Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie

Band: 78 (1998)

Heft: 3

Artikel: Titanium and iron poor zincohögbomite-16H, Zn14(Al,Fe3+,Ti,Mg)8Al24O62(OH)2, from Nezilovo, Macedonia : occurence and crystal structure of a new polysome

Autor: Armbruster, Th. / Bermanec, V. / Zebec, V.

DOI: https://doi.org/10.5169/seals-59301

SCHWEIZ. MINERAL. PETROGR. MITT. 78, 469–477, 1998

Titanium and iron poor zincohögbomite-16*H*, $Zn_{14}(Al,Fe^{3+},Ti,Mg)_8Al_{24}O_{62}(OH)_2$, from Nezilovo, Macedonia: occurrence and crystal structure of a new polysome

by *Th. Armbruster*[1], *V. Bermanec*[2], *V. Zebec*[3] and *R. Oberhänsli*[4]

Abstract

The new polysome zincohögbomite-16*H*, $Zn_{13.03}Mg_{0.49}Fe^{3+}_{2.12}Ti_{1.15}Al_{29.21}O_{62}(OH)_2$, (space group $P6_3mc$, $Z = 1$, $a = 5.729(2)$, $c = 37.097(5)$ Å; $d_{calc.} = 4.52$ g/cm^3) occurring as small plates in pink marbles at Nezilovo, Macedonia, is a mineral of the högbomite group. The hexagonal plates exhibit parallel intergrowth or occur in aggregates up to 2 mm in size. The transparent orange mineral shows a pale yellow streak and has adamantine luster. Zincohögbomite-16*H* is optically uniaxial negative ($\omega_{red} = 1.850$ and $\omega_{yellow} = 1.845$, ε = not determined), pleochroic: ω – brown-yellow, ε – pale greenish-yellow, Mohs hardness 6–7, neither cleavage nor parting were observed. Zincohögbomite-16*H* is a metamorphic reaction product in the high grade metamorphic assemblage of the marbles at Nezilovo (Macedonia): it coexists with gahnite and zinc-rich phlogopite.

The crystal structure of zincohögbomite-16*H* was solved and refined from X-ray single-crystal data to $R = 2.42\%$ with 79 variables and 518 observations $> 4\sigma(F)$. The new polysome has a close packed oxygen array composed of 16 oxygen layers stacked along the *c*-axis in the sequence ABCABCBACBACBABC. The oxygen array consists of cubic close packed subunits (complete gahnite-spinel blocks of six layers) with intercalated units of the hexagonal close packed type. Out of the 15 cation sites seven are tetrahedrally (T) and eight are octahedrally (M) coordinated; taking into account their multiplicities the formula $T_{14}M_{32}O_{62}(OH)_2$ can be derived. The tetrahedra are mainly occupied by Zn, whereas Al, Fe, and Ti have octahedral coordination.

Keywords: zincohögbomite-16*H*, crystal chemistry, X-ray single-crystal structure refinement, Nezilovo, Macedonia.

Introduction

Högbomites are complex Fe–Mg–Al–Ti-oxides with the approximated formula $Fe_5Al_{16}TiO_{30}(OH)_2$ (*e.g.*, PETERSEN et al., 1989). The crystal structure is based on a close packed oxygen array of which various stacking variants have been identified (GATEHOUSE and GREY, 1982). Using single-crystal X-ray methods MCKIE (1963) distinguished 'polytypes' composed of 8, 10, 12, 28, 30, and 36 oxygen layers. However, the accompanying paper (ARMBRUSTER, 1998) suggests on the basis of available crystal structure analyses that most of the stacking variants do not represent polytypes but polysomes. Högbomite related polysomes are composed of spinel- and nolanite-like slabs. PEACOR (1967) introduced the nomenclature with the suffix *nH* or *nR* where *n* equals the number of close packed oxygen layers (ca. 2.3 Å thick) and *H* = hexagonal and *R* = rhombohedral whereas MCKIE (1963) used $n = c_{hex}/4.6$. For these reasons the nomenclature of högbomite stacking variants is highly confusing and in case of doubt the length of the *c*-axis should be consulted. The name zincohögbomite was introduced by OCKENGA et al. (1998) for a Zn-rich 8*H* member found in greenshist-grade metabauxites from Samos (Greece), and along the southern margin of the Menderes

