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Zincohögbomite-8*H* from Samos (Greece): crystal structure, polysomatism, and polytypism in högbomite related structures

by *Thomas Armbruster*[1]

Abstract

The crystal structure of type locality zincohögbomite-8*H*, $Zn_{3.54}Mg_{0.10}Ni_{0.20}Fe^{3+,2+}_{2.33}Al_{14.73}Cr_{0.03}Ti_{0.98}Sn_{0.09}O_{30+x}(OH)_{2-x}$, ($a$ = 5.7097(8), b = 18.333(3) Å, Z = 1, space group $P6_3mc$) was refined from single-crystal X-ray data to R = 1.79% with 43 variables and 505 observations > 4$\sigma(F)$. Zincohögbomite-8*H* with close-packed oxygen layers stacked along the c-axis in the sequence ABCBACBC has the same symmetry and polyhedral articulation as högbomite-8*H* refined by GATEHOUSE and GREY (1982). The structure of Samos zincohögbomite may be interpreted as composed through alternation along c of two gahnite (spinel) layers of approximately $Zn_2Al_4O_8$ composition and two layers of a nolanite-like unit with $(Fe^{3+}_{0.69}Al_{0.31})^{IV}(Fe^{3+,2+}_{0.12}Ti_{0.12}Sn_{0.01}Al_{0.75})^{VI}_4O_7(OH)$ composition. Out of the seven crystallographically independent cation sites three are tetrahedrally (T) and four are octahedrally (M) coordinated; taking into account their multiplicities, the formula $T_6M_{16}O_{30}(OH)_2$ can be derived.

It is suggested that in högbomite related structures with either substantial Ti^{4+} or Sn^{4+} (högbomites, zincohögbomites, pengzhizongites, and nigerites) the observed polysome depends not only on the Ti^{4+}, Sn^{4+} concentration but more probably on a complex interaction of cations of various valence and size responsible for the formation of nolanite-like subunits ('*ch*') of $TM_4O_7(OH)$ composition within a spinel-like host structure (the number of remaining '*c*' layers describes the number of spinel-like layers with TM_2O_4 composition). In addition, the number of nolanite-like layers may also determine the amount of OH in the formula. With increasing number of nolanite units the following stacking types will be favored: (1) 16*H*: 2 x (*cccccc* + *ch*), (2) 12*H*: 2 x (*cccc* + *ch*), (3) 10*H*: 2 x (*ccc* + *ch*), (4) either 8*H*: 2 x (*cc* + *ch*) or 24*R*: 3 x (*cccc* + *hcch*), (5) either 6*H*: 2 x (*c* + *ch*) or 18*R*: 3 x (*cc* + *chhc*).

Keywords: zincohögbomite, nigerite, spinel, nolanite, crystal structure, chemistry, polytypism, polysomatism, Samos.

Introduction

Högbomites, zincohögbomites, pengzhizhongites, and nigerites possess related structures with a close packed oxygen array but with variable stacking sequence of the oxygen layers. The various stacking variants were hitherto considered *polytypes* or *polytypoids*. In this paper the nomenclature of PEACOR (1967) is adopted which uses a suffix composed of the number n of oxygen layers (ca. 2.3 Å thick) and a letter R or H designating either rhombohedral or hexagonal symmetry. This suffix is different from the one suggested by MCKIE (1963) who applied $n = c_{hex} / 4.6$. Furthermore, the '*h*', '*c*' nomenclature is used to describe the sequence of oxygen layers. A '*h*' layer (hexagonal close packed) indicates that the layer above and below are of the same type (*e.g.*, ABA, CBC, CAC, ACA). A '*c*' layer (cubic close packed) indicates that the layer above and below have different shifts (*e.g.*, ABC, CAB, ACB). As shown by GREY and GATEHOUSE (1979) the above minerals have '*cc*' sequences occupied by $\mathbf{T_2}$-type cation layers with spinel-like arrangements of tetrahedra (T) and octahedra (M), with T_2MO_4 composition, or octahedral **O**-type layers of M_3O_4 composition. Cations on a '*ch*' interface are either of the $\mathbf{T_1}$-type with TMO_4 composition or of the **O**-type. Furthermore, **O** and either $\mathbf{T_1}$- or $\mathbf{T_2}$-type layers always alternate along the stacking direction of oxygen layers. The arrangement of octahedra (M) and tetrahedra (T) within $\mathbf{T_1}$, $\mathbf{T_2}$, and **O** layers is depicted in figure 3 of the accompanying paper (ARMBRUSTER et al., 1998). It follows that these

