra, and octahedra share edges and corners. The ...OT_2OT_2... part of the structure represents a 4-layer spinel block, with ordering of Al into the octahedral sites and divalent Fe and Zn into the tetrahedral sites. The Sn atoms are fully ordered into the octahedral sites in the T_1 layers, whereas the tetrahedral sites in these layers contain predominantly Al.

The structural principles which were used to derive the nigerite-24R structure have been applied to predict the structures of related minerals such as nigerite-6H, högbomite-8H, and the taafeite polytypes.

Introduction

Nigerite, a tin-bearing oxide mineral, was discovered by Jacobson and Webb (1947) in 1944 during an investigation of the tin-bearing pegmatites of Kabba Province, central Nigeria. A subsequent study of the physical and chemical properties of the mineral by Bannister *et al.* (1947) showed that the mineral had symmetry $\bar{3}m$, with $a = 5.72$, $c = 13.86$A. The ideal unit-cell composition was given by the formula $(Zn,Mg,Fe^{2+})(Sn,Zn)_2(Al,Fe^{3+})_{12}O_{22}(OH)_2$. The mineral was often found as overgrowths on (111) planes

of gahnite, and Bannister *et al.* noted the structural correspondence in (111) close-packed oxygen layers in gahnite being parallel to equivalent (0001) layers in nigerite. A close structural relationship between nigerite, högbomite, and taafeite polytypes has been suggested by McKie (1963). The minerals all have trigonal or hexagonal symmetry, with similar a values and values of c that are multiples of about 2.3A, the separation between closest-packed oxygen layers. According to McKie's nomenclature, in which a double oxygen layer is taken as a repeat layer, nigerite is designated as a 3H polytype (H for hexagonal

symmetry, $c \simeq 3 \times 4.6A$). A new nigerite polytype, with trigonal symmetry and $c = 56.2A$, was identified by Peacor (1967). In McKie's nomenclature this is a 12R polytype, but Peacor suggested that a more realistic nomenclature system should be based on a single oxygen layer repeat to account for odd-layer number repeats, *e.g.* davidite (Rouse and Peacor, 1968). Using this system the two nigerite polytypes are 6H and 24R respectively. In the present paper we adhere to Peacor's suggested nomenclature system.

In a recent mineralogical examination of polished sections from a tin-bearing magnetite–fluorite–biotite deposit from Mt. Garnet in northern Queensland, we confirmed the presence of a tin-rich aluminum oxide, which had been observed in earlier studies on the deposit (H.W. Fander, private communication, 1976). Single crystals of the phase were excavated from the polished sections and studied by precession and Weissenberg X-ray diffraction methods. These studies, coupled with microprobe analyses, served to characterize the mineral as a 24R nigerite polytype, analogous to the mineral described by Peacor (1967). We report here the single-crystal structure determination for nigerite-24R, and use the results to predict the structures of some polytypes in the related series—nigerite, högbomite, taafeite.

Experimental

Drill-core sections containing nigerite were kindly supplied by Mr. L. A. Newnham, chief geologist at Renison Limited in Tasmania. The samples were from a drilling program carried out by Comalco Ltd. at their Mt. Garnet tin deposits in northern Queensland. In polished section the nigerite appeared as small rods and plates, generally 5–50μm wide and up to ~100 μm long, in a matrix comprising colloform-banded magnetite with fluorite and biotite. Associated minerals included gahnite, corundum, and cassiterite. The elongated lath-like nigerite crystals were often intergrown at an angle of about 120°. Examination of the crystals in a scanning electron microscope fitted with an energy-dispersive analyzer showed dominant Al, Sn, together with minor Fe, Zn, and trace amounts of Ca, Mn.

Crystals excavated from the polished section appeared colorless under the binocular microscope and a very pale green in transmitted light. An elongated tabular crystal measuring $77 \times 35 \times 20$ μm was selected for the X-ray diffraction study. Initially, precession and Weissenberg photographs were used to confirm that it was a single crystal, with trigonal sym-

metry, $R3m$, $R32$, or $R\bar{3}m$, and approximate cell dimensions $a = 5.73$, $c = 55.6A$.

For the intensity data collection the crystal was remounted along its long dimension on a Philips PW1100 4-circle automatic diffractometer. Thirteen reflections with $14° < 2\theta < 29°$ were carefully centered and the 2θ values used in a least-squares refinement to calculate the lattice parameters as reported in Table 1. Intensities were collected with graphite-monochromated Mo$K\alpha$ radiation. A θ–2θ scan, 3–30°, was used with a variable scan width given by $\Delta\theta = (0.9 + 0.3 \tan \theta)$ and a speed of 0.03° sec^{-1}. Two background measurements, each for half the scan time, were made for each scan, one at the lower and one at the upper limit. The intensities were processed using a program written for the PW 1100 diffractometer by Hornstra and Stubbe (1972). An absorption correction was not applied. However, a partial compensation was achieved by averaging the intensities of equivalent reflections, ±(*hkl, lhk, klh*), in the rhombohedral cell. (Interscale R factor for equivalent reflections = 0.054.) Thus, the 2834 reflections measured were reduced to a unique set of 656, of which 477 had $F^2 \geq 3\sigma [F^2]$ and were used in the structure refinement.