[1] Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestr. 3, CH-3012 Bern, Switzerland. <armbruster@krist.unibe.ch>
[2] Mineralosko-petrografski zavod, Geoloski odsjek, PMF, Horvatovac bb, HR-10000 Zagreb, Croatia.
[3] Mineralosko-petrografski odjel, Hrvatski Prirodoslovni Muzej, Demetrova 1, HR-10000 Zagreb, Croatia.
[4] Institut für Geowissenschaften, Mineralogie-Petrologie, Universität Potsdam, POB 601553, D-14415 Potsdam, Germany.

Complex, Turkey (YALÇIN et al., 1987). The detailed work of FEENSTRA (1997) discusses the crystal chemisty and paragenesis of zincohögbomite-8*H* in the diaspore-bearing metabauxites from eastern Samos. A review of högbomite group minerals and observed stacking variants is provided in the accompanying paper (ARMBRUSTER, 1998).

Occurrence and description

Zincohögbomite-16*H* occurs in a dolomitic marble in the Nezilovo area (Macedonia) together with zinc-rich phlogopite-1*M*, white mica, epidote-piemontite (BERMANEC et al., 1994), hematite and white amphibole with accessory rutile and gahnite. Such mineralized marbles are usually found close to the contact of Precambrian gneisses and marbles. After treatment of these carbonate rocks with HCl, zincohögbomite concentrates in the insoluble residue. Zincohögbomite-16*H* crystals are frequently epitactically intergrown with phlogopite and thus difficult to distinguish and to separate from mica. Zincohögbomite-16*H* is formed under metamorphic conditions. Nezilovite (BERMANEC et al., 1996), a mineral of the magnetoplumbite group, and zincohögbomite-16*H* are developed in the same association but they never occur in the same sample.

Zincohögbomite-16*H* is orange in color with pale yellow streak and adamantine luster. Single crystals, 0.01 to 0.1 mm in size, are rather rare. They show intense pleochroism (ω = brown-yellow; ε = pale greenish yellow). Idiomorphic crystals are transparent, brittle, the Mohs hardness is between 6–7. Hexagonal platy crystals commonly grow parallel to each other (Fig. 1) or form clusters up to 2 mm in size. Cleavage, parting and fluorescence were not observed.

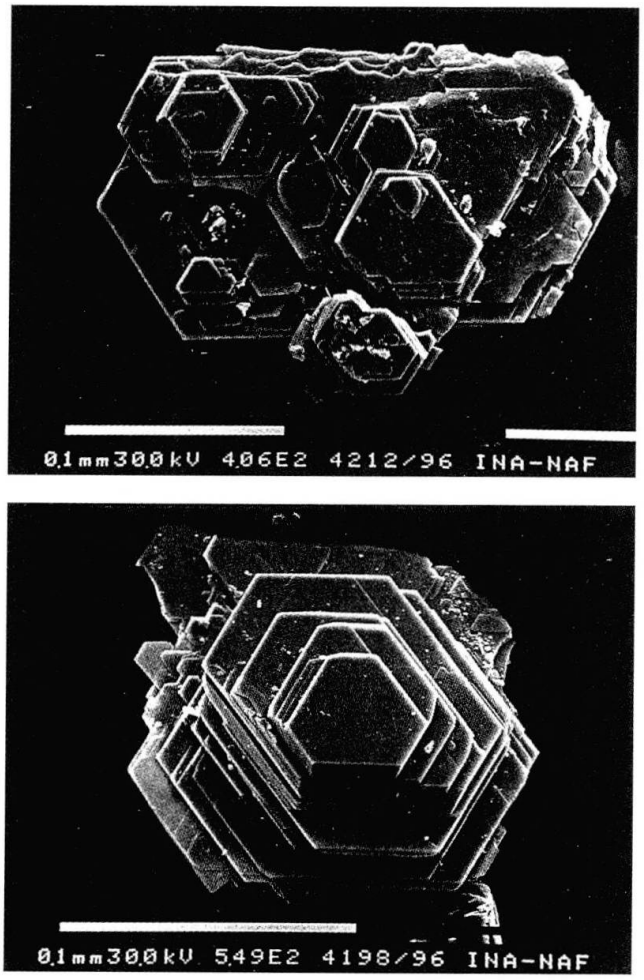

Fig. 1 Scanning electron microscopic photograph of zincohögbomite-16*H* clusters from Nezilovo, Macedonia.