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structures have compositions between $T_2M_4O_8$ (spinel) and TM_4O_8 or TM_4O_7OH (nolanite). Related to the above minerals are the members of the taaffeite series, Be–Mg–Al oxides, (*e.g.*, NUBER and SCHMETZER, 1983) which differ from the former because the $\mathbf{T_1}$ layers have the composition T_2MO_4 just as the $\mathbf{T_2}$ layers. Thus for taaffeite related structures the T/M ratio does not change with stacking sequence.

As mentioned above, the stacking variants of högbomites, zincohögbomites, pengzhizhongites, and nigerites were hitherto interpreted as *polytypes* which is only correct for the anion layers but not for the cations. For members of a polytypic series *sensu stricto* the chemical composition should be the same. The above examples, however, indicate that the ratio tetrahedra/octahedra and the stoichiometry (the ratio cation/anion) alters. The term polytypism was originally introduced by BAUMHAUER (1912, 1915) as a result of his studies on SiC single crystals by optical goniometry. Subsequent structure determinations showed that these polytypes consist of identical layers stacked in a different sequence. A recent review on polytypism is provided by DUROVIC (1997). The present official crystallographic definition (GUINIER et al., 1984) reads: 'An element or compound is polytypic if it occurs in several structural modifications, each of which may be regarded as built by stacking layers of (nearly) identical structure and composition, and if the modifications differ only in their stacking sequence. Polytypism is a special case of polymorphism: the two-dimensional translations within the layers are (essentially) preserved whereas the lattice spacings normal to the layers vary between polytypes and are indicative of the stacking period.' For application of this definition to högbomite related structures the question arises how 'nearly identical compositions' are limited. The Committee chaired by Guinier (GUINIER et al., 1984) comments in its report on this question: 'deviation in composition up to 0.25 atoms per formula unit are permitted within the same polytypic series: two layer structures that differ by more than this amount should not be called polytypic.' Valid for mineralogical nomenclature is still the definition proposed by the IMA-IUCr Joint Committee on Nomenclature (BAILEY et al., 1977). This latter report included the tolerance of 0.25 apfu in the text of the definition and even specified: '0.25 apfu of any constituent element'. The report continues: 'Layer structures that differ from one another by more than this amount are to be called *polytypoids* rather than *polytypes*. One may argue that several stacking variants of högbomite related minerals do not fulfill the requirements for *polytypes* (GUINIER et al., 1984) because the structures are assembled of two kinds of structural layers (the spinel layer and the nolanite layer). Another question arises: **what is the formula unit for normalization of two compounds with different stoichiometry and symmetry?** If we analyze, based on the respective crystal structures (GREY and GATEHOUSE, 1979; GATEHOUSE and GREY, 1982; CHEN et al., 1989; ARAKCHEEVA et al., 1995; ARMBRUSTER et al., 1998), the composition of various högbomite, zincohögbomite, pengzhizhongite, and nigerite polytypes and normalize the formula to 8 oxygen atoms (required for nolanite) we find a range between $T_{1.75}M_4O_8$ (16*H*) and $T_{1.33}M_4O_8$ (6*H*) which exceeds the 0.25 apfu limit for polytypic layer structures. If we arbitrarily normalize to 4 oxygen atoms (spinel) the above minerals may be considered a series of polytypes. It is clear that possible polytypic series must be defined for each of the chemically distinct minerals: högbomite, zincohögbomite, pengzhizhongite, and nigerite. Nevertheless, the same architectural principles are observed in the structures of all for of them and it must be assumed that also the same stacking variants may occur. The arguments elucidated above clearly suggest that stacking variants of högbomite-related minerals are not necessarily polytypes (as shown below, some may be considered polytypes but others not).