Scattering factor curves for Sn, Fe, Al, Ca, Zn, and Mn 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 CDC 3200 and Burroughs 6700 and the CSIRO CDC 7600 computers.

Two nigerite grains in close proximity to the one excavated for XRD studies were subjected to microprobe analyses. The results (given in Table 2) show variations of up to 10 percent in individual element analyses; the two data sets were averaged to obtain a typical analysis applicable to the XRD crystal. The derived unit-cell composition, normalized to 32 anions, is given in Table 2.

A structural model for nigerite and related mineral polytype—general considerations

The diffraction patterns for nigerite and related mineral polytypes are dominated by strong spinel-like subcell reflections. In the case of the nigerite-24R described here, the strongest reflections define a 6R type sublattice with $a = 5.73$, $c = 13.90A$. For comparison the unit cell for the spinel gahnite, when referred to hexagonal axes, is also 6R in type and has $a = 5.73$, $c = 14.04A$. As a consequence the three-dimensional Patterson map for nigerite showed only

Table 1. Nigerite-24R: unit-cell parameters

a_{rh} = 18.826(10) Å	a_{hex} = 5.730(3) Å
α_{rh} = 17.508(3)°	c_{hex} = 55.60(3) Å
Z_{rh} = 1	Z_{hex} = 3
Space group $R\bar{3}m$	
D_{calc} = 4.42 g cm^{-3}	
μ = 70.4 cm^{-1}	

spinel-type subcell vectors, and was thus not very useful in helping to establish a structural model. However, the similarities in the diffraction data and unit-cell parameters for nigerite, högbomite, and taafeite polytypes suggested that a simple structural principle, such as intergrowth of two basic structure types, should relate the structures of the various polytypes. An attempt was thus made to solve the structure of nigerite-24R by using crystallochemical reasoning to establish the underlying general structural principle for the polytypes. In this approach we were aided by the available structural information for nigerite and related minerals, as well as published data for related compounds with known structures.

Initially, a survey was made of compounds with known structures, containing close-packed oxygen frameworks, which could be described by hexagonal/trigonal unit cells with $a \simeq 5.7$, $c \simeq$ n × 2.3A. [Compounds with large cations occupying anion sites, such as various ferrites, e.g. $BaFe_{12}O_{19}$ (Townes et al., 1967), were not considered because the nigerite–högbomite–taafeite polytypes do not contain such ions.] In addition to spinel, with cubic stacking of close-packed oxygen layers, (c...), n = 6, there are a number of compounds with double-hexagonal stacking, i.e. (ch...), n = 4, and also series of compounds with simple hexagonal stacking of the oxygen layers, (h...), n = 2. The former are typified by the mineral nolanite, an iron vanadate, $(Fe,V)_5O_8$ (Hanson, 1958), and also by compounds $A_2Mo_3O_8$, A = Zn, Mg, Mn...(McCarroll et al., 1957), and the simple hexagonal structures are represented by the series $LiRMo_3O_8$, R = Sc, Y, In, Sm...(McCarroll, 1977). The three types of structures, designated (c...), (ch...), and (h...) according to the oxygen layer stacking, (ABC...), (ABAC...) (AB...) respectively, have some important features in common. For instance, the layer of octahedrally coordinated metal atoms as shown in Figure 1(i) occurs in all three structures and

alternates with layers containing both octahedrally and tetrahedrally coordinated metal atoms [Figs. 1(ii) and 1(iii)]. To simplify the discussion we have designated these layers as O (for octahedral cations only), T_2 (two tetrahedral cations per layer in the unit cell), and T_1 (one tetrahedral cation) respectively [Fig. 1, (i)–(iii)]. For spinel, O and T_2 layers alternate, whereas in both the (ch...) and (h...) structures O and T_1 metal atom layers alternate along [0001]. The interlayer articulation of polyhedra (i.e. between metals in the O and T layers) depends on the oxygen stacking sequence. Octahedron–octahedron articulation occurs by edge-sharing only in (c...), by corner-sharing only in (h...), and by both corner- and edge-sharing in (ch...). These are shown in Figure 2. Tetrahedron–octahedron articulation occurs only by corner-sharing in both the (c...) and (ch...) structures, and by corner- and edge-sharing (as in olivine) in the (h...) structures (see Fig. 3). Note that this latter type of tetrahedron–octahedron articulation is avoided in the (ch...) structures by having only one of the two available tetrahedral sites in the T_1 layers occupied.

The unit-cell compositions of the O, T_2, and T_1 layers (including surrounding oxygens) are M_3O_4, M_3O_4, and M_2O_4 respectively, and so the overall compositions of the (c...), (ch...), and (h...) type compounds (normalized to 8 oxygens for comparison) are M_6O_8, M_6O_8, and M_5O_8 respectively. It follows that long-periodicity structures with mixed stacking sequences, e.g. cchcchh..., will have compositions intermediate to M_5O_8 and M_6O_8. This in fact is true for all the known polytypes of nigerite, högbomite, and taafeite, range $M_{5.297}O_8$ to M_6O_8 (McKie, 1963; Hudson et al., 1967; Wilson, 1977). We were able to es-

Table 2. Nigerite-24R: electron microprobe analyses

	Weight percent		Atoms*	
	1	2**	1	2
Al	27.78	27.93	14.66	14.73
Sn	17.62	15.89	2.11	1.91
Fe	10.50	11.12	2.68	2.83
Zn	6.23	6.81	1.36	1.48
Ca	0.81	0.75	0.29	0.27
Mn	0.26	0.25	0.07	0.06
Si	0.40	0.43	0.20	0.22

* Number of atoms per unit cell, normalized to 30 O + 2 OH, and with all iron as ferrous. The averaged unit cell composition from 1 and 2 is $Al_{14.69}Sn_{2.01}Fe_{2.76}Zn_{1.42}Ca_{0.28}Mn_{0.06}Si_{0.21}O_{30}(OH)_2$.