Experimental

X-ray powder diffraction investigations were performed on a Philips vertical X-ray goniometer, using graphite monochromated Cu$K\alpha$ radiation (Tab. 1). The strong chemical and structural similarity between zincohögbomite-16*H* and gahnite, $ZnAl_2O_4$, leads to an overlap of the gahnite X-ray powder reflections with those of zincohögbomite-16*H* (Tab. 1). The powder pattern was calculated using the program LAZY PULVERIX (YVON et al., 1977).

Refractive indices were measured by the immersion method with white light, using the Becke line method, and with monochromatized light (sodium D line on 589.3 nm and filter on 630 nm). The flaky habit of the crystals allowed only determination of the refractive index ω which is 1.850 for 630 nm and 1.845 for 589.3 nm. Zincohögbomite-16*H* is optically negative.

X-ray precession photographs show hexagonal symmetry with $a \approx 5.7$, $c \approx 37.1$ Å. A morphological study (Fig. 2) yielded following forms: {001}, {00$\bar{1}$}, {409}, {102}, {304}, {301} and {031}. The different luster of {001} and {00$\bar{1}$} faces is a strong

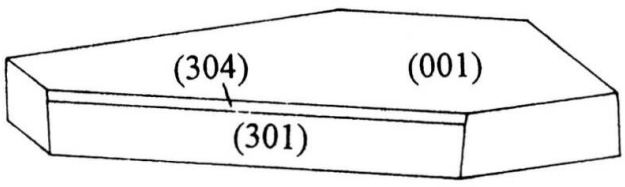

Fig. 2 Schematic representation of the morphology of zincohögbomite-16*H* from Nezilovo, Macedonia.

Tab. 1 Calculated and observed X-ray powder pattern (Cu$K\alpha$ X-radiation) for zincohögbomite-16*H* and gahnite (calculated with a = 8.086 Å; FISCHER, 1967). Only reflections with $I_{calc} > 5$ are displayed.

zincohögbomite-16*H*					gahnite		
h k l	d_{calc}	I_{calc}	d_{obs}	I_{obs}	h k l	d_{calc}	I_{calc}
1 0 1	4.918	7					
1 0 10	2.971	28	2.970	10			
1 1 0	2.865	68	2.876	55	2 2 0	2.859	73
1 0 11	2.789	35	2.797	12			
1 0 12	2.624	20	2.628	7			
1 0 13	2.474	33	2.474	13			
2 0 2	2.459	18	2.446				
1 1 8	2.437	100	2.446	100	3 1 1	2.438	100
2 0 3	2.432	28	2.446				
2 0 4	2.397	6	2.389	4			
1 0 14	2.337	10					
2 0 10	2.062	6	2.063	8	4 0 0	2.022	6
2 0 11	1.998	6					
2 1 3	1.8541	4			3 3 1	1.8551	8
2 1 10	1.6736	9					
1 0 21	1.6642	7					
3 0 0	1.6538	10	1.6560	10	4 2 2	1.6505	23
2 1 11	1.6385	11					
2 1 12	1.6033	10					
2 0 18	1.5852	7					
2 1 13	1.5672	21	1.5704	5			
3 0 8	1.5577	22	1.5607	20	5 1 1	1.5562	38
2 0 19	1.5343	8					
2 1 14	1.5307	8					

zincohögbomite-16*H* cell dimensions refined from X-ray powder data yielded a = 5.737(4), c = 37.18(8) Å.

indication for a hemimorphic crystallographic class.