A better description of högbomite related structures is based on the concept of *polysomatism* where a *polysome* characterizes a structure composed of various structural modules (THOMPSON, 1978; FERRARIS, 1997; MERLINO and PASERO, 1997). In case of högbomite related structures these modules comprise spinel and nolanite units. A review on crystal chemistry and hitherto observed stacking variants of högbomite was given by PETERSEN et al. (1989). Polysomatism in nigerite was recently studied by NEIVA and CHAMPNESS (1997) with electron diffraction.

The mineral name zincohögbomite was introduced by OCKENGA et al. (1998) for a Zn-rich 8*H* polysome found in metabauxites at Mikiri East-Samos, Kerkis West-Samos (Greece) and in the greenshist grade metabauxites along the southern margin of the Menderes Complex, Turkey (YALÇIN et al., 1987). The detailed work of FEENSTRA (1997) discusses the crystal chemistry and paragenesis of zincohögbomite-8*H* in the diaspore-bearing metabauxites from E-Samos.

The aim of the present study is manifold: (1) to solve the structure of zincohögbomite-8*H* from Samos and to compare the results with the structure of högbomite-8*H* (GATEHOUSE and GREY, 1982); (2) to compare the polysomatic structures of the hitherto known högbomites, zincohög-

Tab. 1 Electron-microprobe analyses and chemical formula normalized on 22 cations. With all Fe assumed as Fe^{3+} and 32 O pfu (crystal structure) charge balance yields $O_{31.22}(OH)_{0.78}$. In order to obtain stoichiometric $O_{30}(OH)_2$ 1.107 Fe^{3+} and 1.220 Fe^{2+} must be assumed.

	minimum	maximum	mean	σ	elements	apfu
MgO	0.29	0.36	0.31	0.02	Mg	0.104
NiO	0.80	1.23	1.10	0.10	Ni	0.198
ZnO	20.25	22.17	21.36	0.58	Zn	3.536
MnO	0.02	0.08	0.05	0.02	Mn	0.009
Al_2O_3	54.89	57.44	55.75	0.61	Al	14.732
Fe_2O_3	13.18	15.57	13.79	0.66	Fe	2.327
Cr_2O_3	0.01	0.37	0.15	0.11	Cr	0.027
TiO_2	4.52	6.25	5.82	0.40	Ti	0.981
SnO_2	0.08	1.64	0.97	0.46	Sn	0.087
Sum			99.30		Sum	22.00

bomites, pengzhizhongites, and nigerites; and (3) to find rules which are responsible for the development of the various close packed stacking variants.

Experimental

The investigated crystal originates from the Kerketefs Mountain West Samos (Greece). The crystal was kindly supplied by O. Medenbach (Bochum) and is identical to the specimen from Samos studied by OCKENGA et al. (1998). The chemical composition of the same crystal as used for the structure refinement was determined with a CAMEBAX SX 50 electron-microprobe. The accelerating voltage was 20 kV and the sample current was 20 nA. Synthetic and natural samples were used as standards: MgO Mg *K*α, Al_2O_3 Al *K*α, TiO_2 Ti *K*α, Cr_2O_3 Cr *K*α, andradite Fe *K*α, NiO Ni *K*α, ZnO Zn *K*α, SnO_2 Sn *L*α, spessartine Mn *K*α. Analyses on 15 spots were collected and the minimum, maximum, and mean values for zincohögbomute-8*H* are given in table 1. As evidenced by electron microprobe analyses, the small crystal was actually composed of three distinct phases: ca. 83% zincohögbomite (composition given in Tab. 1), 15% of a phase composed of Al and O (diaspore?), and 2% TiO_2 (rutile?). If these phases are coherently intergrown (with common reflection positions), the composition refined by single-crystal X-ray methods may reflect the composition of the entire crystal rather than only the zincohögbomite component.