** 1 and 2 are point analyses for two different grains.
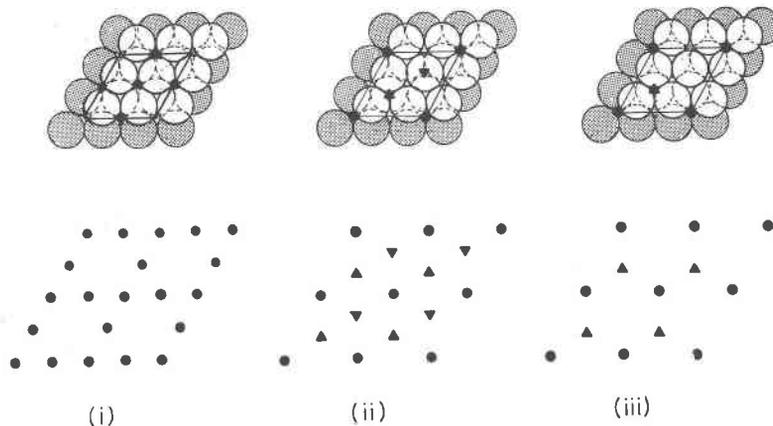
Fig. 1. Metal atom arrangements between close-packed oxygen layers for (i) the O layer in spinel and nolanite, (ii) the T_2 layer in spinel, and (iii) the T_1 layer in nolanite. The small solid circles and triangles represent octahedrally and tetrahedrally coordinated metals, respectively. Oxygen layers and unit-cell outlines are shown in the upper parts of the figure; the lower half shows the extended metal atom arrangements.

tablish the correct structural model for nigerite-24R, and predict models for other polytypes, on the basis that they were built up from a stacking of O, T_2, and T_1 layers, the sequence being determined by the oxygen-layer stacking scheme. This is outlined below.

Model for nigerite-24R

Using the realistic assumption that the c-axis periodicity (n = 24) is determined by the oxygen stacking sequence (rather than by subtle changes in metal atom ordering), the possible layer sequences may be obtained from Patterson and Kasper's Table in *International Tables for X-ray Crystallography*, Vol. II (1962), p. 342–355. Nigerite-24R has an even period, N = 8, and a primitive rhombohedral lattice, and the appropriate table shows that eight different stacking sequences are possible. These were reduced to two probable sequences using the criterion that cubic stacking should predominate, as suggested by the strong spinel-like subcell. These two possibilities are designated (6)(2) and (5)(3) by Patterson and Kasper and comprise stacking sequences (ccccchch...) and (ccchcch...). The observation of an even number of layers for nigerite-24R (as indeed is the case for all the reported polytypes of nigerite, högbomite, and taafeite) required that O and T metal atom layers alternate. A further restriction suggested by the survey of known related structures given above was that T_2 layers lay between pairs of cubic stacked oxygen layers, *i.e.* c–T_2–c, and T_1 layers lay between cubic- and
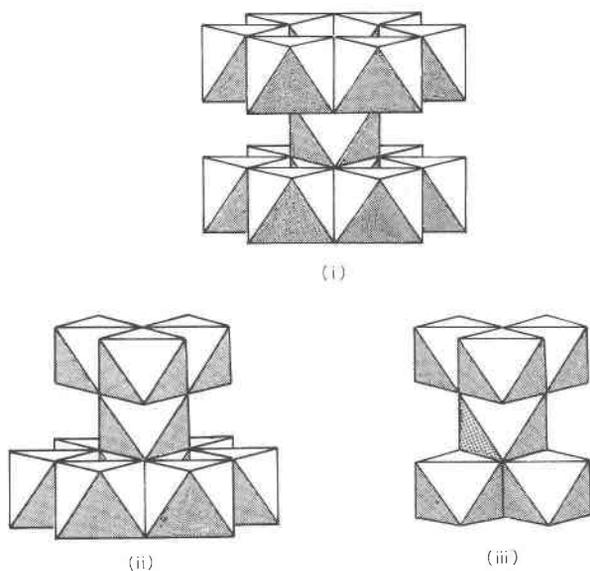
Fig. 2. Polyhedral representations of interlayer articulation of octahedra in (i) $LiRMo_3O_8$, (ii) nolanite, and (iii) spinel-type structures.
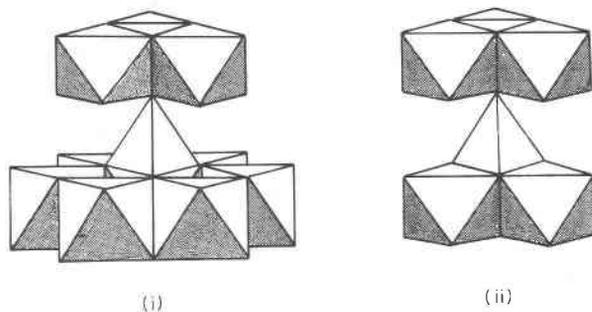
Fig. 3. Polyhedral representations of interlayer articulation of tetrahedra and octahedra in (i) $LiRMo_3O_8$ and (ii) spinel and nolanite type structures.