Nine electron microprobe analyses were performed on several grains of zincohögbomite to examine homogeneity and chemical composition. In addition, coexisting gahnite and Zn-rich phlogopite were analyzed (Tab. 2). The accelerating voltage was 15 kV and the sample current was 10 nA, natural and synthetic oxides were used as standards: wollastonite Ca and Si $K\alpha$, corundum Al $K\alpha$, $MnTiO_3$ Ti $K\alpha$, MgO Mg $K\alpha$, albite Na $K\alpha$, hematite Fe$K\alpha$, willemite Zn $L\alpha$, antimonite Sb $L\alpha$, and chromite Cr $K\alpha$. No significant inhomogeneity was detected for zincohögbomite-16*H* and the average chemical composition was calculated on the basis of 46 cations. Possible H_2O or OH could not be determined due to the close intergrowth of zincohögbomite-16*H* with mica (which also contains OH). However, there are strong crystal chemical arguments for the presence of OH discussed below.

Single-crystal data collection on a hexagonal plate, 0.07 mm in diameter and 0.01 mm thick, was performed on an ENRAF NONIUS CAD4 single-crystal X-ray diffractometer with graphite monochromated Mo$K\alpha$ X-radiation. Cell dimensions were refined from the angular settings of 25 reflections with $8 < \theta < 17°$ yielding hexagonal symmetry with a = 5.729(2), c = 37.097(5) Å. Diffraction data were collected up to $\theta = 30°$, yielding 678 unique reflections of which 518 had $F > 4\sigma(F)$ used for structure solution and refinement. Experimental details are given in table 3. Data reduction, including background and Lorenz 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*31*c*, *P*$\bar{3}$1*c*, *P*6$_3$*mc*, *P*6$_3$/*mmc* or *P*$\bar{6}$2*c* as possible space groups. Structure solution by direct methods using the program SHELXS-97 (SHELDRICK, 1997) was only successful in the acentric space group *P*31*c*. However, following the arguments stated by PATTERSON and KASPER (1962), the structure could successfully be transformed into the space group *P*6$_3$*mc*. The observation that the structure solution was only possible in the lower symmetry space group is probably related to the strong spinel-like pseudo-symmetry discussed below. Subsequent refinement cycles in space group *P*6$_3$*mc* with neutral atom scattering factors (program SHELXL-97 by SHELDRICK

Tab. 2 Electron microprobe analyses of Nezilovo zincohögbomite-16*H* and coexisting gahnite and zinc-rich phlogopite.

	Zincohögbomite-16*H*		Gahnite		Zn-rich phlogopite			
	average	range						
SiO_2					41.31	41.06	41.06	40.96
Al_2O_3	52.99	52.35–53.41	47.59	48.25	11.94	12.11	11.59	11.80
MgO	0.70	0.60–0.91	0.14	0.15	20.57	20.44	20.48	20.14
ZnO	37.74	35.98–38.86	42.94	42.60	4.99	5.24	5.03	4.96
Fe_2O_3–FeO*	6.02	5.90–6.39	4.54	4.70	1.84*	1.88*	1.82*	1.58*
TiO_2	3.27	3.03–3.68	0.00	0.02	0.13	0.12	0.10	0.17
Mn_2O_3–MnO*			3.74	3.30	2.01*	2.00*	2.02*	2.01*
Cr_2O_3			0.01	0.02	0.00	0.00	0.00	0.03
Na_2O					0.23	0.26	0.28	0.25
K_2O					9.49	9.42	9.40	9.41
CaO					0.05	0.07	0.03	0.08
BaO					0.56	0.78	0.73	0.49
Σ	100.72		98.96	99.04	93.12	93.38	92.54	91.88
Calculated formula								
Si					3.07	3.05	3.08	3.08
Al	29.21		1.79	1.80	1.05	1.06	1.02	1.05
Mg	0.49		0.01	0.01	2.28	2.27	2.29	2.26
Zn	13.03		1.01	1.00	0.27	0.29	0.28	0.28
Fe^{3+}– Fe^{2+}*	2.12		0.11	0.11	0.11*	0.12*	0.11*	0.10*
Ti	1.15		0.00	0.00	0.01	0.01	0.01	0.01
Mn^{3+}– Mn^{2+}*			0.09	0.08	0.13*	0.13*	0.13*	0.13*
Cr			0.00	0.00	0.00	0.00	0.00	0.00
Na					0.03	0.04	0.04	0.04
K					0.90	0.89	0.90	0.90
Ca					0.00	0.01	0.00	0.01
Ba					0.02	0.02	0.02	0.01
O	62.82		4.0**	4.0**	11.0**	11.0**	11.0**	11.0**

* Analyses flagged with an asterisk were calculated with all Fe and Mn assumed to be two-valent; for those without asterisk Fe and Mn were assumed to be three-valent.