Single-crystal X-ray data collection on a hexagonal plate, 0.125 mm in diameter and 0.050 mm thick, and brown in color, was performed on an ENRAF NONIUS CAD4 single-crystal X-ray diffractometer with graphite monochromated Mo*K*α X-radiation. Cell dimensions were refined from 15 reflections with $12 < \theta < 21°$ yielding hexagonal symmetry with $a = 5.7097(8)$, $c = 18.333(3)$ Å. The single-crystal diffraction pattern did not show evidence of the admixed phases determined by electron-microprobe analyses. Experimental details are given in table 2. Diffraction data were collected up to $\theta = 30°$, yielding 1604 reflections of which 670 were unique and 505 had $F > 4\sigma(F)$ used for structure solution and refinement. Data reduction, including background and Lorentz polarization correction, was carried out with the SDP program system (ENRAF NONIUS, 1983). An empirical absorption correction using the ψ-scan technique was applied. Systematic absences indicated $P\bar{3}1c$, $P31c$, $P6_3mc$, $P6_3/mmc$, or $P\bar{6}2c$ as possible space groups. Following GATEHOUSE and GREY (1982) the space group of zincohögbomite-8*H* was assumed to be the same as for högbomite-8*H* and space group $P6_3mc$ was used for structure solution by direct methods with the program SHELXS-97 (SHELDRICK, 1997). Subsequent refinement cycles with neutral atom

Tab. 2 Details of X-ray data collection and refinement

Space group	$P6_3mc$
a, c (Å)	5.7097(8), 18.333(3)
X-radiation	Mo*K*α
Upper θ limit	30°
h, k, l limit	$10 \geq h \geq -1, 10 \geq k \geq 0,$ $33 \geq l \geq 0$
Reflections measured	1604
Unique reflections	670
Reflections > 4σ (F)	505
Absorption corr.	empirical: ψ scans
Absolute configuration	10(3)% enantiomorph twinning
Number of parameters	43
R (on F)	1.79%
ωR (on F^2)	4.80%

$$R = (\Sigma||F_o|-|F_c||)/(\Sigma|F_o|) \qquad \omega R = \sqrt{(\Sigma(F_o^2-F_c^2)^2)/(\Sigma w(F_o^2)^2)}$$

Tab. 3 Atomic positional parameters and B_{eq} values, with standard deviations in parentheses, for zincohögbomite-8*H* from Samos.

atom	pop.	*x/a*	*y/b*	*z/c*	B_{eq} (Å^2)
M1	1. Al	0.1640(1)	0.3281(2)	0.06996(7)	0.30(1) *
M2	0.60(1)Ti + 0.40 Fe	0	0	0.21385(5)	0.31(1) *
T3	0.69(1)Fe + 0.31 Al	2/3	1/3	0.16044(6)	0.38(2) *
M4	1 Al	0.4983(1)	0.9967(3)	0.31480(7)	0.32(1) *
M5	1 Al	2/3	1/3	0.4441(1)	0.38(2) *
T6	0.84(1)Zn + 0.16 Al	1/3	2/3	0.47482(5)	0.38(2) *
T7	0.75(1)Zn + 0.25 Al	0	0	–0.09223(5)	0.42(2) *
O1	1	0	0	0.0160(3)	0.57(6) *
O2	1	0.0382(5)	0.5191(2)	0.0120(1)	0.52(3) *
O3	1	1/3	2/3	0.1258(2)	0.47(5) *
O4	1	0.8476(3)	0.6951(5)	0.1287(1)	0.66(3) *
O5	1	2/3	1/3	0.2624(3)	0.62(7) *
O6	1	0.1697(3)	0.3393(6)	0.2616(1)	0.60(3) *
O7	1	1/3	2/3	0.3682(3)	0.53(6) *
O8	1	0.1873(3)	0.3746(6)	–0.1219(1)	0.61(3) *

Note: An Al scattering curve was used to model Al with minor Mg. A Zn scattering curve was applied to model Zn with minor Ni.
* Starred atoms were refined isotropically.

Tab. 4 Cation and oxygen stacking sequence, nomenclature explained in the text.