Table 3. Nigerite-24R: final atomic coordinates and isotropic temperature factors

Atom site		Occupancy	x	y	z	B $(\overset{O}{A}^2)$
M(1)	OCT.	2.1 Al + 0.9 □*	0.50000	0.00000	0.50000	0.24(10)
M(2)	OCT.	2 Sn	0.28684(2)	0.28684(2)	0.28684(2)	0.31(2)
M(3)	TET.	1.2 Al + 0.8 Fe	0.03070(6)	0.03070(6)	0.03070(6)	0.52(6)
M(4)	OCT.	6 Al	0.75013(7)	0.75013(7)	0.25328(14)	0.35(5)
M(5)	OCT.	2 Al	0.12488(8)	0.12488(8)	0.12488(8)	0.22(9)
M(6)	TET.	Fe + 0.8 Zn + 0.2 Al	0.53153(4)	0.53153(4)	0.53153(4)	0.39(4)
M(7)	TET.	Fe + 0.6 Zn + 0.4 Al	0.22047(5)	0.22047(5)	0.22047(5)	0.66(5)
M(8)	OCT.	3 Al	0.00000	0.00000	0.50000	0.33(8)
O(1)		6 O	0.1558(2)	0.1558(2)	0.6257(3)	0.94(15)
O(2)		2 OH	0.3504(2)	0.3504(2)	0.3504(2)	0.91(25)
O(3)		6 O	0.4420(2)	0.4420(2)	0.9213(3)	0.98(15)
O(4)		2 O	0.0644(2)	0.0644(2)	0.0644(2)	0.88(25)
O(5)		6 O	0.0439(2)	0.0439(2)	0.6026(3)	0.82(13)
O(6)		2 O	0.5666(2)	0.5666(2)	0.5666(2)	0.26(22)
O(7)		6 O	0.7056(2)	0.7056(2)	0.1467(3)	0.97(14)
O(8)		2 O	0.1844(2)	0.1844(2)	0.1844(2)	0.72(24)

* = vacancy

Table 4. Nigerite-24R: selected interatomic distances (A) and angles (degrees)

M(1) (Al) Octahedron

M(1)-O(1)	1.982*(x4)	O(1)-M(1)-O(2)	84.73 (x4)
M(1)-O(2)	1.908 (x2)	O(1)-M(1)-O(1)'	85.56 (x2)
Mean	1.957	O(1)-M(1)-O(1)''	94.44 (x2)
		O(1)'-M(1)-O(2)	95.27 (x4)
O(1)-O(2)	2.622 (x4)		
O(1)-O(1)'	2.693 (x2)		
O(1)-O(1)''	2.910 (x2)		
O(1)'-O(2)	2.875 (x4)		

M(2) (Sn) Octahedron

M(2)-O(1)	2.108 (x3)	O(1)-M(2)-O(1)'	79.38 (x3)
M(2)-O(3)	2.003 (x3)	O(1)-M(2)-O(3)	91.59 (x6)
Mean	2.056	O(3)-M(2)-O(3)'	96.26 (x3)
O(1)-O(1)'	2.692 (x3)		
O(1)-O(3)	2.948 (x6)		
O(3)-O(3)'	2.984 (x3)		

M(3) (Al,Fe) Tetrahedron

M(3)-O(1)	1.837 (x3)	O(1)-M(3)-O(1)'	111.57 (x3)
M(3)-O(4)	1.873	O(1)-M(3)-O(4)	107.28 (x3)
Mean	1.846		
O(1)-O(4)	2.987 (x3)		
O(1)-O(1)'	3.037 (x3)		

M(4) (Al) Octahedron

M(4)-O(3)	1.879 (x2)	O(5)-M(4)-O(5)'	80.37
M(4)-O(6)	1.923	O(3)-M(4)-O(6)	82.97 (x2)
M(4)-O(4)	1.936	O(4)-M(4)-O(5)	83.95 (x2)
M(4)-O(5)	1.960 (x2)	O(3)-M(4)-O(5)	92.82 (x2)
Mean	1.923	O(3)-M(4)-O(3)'	93.92
		O(5)-M(4)-O(6)	95.63 (x2)
O(5)-O(5)'	2.529	O(3)-M(4)-O(4)	97.40 (x2)
O(3)-O(6)	2.519 (x2)		
O(4)-O(5)	2.605 (x2)		
O(3)-O(5)	2.781 (x2)		
O(3)-O(3)'	2.747		
O(5)-O(6)	2.877 (x2)		
O(3)-O(4)	2.866 (x2)		