** Basis of formula normalization, the högbomite-16*H* analysis was normalized on 46 cations.

[1997]) accompanied by difference-Fourier maps yielded 15 cation and 16 oxygen positions. Because of limited diffraction data, due to the small crystal size and the high number of variables caused by the acentric symmetry, isotropic displacement parameters were refined for all atoms. In addition, cation positions of similar occupancy, symmetry, and coordination were constrained to the same displacement parameter. Cation assignment was based on interatomic distances and scattering power. Least squares refinements converged at $R = 2.42\%$ with 79 variables for 518 observations $> 4\sigma(F)$. The absolute configuration was evaluated using the FLACK (1983) x parameter which was 0.02(2), thus twinning or an inverted absolute structure could be excluded. Final atomic coordinates, populations and B_{eq} values are listed in table 4. A schematic representation of cation and oxygen stacking is given in table 5 and selected interatomic distances are summarized in table 6.

Tab. 3 Details of X-ray data collection and refinement.

space group	$P6_3mc$
a, c (Å)	5.729(2), 37.097(5)
X-radiation	Mo$K\alpha$
upper θ limit	30°
h, k, l limit	$7 \geq h \geq -8, 8 \geq k \geq -1,$ $52 \geq l \geq -1$
reflections measured	4439
unique reflections	678
reflections $> 4\sigma$ (F)	518
absorption corr.	empirical: ψ scans
absolute configuration	no enantiomorph twinning
number of parameters	79
R (on F)	2.42%
ωR (on F^2)	7.63%

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

Tab. 4 Final atomic coordinates, populations and B_{eq} values for zincohögbomite-16*H*.

atom	pop.	x/*a*	y/*b*	z/*c*	B_{eq} (Å^2)
T1	0.84(1)Zn + 0.16 Al, Mg	2/3	1/3	0.27662(4)	0.48(1) *
T2	0.95(1)Zn + 0.05 Mg, Al	0	0	0.52706(4)	0.48(1) *
T3	0.91(1)Zn + 0.09 Mg, Al	2/3	1/3	0.55878(4)	0.48(1) *
T4	0.95(1)Zn + 0.05 Mg, Al	2/3	1/3	0.65229(4)	0.48(1) *
T5	0.93(1)Zn + 0.07 Mg, Al	1/3	2/3	0.68484(4)	0.48(1) *
T6	0.88(1)Zn + 0.12 Mg, Al	1/3	2/3	0.40084(4)	0.48(1) *
T7	0.91(1)Zn + 0.09 Mg, Al	0	0	0.43266(4)	0.48(1) *
M8	1.0 Fe	1/3	2/3	0.30155(5)	0.44(3) *
M9	0.26(1)Ti + 0.74Al	–0.1660(2)	–0.3321(4)	0.35345(4)	0.51(3) *
M10	1.0 Al	0.1665(3)	0.3330(6)	0.60593(6)	0.43(3) *
M11	1.0 Al	0	0	0.6690(1)	0.49(5) *
M12	1.0 Al	2/3	1/3	0.4176(1)	0.56(5) *
M13	1.0 Al	0.5001(3)	0.0002(6)	0.48009(6)	0.44(3) *
M14	1.0 Al	–0.1698(2)	–0.3395(4)	0.73135(6)	0.48(3) *
M15	1.0 Al	1/3	2/3	0.5429(1)	0.45(5) *
O1	1.0	1/3	2/3	0.6329(2)	0.9(1) *
O2	1.0	2/3	1/3	0.5070(2)	0.9(1) *
O3	1.0	0.1867(6)	0.373(1)	0.5100(1)	0.61(9) *
O4	1.0	0	0	0.3796(2)	0.9(1) *
O5	1.0	–0.1469(5)	–0.293(1)	0.6357(1)	0.66(8) *
O6	1.0	0.5197(5)	0.039(1)	0.3852(1)	0.69(8) *
O7	1.0	0.4821(5)	0.964(1)	0.2611(1)	0.79(8) *
O8	1.0	0.1479(5)	0.2959(9)	0.7026(1)	0.53(8) *
O9	1.0	0.4824(5)	0.964(1)	0.5766(1)	0.59(8) *
O10	1.0	–0.1838(6)	–0.368(1)	0.4508(1)	0.52(9) *
O11	1.0	0	0	0.7588(2)	0.6(1) *
O12	1.0	0.1658(7)	0.332(1)	0.3260(1)	0.58(8) *
O13	1.0	0	0	0.5800(2)	0.4(1) *
O14	1.0	1/3	2/3	0.4544(2)	0.6(2) *
O15	1.0	2/3	1/3	0.3285(2)	0.8(2) *
O16	1.0	1/3	2/3	0.2054(2)	0.4(1) *