C	c	O7, O8		
			O	M4
B	h	O5, O6		
			$\mathbf{T_1}$	M2, T3
C	c	O3, O4		
			O	M1
A	c	O1, O2		
			$\mathbf{T_2}$	M5, T6, T7
B	c	O7, O8		
			O	M4
C	h	O5, O6		
			$\mathbf{T_1}$	M2, T3
B	c	O3, O4		
			O	M1
A (origin)	c	O1, O2		
			$\mathbf{T_2}$	M5, T6, T7

scattering factors (program SHELXL-97 by SHELDRICK [1997]) were accompanied by difference Fourier maps yielding 7 cation and 8 oxygen positions. Isotropic displacement parameters were refined for all atoms. Cation assignment was based on interatomic distances and scattering power. The minor Ni concentrations cannot be distinguished from dominant Zn thus a Zn scattering curve was used to model Zn and Ni. Minor Mg and Al concentrations on Zn-rich tetrahedral sites can not be differentiated and an Al scattering curve was used to model the amount of both elements. The absolute configuration was evaluated using the absolute structure parameter introduced by FLACK (1983). This parameter indicated that partial enantiomorph twinning had to be assumed leading to a twinning contribution of 10(3)%. Final least squares cycles converged at $R = 1.79\%$ for 505 observation $> 4\sigma(F)$ and 43 parameters. For better comparison with the data by GATEHOUSE and GREY (1982) the same cation and oxygen numbering scheme was used where T and M designate tetrahedral and octahedral positions. Atomic coordinates and isotropic displace-

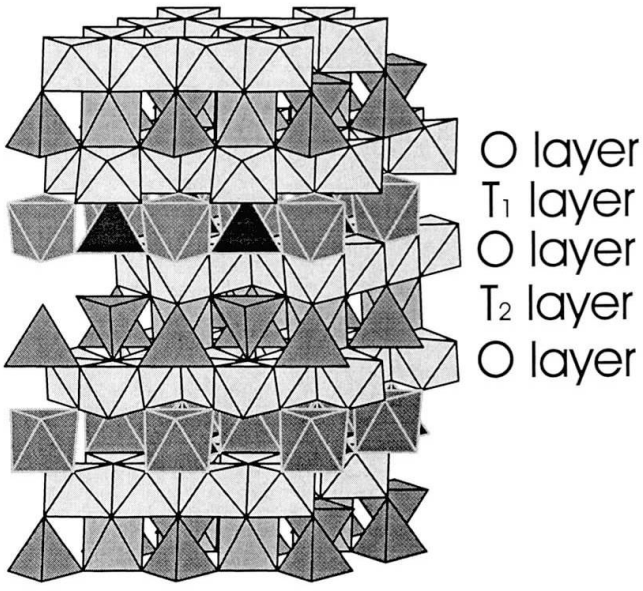

Fig. 1 Polyhedral representation of the zincohögbomite-8*H* structure. **O**-type octahedral layers are light gray with dark rims. $\mathbf{T_2}$-type spinel layers are dark gray with black rims and nolanite-like $\mathbf{T_1}$ layers have light rims.

ment parameters for zincohögbomite-8*H* from Samos are given in table 3. The stacking sequence of cations and oxygen layers is elucidated in table 4 and shown in figure 1. Table 5 displays selected interatomic distances.

Tab. 5 Interatomic distances (Å) for zincohögbomite-8*H* from Samos.

M1	O1	1.905(3)			
M1	O2 2x	1.902(2)			
M1	O4 2x	1.902(2)	M5	O8 3x	1.884(3)
M1	O3	1.962(2)	M5	O2 3x	1.919(3)
	average	1.913		average	1.901
M2	O6 3x	1.892(3)	T6	O7	1.955(5)
M2	O4 3x	2.171(3)	T6	O2 3x	1.960(3)
	average	2.031		average	1.958
T3	O5	1.869(5)	T7	O8 3x	1.930(3)
T3	O4 3x	1.881(3)	T7	O1	1.983
	average	1.878		average	1.944
M4	O6 2x	1.896(2)			
M4	O7	1.903(3)			
M4	O5	1.922(2)			
M4	O8 2x	1.949(2)			
	average	1.919			