M(5) (Al) Octahedron

M(5)-O(5)	1.894 (x3)	O(7)-M(5)-O(7)'	82.22 (x3)
M(5)-O(7)	1.922 (x3)	O(5)-M(5)-O(5)'	83.79 (x3)
Mean	1.908	O(5)-M(5)-O(7)	96.99 (x6)
O(7)-O(7)'	2.527 (x3)		
O(5)-O(5)'	2.529 (x3)		
O(5)-O(7)	2.858 (x6)		

M(6) (Fe,Zn) Tetrahedron

M(6)-O(6)	1.949	O(7)-M(6)-O(7)'	108.73 (x3)
M(6)-O(7)	1.970 (x3)	O(6)-M(6)-O(7)	110.21 (x3)
Mean	1.965		
O(7)-O(7)'	3.203 (x3)		
O(6)-O(7)	3.215 (x3)		

M(7) (Fe,Zn) Tetrahedron

M(7)-O(5)	1.925 (x3)	O(5)-M(7)-O(8)	106.22 (x3)
M(7)-O(8)	2.005	O(5)-M(7)-O(5)'	112.52 (x3)
Mean	1.945		
O(5)-O(8)	3.144 (x3)		
O(5)-O(5)'	3.201 (x3)		

M(8) (Al) Octahedron

M(8)-O(7)	1.898 (x4)	O(7)-M(8)-O(8)	82.58 (x4)
M(8)-O(8)	1.926 (x2)	O(7)-M(8)-O(7)	83.50 (x2)
Mean	1.907	O(7)-M(8)-O(7)''	96.50 (x2)
		O(7)'-M(8)-O(8)	97.42 (x4)
O(7)-O(8)	2.523 (x4)		
O(7)-O(7)'	2.527 (x2)		
O(7)-O(7)''	2.832 (x2)		
O(7)'-O(8)	2.873 (x4)		

* Standard deviations for M-M, M-O, and O-O are 0.003, 0.005, and 0.008 $\overset{O}{A}$, respectively, and for angle O-M-O 0.16 degrees.

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   Origin
          ↓
A    C    B    A    B    C    A    B    C    B    A    C

h    c    c    h    c    c    c    c    h    c    c    h

T₁   O    T₁   O    T₂   O    T₂   O    T₁   O    T₁
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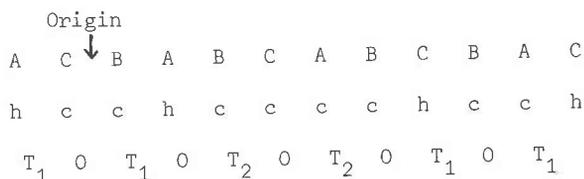
Fig. 4. Anion layer sequence (first two lines) and metal atom layer sequence (third line) for nigerite-24R.

hexagonal-stacked oxygen layers, *i.e.* c–T_1–h. It was also possible to make some reasonable assumptions concerning the metal atom distributions in the trial models. Firstly, by analogy with gahnite, it was expected that the spinel-like slabs would contain aluminum in octahedral sites and large divalent ions, Zn^{2+} and Fe^{2+}, in the tetrahedral sites. Secondly, Sn^{4+} has a marked preference for octahedral coordination in spinel (Djega-Mariadassou *et al.,* 1973). It is not expected to order with the much smaller Al^{3+} in the O layers and was thus assigned to T_1 layers.

Subject to the restrictions outlined above, only a small number of models remained to be tested. Structure factor calculations for these possible models indicated a centrosymmetric model ($R\bar{3}m$), with the (5)(3) oxygen stacking sequence as correct.

Refinement of the structure

The origin location was established in the space group $R\bar{3}m$ by assigning O-layer metals (aluminums) to the special positions 3(e) and 3(d), *i.e.* 0 ½ ½ and ½ 0 0 (rhombohedral axes). Initially, with Al atoms assigned to the O-layers and an average structure factor curve for M atoms in the T layers, full refinement of coordinates of all atoms proceeded smoothly to an *R* of about 0.15. At this stage, a difference Fourier and temperature factor refinement allowed a specific assignment of Sn, Fe, *etc.* to the different metal atom sites in the T layers. With a new set of scattering curves, refinement of all coordinates and isotropic temperature factors proceeded to an *R* value of 0.065. The refined temperature factors showed a wide range of values, from −0.40(20) to 1.57(33), and a difference Fourier displayed a number of peaks of density greater than 2e A^{-2}, in unrealistic positions (*e.g.* within ~2A from metal atoms). Examination of the structure factor table showed that 30 of the weakest reflections ($3\sigma[F^2] < F^2 < 4\sigma[F^2]$) had F_o values systematically higher than F_c by a factor of 2 or more. These reflections were given zero weight in the subsequent refinement. Further cycles of full matrix refinement of positional and isotropic thermal parame-

ters led to convergence at $R = 0.044$, $wR = 0.033$, and $R(F^2) = 0.058$, for 448 observed reflections. The refined atomic coordinates (in the rhombohedral cell) and thermal parameters are listed in Table 3. The thermal parameters for oxygens are now within the narrow range expected for a close-packed oxide [except for O(6), which had a B value of −0.40(20) before removal of the 30 affected reflections]. A final difference Fourier showed no features above 0.5eA^{-2}.

Calculated bond lengths are given in Table 4 and observed and calculated structure factors are listed in Table 5.[1]

Description of the structure

The structure of nigerite is based on a close-packed oxygen framework with a 24-layer repeat along the hexagonal *c* axis (8-layer true repeat in the primitive rhombohedral cell). The layer sequence is shown in Figure 4, together with the stacking representation for each oxygen layer (c or h) and the metal atom layer sequence. The oxygen sequence is (cchccch...) and the metal atom layer sequence is ($OT_1OT_1OT_2OT_2...$). The... $OT_2OT_2...$ sequence represents a four-layer slab of spinel structure. The ...OT_1OT_1... metal layer sequence is the same as that for the double-hexagonal-close-packed nolanite structure, and the O–T_1–O interlayer polyhedral articulations are the same [see Figs. 2(ii) and 3(i)]. However, the oxygen layer sequence is different, *viz.* hcch for nigerite and hchc for nolanite, and this results in different T_1–O–T_1 interlayer polyhedral linkages, as shown in Figure 5, which gives a polyhedral representation corresponding to the asymmetric unit in the triply-primitive hexagonal cell. The O, T_1, and T_2 layers are marked, as well as the various metal atoms. For convenience in interpreting Figure 5, the atomic coordinates have been converted to those pertaining to the hexagonal cell and are given in Table 6. To show the magnitude of the various deviations from an ideal close-packed model, the *z* parameters are also given in angstroms. It is apparent that there are considerable distortions both in the planarity of the oxygen layers, and in the close packing of the oxygens within the layers. For example, the ideally coplanar O(1) and O(2) atoms differ by more than 0.2A in their *z* parameter, and the *y* parameters of 0(5) and 0(7) also differ by more than 0.2A from the
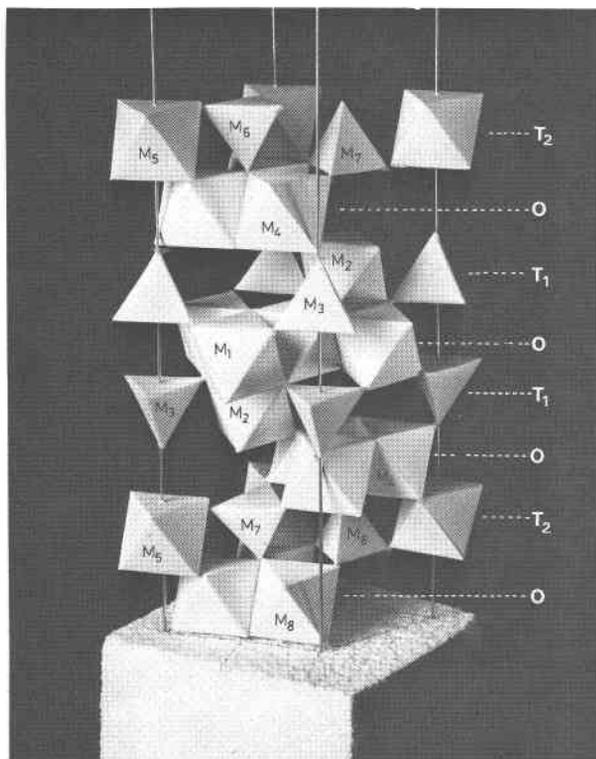
Fig. 5. Polyhedral model of nigerite-24R in a hexagonal cell representation.

ideal values ($y = 5/6$ and $2/3$ respectively). The octahedral metal M(2) (tin) in the T_1 layer shows a displacement of 0.27A, whereas the metals in the O layers are almost exactly midway between the sandwiching oxygen layers.

Metal atom ordering

Metal atom ordering in a number of sites is quite unambiguous. In particular the octahedral site in the T_1 layers is fully occupied by tetravalent tin. The average Sn^{2+}–O bond length of 2.056(5)A agrees with a calculated value of 2.06A, using Shannon and Prewitt's (1969) ionic radii tables. (The oxygen radius appropriate to the average coordination number 3.5 was used.) The ordering of Al into the octahedral sites in the spinel block is also clearly established from the structure refinement. The observed $\overline{Al–O}$ bond lengths of 1.908(5) [M(5) in T_2 layer] and 1.907(5) [M(8) in O layer] and 1.923(5) [M(4) in O layer] lie within the range 1.885–1.924 observed for Al atoms in the octahedral sites in the spinel blocks of various β-aluminas (e.g. Dernier and Remeika, 1976; Kodama and Muto, 1976). In fact the spinel block in nigerite resembles quite closely gahnite, $ZnAl_2O_4$ (Saalfeld, 1964), on which nigerite is often

found as an overgrowth. Complete correspondence requires divalent ions Fe^{2+}, Zn^{2+} in the tetrahedral sites, whereas the observed average bond lengths (Table 3) suggest some trivalent Al in these sites. Note the opposite senses of the ratios of the apical to basal M–O bond lengths for the two tetrahedral sites, M(6) and M(7), in the spinel block.

A difficulty was encountered in determining the occupancy of the octahedral site M(1) in the O layer. With Al assigned to this site, a reasonable temperature factor was obtained only when the occupancy was reduced to 0.70 (Table 3). The average M(1)–O bond length, 1.957(5)A, is somewhat higher than expected for Al, reflecting a lower average polyhedral bond strength due to the partial occupancy. Allowance for iron in this site would decrease the partial occupancy parameter still further.