Structure description

Stacking sequence ABCBACBC or '*cchccchc*' (as defined above) and polyhedral articulation of zincohögbomite-8*H* are the same as found for högbomite-8*H* by GATEHOUSE and GREY (1982). The tetrahedral sites of the $\mathbf{T_2}$-type layer (T6 and T7) are occupied by 3.2 Zn pfu and 0.8 pfu light elements (Al, Mg). If we assume that Mg will preferentially share the tetrahedral sites with Zn and subtract 0.1 Mg pfu (according to the chemical composition) 0.7 Al pfu remain in tetrahedral coordination. The sum of tetrahedral Zn + Ni, obtained by site population refinement is 3.2 apfu which is in fair agreement with 3.7 apfu from the chemical formula. The octahedral site M5 in the $\mathbf{T_2}$ layer has only Al. The octahedral sites in the **O**-type layer (M1, M4) are also both pure Al sites. The tetrahedral site (T3) of the $\mathbf{T_1}$-type layer shares Fe^{3+} and Al. The relatively short average T3-O distance of 1.878 Å confirms Fe^{3+}. M2, also in the $\mathbf{T_1}$-type layer, shares Fe and Ti. Site population refinements for M2 converge at 1.2 Ti pfu (versus 0.98 Ti and 0.09 Sn pfu measured). The refined Fe concentration of 2.2 apfu on M2 and T3 is in good agreement with 2.3 Fe pfu from the chemical analysis. Due to the complex Fe, Ti, Sn occupation on M2 it seems impossible to decide whether Fe on M2 is ferrous, ferric, or of mixed valence. Table 5 indicates that in the $\mathbf{T_1}$ layer the octahedron M1 is larger than T3 whereas in the $\mathbf{T_2}$ layer the tetrahedra T6 and T7 are larger than M5. The cation distributions, elucidated above, are qualitatively very similar to those derived by GATEHOUSE and GREY (1982) for högbomite-8*H*. If we further account M5, T6 and T7 ($\mathbf{T_2}$-type layer) and M1 or M4 (**O**-type layers) to a spinel-like unit we obtain a gahnite-like composition of $4\,[(Zn_{0.73}Ni_{0.04}Mg_{0.04}Al_{0.19})^{IV}Al_2^{VI}O_4]^{0.19+}$ and the remaining cations (T3 and M2 in the $\mathbf{T_1}$-type layer and M1 or M4 on the **O**-type layer) assemble the nolanite like-unit of approximately 2 $(Fe^{3+}_{0.69}Al_{0.31})^{IV}(Ti_{0.5}Fe^{2+}_{0.5})^{VI}Al_3^{VI}O_7(OH)$. To account for the excess charge in the spinel layers the number of OH groups in the nolanite layers must be decreased to $O_{7.38}(OH)_{0.62}$. Additional Fe^{3+} instead of Fe^{2+} in the nolanite-like unit leads to a further decrease of OH.

The prediction of OH (or possibly F) in the structures of the various högbomite related minerals comes from crystal chemical considerations. In zincohögbomite-8*H* (this study) and högbomite-8*H* (GATEHOUSE and GREY, 1982) all oxygen atoms, except O3 and O6, are four-coordinated. The additional tetrahedral vacancy (formed by 3 x O6 and 1 x O3) in the nolanite type $\mathbf{T_1}$-layer is responsible for the three-fold coordination of O3 and O6. Oxygen O3 forms three bonds to the Al octahedron M1. Within the M1 octahedron the M1-O3 bond is the longest (1.962 Å). Thus O3 is strongly underbonded and a privileged site for OH (or F). In contrast, O6 bonds to 2 x M4 (Al) and 1 x M2 (Fe,Ti) and exhibits the shortest bonds in these coordination polyhedra. In addition, M2 is partially Ti^{4+} bearing which reduces underbonding. Thus O6 is not underbonded enough to bear an OH group but privileged to accept a weak hydrogen bond. GATEHOUSE and GREY (1982) already stated similar arguments based on valence sums for högbomite-8*H*. These arguments strongly suggest that the formula of högbomite-8*H* and zincohögbomite-8*H* is $T_6M_{16}O_{30}(OH)_2$. Nevertheless, neither in the crystal structure study by GATEHOUSE and GREY (1982) nor in this investigation a proton position could be refined. The reasons are probably partial occupancy and positional disorder. Oxygen O3 resides on a three-fold axis whereas the adjacent (above or below) O6 sites, accepting the hydrogen bond, form a triangle centered by the three-fold axis. We may further assume that the proton resides approximately at the O3-O6 connection lines (O3 and O6 are 2.97 Å apart) and thus deviates from the three-fold axis. Consequently each proton site is only 1/3 occupied. Electron density at such a position (0.38, 0.76, 0.16) could be located in difference Fourier maps. However, subsequent refinement of