Whereas in the T_2 layers small ions (Al^{3+}) occupy the octahedral site and large ions (Fe^{2+},Zn^{2+}) occupy the tetrahedral sites, the reverse is true in the T_1 layers, with large octahedral Sn^{4+} and small tetrahedral Al^{3+}. As a consequence of adjusting to the various-sized polyhedra, the M(4)O$_6$ octahedra in the intervening O layer are considerably distorted, with M(4)–O bond lengths in the range 1.879(5)– 1.960(5)A. By comparison, the M(8)O$_6$ octahedra in the O layers in the spinel block are more regular, with a M(8)–O range of 1.898(5)–1.926(5)A.

Table 6. Nigerite-24R: atomic coordinates in the hexagonal cell representation

Atom site	Atom type	Fractional coordinates			z(Å)	Layer type
		x	y	z		
M(1)	Al	½	0	0	0.00	O
O(1)	O	0.8233	0.6466	0.0210	1.17	c
O(2)	OH	1/3	2/3	0.0171	0.95	
M(2)	Sn	2/3	1/3	0.0465	2.59	
M(3)	Al,Fe	0	0	0.0307	1.71	T_1
O(3)	O	0.4931	0.9862	0.0649	3.61	h
O(4)	O	0	0	0.0644	3.58	
M(4)	Al	0.1677	0.3355	0.0822	4.57	O
O(5)	O	0.8529	0.7058	0.1032	5.74	c
O(6)	O	1/3	2/3	0.1001	5.57	
M(5)	Al	0	0	0.1248	6.94	
M(6)	Fe,Zn	1/3	2/3	0.1351	7.51	T_2
M(7)	Fe,Zn	2/3	1/3	0.1129	6.28	
O(7)	O	0.1470	0.2941	0.1474	8.20	c
O(8)	O	2/3	1/3	0.1489	8.28	
M(8)	Al	1/3	1/6	1/6	9.27	O

```
      Origin
         ↓
 A   B   C   A   C   B   A

 h   c   c   h   c   c   h

   O   T₂   O   T₁   O   T₁
```
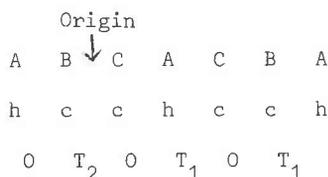
Fig. 6. Anion layer sequence (first two lines) and metal atom layer sequence (third line) for nigerite-6H.

A further consequence of metal atom ordering is an alternation in the magnitude of the oxygen layer separations, corresponding to the T and O metal atom layer alternation. The average oxygen inter-layer separations are about 2.55 and 2.05A across T and O metal atom layers respectively. A similar alternation (2.67 and 2.02A) was observed in the oxygen layer separations in the (ch . . .) structure $Co_2Mn_3O_8$ (Riou and Lecerf, 1975).

The site occupancies derived during the structure refinement (Table 3) give a unit-cell composition $Al_{14.9}Sn_{2.0}Fe_{2.8}Zn_{1.4}O_{30}(OH)_2$. This is in reasonable agreement with the average composition calculated from the microprobe analysis (Table 2), especially if the minor elements, Si and Mn, are grouped with Al and Fe respectively. The location of the large calcium atom was not ascertained from the structure refinement. It may be distributed over some of the anion sites [calcium occupies an anion site in the close-packed oxide mineral loveringite (Gatehouse et al., 1978)]. Note that the above composition requires some iron as ferric to achieve charge balance. Ferric iron is most likely located with aluminum in the tetrahedral site M(3).

Electrostatic valence sums

Indirect support for partial occupancy of the various sites in nigerite is that the resulting calculated electrostatic valence sums for the oxygens are generally close to theoretical (see Table 7). If we allow for full occupancy of site M(1), oxygen O(1) becomes se-

verely oversaturated, with a ΣVi value of 2.32. Table 7 shows that the O(2) site is occupied by OH, having a ΣVi of 1.05. In the calculation of the unit-cell composition, we thus normalized to 30 O + 2 OH. Finally, the undersaturated O(3) site, $\Sigma Vi = 1.67$, is reflected in the O(3)–M bonds all being about 0.05A shorter than the average values.

Prediction of structures for nigerite-6H and related structures

As discussed above, the correct structural model for nigerite-24R was arrived at using crystallochemical reasoning based on the following principles:

(a) The structure is based on a close-packed oxygen framework with a mixed (cubic, hexagonal) stacking sequence. The long c_{hex} axis periodicity is due to the ordering sequence of cubic- and hexagonal-stacked layers. This sequence must be consistent with the symmetry and size of the unit cell and the requirement of dominant cubic stacking.

(b) Between the oxygen layers, ordering of metal atoms gives rise to three possible arrangements, O, T_1, and T_2 (see Fig. 1).

(c) The sequence of O and T layers is determined by the oxygen-layer stacking sequence. Type O layers must alternate with type T layers. T_1 layers occur between cubic- and hexagonal-stacked oxygen layers. T_2 layers lie between cubic-stacked oxygen layers.

(d) In the T_1 layers, the unoccupied tetrahedral site is an olivine-like site, i.e. sharing the basal edges with three octahedra from the adjacent layer (although partial occupancy of this site may be possible).