1/3 occupied H was not successful even after introduction of an O–H bond-length constraint of 0.9 Å. A proton position in a similar structural environment but on the three-fold axis was determined by ARAKCHEEVA et al. (1995) for nigerite-6*H*.

Comparison with related polysomes and polytypes

As discussed above, the privileged OH site in högbomite, zincohögbomite, pengzhizongite, and nigerite is within the cation $\mathbf{T_1}$ layer of the nolanite-like unit. Thus the relative abundance of nolanite layers in these structures governs the degree of hydroxylation. Some restrictions need to be stated. There are several structures, exemplified by the mineral kamiokite $Fe_2^{2+}Mo_3^{4+}O_8$ (KANAZAWA and SASAKI, 1986), which have the same polyhedral topology as nolanite (HANSON, 1958; GATEHOUSE et al., 1983) but do not bear OH. The reason for their anhydrous character is the high concentration of four-valent cations. One three-coordinated oxygen bonds 3 x to octahedral Mo^{4+}, the other three-coordinated O site bonds 2 x to octahedral Mo^{4+} and 1 x to octahedral Fe^{2+}.

Cubic spinels of *Fd*3*m* space group symmetry and a setting with the origin at the center have an ideal oxygen close-packing if oxygen resides at 1/4, 1/4, 1/4 (u, u, u). Deviation from this value leads to a puckered (111) oxygen sheet. If u > 0.2625 the spherical volume of the occupied tetrahedral site is larger than the volume of the occupied octahedral site. Gahnite $ZnAl_2O_4$ and hercynite $FeAl_2O_4$, the 'mother' structures of högbomite related minerals, have both u = 0.264 (*e.g.*, WAERENBORGH et al., 1994). The same pattern (tetrahedron > octahedron) is found in the spinel units of högbomite, zincohögbomite, and nigerite.

In the mineral nolanite (GATEHOUSE et al., 1983) the size of the octahedron is larger than the one of the tetrahedron. This relationship is also found in the nolanite unit of nigerite-24*R* (GREY and GATEHOUSE, 1979) and nigerite-6*H* (ARAKCHEEVA et al., 1995). The reason is that in nigerite the tetrahedral site in the $\mathbf{T_1}$-type layers is occupied by mainly three-valent cations (Al with additional Fe) whereas the two octahedral sites are occupied by Sn ($\mathbf{T_1}$ layer) and Al with supposed vacancies (**O** layer). The relatively high concentration of octahedral vacancies in the nolanite **O** layer, 25% (ARAKCHEEVA et al., 1995) and 30% (GREY and GATEHOUSE, 1979) is rather suspicious. This suspicion is confirmed by the increased size of this octahedron. In further studies on nigerite one should consider the possibility of octahedral Li (WENGER and ARMBRUSTER, 1991). The scattering power attributed in both nigerite studies to Al and vacancies could also be explained by a completely occupied site with Al and Li (ca. 0.4 Li and 0.6 Al). This would remove (from an electrostatic point of view) unfavorable vacancies and would be in accordance with the frequent geochemical association of Sn and Li. The same size relationship in the nolanite unit (octahedron > tetrahedron) is also found in högbomite-8*H* (GATEHOUSE and GREY, 1982) and zincohögbomite-8*H* (this study) where the tetrahedral site is occupied by mainly Fe^{3+} and Al and to a lesser degree in zincohögbomite-16*H* (ARMBRUSTER et al., 1998) where the tetrahedron in the $\mathbf{T_1}$ layer is occupied by mainly Zn and Mg. An exception is the predominantly two-valent character of the tetrahedral ions in the $\mathbf{T_1}$ layer of zincohögbomite-16*H*. The latter exception is also responsible for a different position of Ti^{4+} in zincohögbomite-16*H*. In all other hitherto studied högbomites, zincohögbomites, pengzhizhongites or nigerites the four-valent cations (Ti or Sn) reside in the $\mathbf{T_1}$ layer whereas in zincohögbomite-16*H* Ti is in the **O**-type layer. This has electrostatic reasons: three oxygen atoms forming the base parallel (001) of the tetrahedron in the $\mathbf{T_1}$ layer accept insufficient charge due to the two-valent tetrahedral cations which is balanced by incorporation of Ti^{4+} in the adjacent **O**-type layer.