Having confirmed these general structural principles for nigerite-24R, it should be possible to apply them to predict the structure of other compounds related to nigerite, but with different c_{hex} axis periodicities. These include other nigerite polytypes, högbomites, and taafeites.

Table 7. Nigerite-24R: electrostatic valence sums of cations about anions

Anions	Coordination Cations	ΣVi
O(1)	1 M(1) + M(2) + M(3)	2.02
O(2)	3 M(1)	1.05
O(3)	M(2) + 2 M(4)	1.67
O(4)	M(3) + 3 M(4)	2.15
O(5)	2 M(4) + M(5) + M(6)	2.03
O(6)	3 M(4) + M(6)	2.03
O(7)	M(5) + M(6) + 2 M(8)	2.03
O(8)	M(7) + 3 M(8)	2.05

```
            Origin
               ↓
 C   B   A   C   B   C   A   B   C

 h   c   c   c   h   c   c   c   h

   O   T₂   O   T₁   O   T₂   O   T₁
```
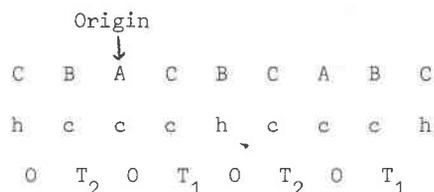
Fig. 7. Anion layer sequence (first two lines) and metal atom layer sequence (third line) for högbomite-8H.

An almost trivial example is provided by the six-layer nigerite polytype first described by Bannister *et al.* (1947). This mineral has trigonal symmetry, $\bar{3}m$, with $c = 13.86A = 6 \times 2.31A$ and with possible space groups $P\bar{3}m1$ or $P\bar{3}1m$. From Table 7.1.5B of Patterson and Kasper (1962), there is only one possible anion layer sequence with dominant cubic stacking. It is designated $|(3)|(3)|$ and has symmetry $P6_3/mmc$ (*i.e.* the trigonal symmetry for nigerite-6H must result from the metal atom arrangement). The oxygen and metal atom layer stacking sequences are given in Figure 6; *i.e.* the oxygen sequence is (cch...) and the metal sequence is $OT_2OT_1OT_1...$. Nigerite-6H differs from nigerite-24R in having only two, rather than four, metal layers in the spinel block. If we use the known occupancies in the $...OT_1OT_1...$ and $...OT_2...$ blocks obtained for nigerite-24R, we can derive a unit-cell composition for nigerite-6H. Allowing the same fractional occupancies, OH^- at a two-fold site, *etc.* (see Table 3) we have

$$Sn_2Al_{10.6}Fe_{1.81}Zn_{0.71}O_{22}(OH)_2 \text{ (not balanced)} \quad (1)$$

For comparison, the analysis obtained by Bannister *et al.* (1947) for nigerite-6H is

$$Sn_{1.77}Al_{10.52}Fe_{1.96}Zn_{0.59}Mn_{0.33}O_{22.16}(OH)_{1.84} \quad (2)$$

It appears that in nigerite polytypes the stacking sequence adopted depends on the tin content, *i.e.* the mineral adopts the sequence that allows all the tin atoms to fully occupy (or almost so) the available octahedral sites in T_1 layers. In going from nigerite-24R to nigerite-6H, the ratio of T_1 to T_2 layers increases to accommodate the higher tin content of the latter.

The prediction of the structure for högbomite-8H (*i.e.* högbomite-4H using McKie's nomenclature) is quite straightforward, using the principles listed (a)–(d) above. This mineral has hexagonal symmetry, possible space groups $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$, with $c_{hex} = 18.35A = 8 \times 2.29A$ (McKie, 1963). From Table 7.1.5B of Patterson and Kasper (1962) the only stacking sequence with dominant cubic stacking is that designated $|(4)|(4)|$. This has symmetry $P6_3mc$, and the origin for the oxygen stacking is located on an oxygen. In order that O and M metal atom layers alternate across the origin oxygen layer, a non-centrosymmetric space group has to be used. The oxygen and metal atom layer sequences are given in Figure 7. Thus, in this structure both the spinel block and the M_5O_8 block are only two metal-atom layers wide. The ideal unit-cell composition (*i.e.* partial occupancy not considered) is $M_{22}O_{32} = M_{5.5}O_8$. Generally, compositions reported for 8H-högbomites contain higher metal contents and suggest partial occupancy of the second tetrahedral site in the T_1 layers; *e.g.* the composition recently determined for zincian högbomite-8H by Wilson (1977), $(Mg,Fe,Zn,Al,Ti...)_{5.762}(O,OH)_8$, requires 50% occupancy of each of the second tetrahedral sites in the T_1 layers. We are currently refining the structure of an 8H-högbomite polytype, and the present R factor of ~0.08 confirms our correct prediction of the structure using the principles described above.

The taafeite minerals are interesting in that they form 8H and 18R polytypes with similar diffraction patterns to högbomite and nigerite polytypes, but the compositions of both are M_6O_8, within experimental error (Hudson *et al.*, 1967). In this case it seems the same structural principles apply, but the second tetrahedral site in the T_1 layers is fully occupied, presumably by the very small Be^{2+} ion which compositionally characterizes the taafeite minerals.

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