The published structures of högbomites, zincohögbomites, pengzhizhongites, nigerites and taaffeite minerals allow deriving the crystal chemical formulas of various högbomite-related *polysomes* or *polytypes*. For each spinel unit ('*c*') the formula contribution TM_2O_4 and for each nolanite unit ('*ch*') the formula contribution $TM_4O_7(OH)$ has to be considered. Thus the 16*H* type (ARMBRUSTER et al., 1998) has the formula $T_{14}M_{32}O_{62}(OH)_2$ with a 2 x (*cccccc* + *ch*) oxygen stacking. The observed 12*H* type (MCKIE, 1963) with a 2 x (*cccc* + *ch*) oxygen stacking sequence (predicted) has the formula $T_{10}M_{24}O_{46}(OH)_2$; the 10*H* type (*e.g.*, ZAKREZEWSKI, 1977) with a 2 x (*ccc* + *ch*) oxygen stacking sequence (predicted) has the formula $T_8M_{20}O_{38}(OH)_2$; the 8*H* type (this study and GATEHOUSE and GREY, 1982) has 2 x (*cc* + *ch*) and the formula $T_6M_{16}O_{30}(OH)_2$. The 24*R* type has the same formula (GREY and GATEHOUSE, 1979; SCHMETZER and BERGER, 1990) with the stacking sequence 3 x (*cccc* + *hcch*). Thus 8*H* and 24*R* may be *polytypes sensu stricto*. The 6*H* type (CHEN et al., 1989; ARAKCHEEVA et al., 1995) with the stacking sequence 2 x (*c* + *ch*) and its *polytype* 18*R* (NUBER and SCHMETZER, 1983) with the stacking sequence 3 x (*cc* + *chhc*) have the same formula $T_4M_{12}O_{22}(OH)_2$. The chemical analyses for which

also the stacking type was determined indicate that per nolanite unit ca. 0.5–1 Ti^{4+} or Sn^{4+} (*e.g.*, PETERSEN et al., 1989; MCKIE, 1963) must be considered where the values close to 1 Sn^{4+} seem to be characteristic of nigerite or pengzhizhongite and values of ca. 0.5 Ti^{4+} for högbomite and zincohögbomite. On the basis of a formula normalized to 8 oxygen atoms 16*H* has 0.125–0.25 M^{4+}, 12*H* has 0.167–0.333 M^{4+}, 10*H* has 0.2–0.4 M^{4+}, 8*H* and 24*R* have 0.25 to 0.5 M^{4+}, 6*H* and 18*R* have 0.333 to 0.666 M^{4+}. It is evident that the knowledge of M^{4+} per 8 oxygen atoms is not sufficient to determine the stacking type. Furthermore, there is a high probability that in a given stacking type high concentrations of M^{4+} ions are balanced within the nolanite unit by a high concentration of cations with low valence (see the discussion above concerning possible vacancies or more probably Li^{+} in nigerite). The example of the mineral kamiokite $Fe_2^{2+}Mo_3^{4+}O_8$ with a nolanite-like structure (KANAZAWA and SASAKI, 1986) indicates that even up to 3 M^{4+} cations are possible in a nolanite unit, provided no OH is present. The other extreme would be a M^{4+}-free nolanite-like unit where all cations are three-valent $T^{3+}M_4^{3+}O_7(OH)$. It seems that a very complex interaction of cations of various valence and size is responsible for the formation of a nolanite unit, which governs the stacking type.

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