* Starred atoms were isotropically refined.

Mineral chemistry

Results of the electron-microprobe analyses on zincohögbomite-16*H* show that there is no significant intragranular variation in composition (Tab. 2). The Zn concentration of Nezilovo zincohögbomite with up to 39 wt% ZnO is significantly higher than in any other högbomite hitherto reported. Up to 21 wt% ZnO were measured by OCKENGA et al. (1998) for a 8*H* sample from Samos which was confirmed by FEENSTRA (1997) who analyzed up to 23 wt% ZnO. ZnO concentrations up to 20 wt% were reported (YALÇIN et al., 1993) for zincohögbomite from the Menderes Massif (SW Turkey). Another striking chemical pecularity of the Nezilovo zincohögbomite-16*H* is the low TiO_2 content of 3.0–3.7 wt%. Samples from the Menderes Massif have 3.2–6.5 wt% TiO_2 (YALÇIN et al., 1993) and those from Samos between and 6 and 10 wt% (FEENSTRA, 1997). The gahnite analyses from Nezilovo indicate that the coexisting spinel is saturated with respect to Zn but gahnite reveals a minor substitution of Al by Mn^{3+} and Fe^{3+} indicating rather oxidizing conditions of gahnite formation. In contrast to the metabauxites of Samos and the Menderes Massif, the Nezilovo zincohögbomite-bearing marbles also contain Zn-rich phlogopite.

Structure description

Zincohögbomite-16*H* possesses a close packed oxygen array composed of 16 oxygen layers stacked along the *c*-axis in the sequence ABCABCBACBACBABC (Tab. 5). Thus, the oxygen array consists of cubic close packed subunits with intercalated units of the hexagonal close packed type. In this structure seven cations are tetrahedrally (T sites) and eight are octahedrally coordinated (M sites); taking into account the multiplicities of the corresponding sites the crystal chemical formula $T_{14}M_{32}O_{64}$ is obtained. All tetrahedra are mainly occupied by Zn, with minor Al and/or

Mg. Six octahedra are filled with only Al (M10–M15) and two (M8 and M9) with Fe and (Ti, Al), respectively.

Inspection of the oxygen coordination indicates that, except O11 and O12 which are three-coordinated by cations, all other oxygen sites are four-coordinated. In particular, O11 participates in three rather long Al14–O11 bonds of 1.969 Å. Hence O11 is underbonded as characteristic of an OH group. In contrast, O12 is electrostatically balanced by adopting short bonds to two Ti-rich octahedra (M9) and to one Fe^{3+} octahedron (M8). Therefore, only O11 represents an OH group and the formula has to be modified to $T_{14}M_{32}O_{62}(OH)_2$. GATEHOUSE and GREY (1982) also inferred the presence of some hydroxyl groups for högbomite-8*H*, the amount of which may depend on the valence state of the cation (*e.g.*, Fe^{2+}, Fe^{3+} on M8 or Ti^{4+}, Al on M9) bonding to the potential OH group. Parallel to (001), layers of cations only occupying octahedral interstices alternate with mixed layers where octahedral and tetrahedral sites are occupied. The same two types of alternating two-dimensional cation arrangements also occur parallel to (111) in the spinel structure-type. As a matter of fact, gahnite shows a corresponding cation distribution with Zn on the tetrahedral and Al on the octahedral sites. The three-coordinated sites O11 and O12 are associated with tetrahedral vacancies in the mixed layers (Fig. 3).

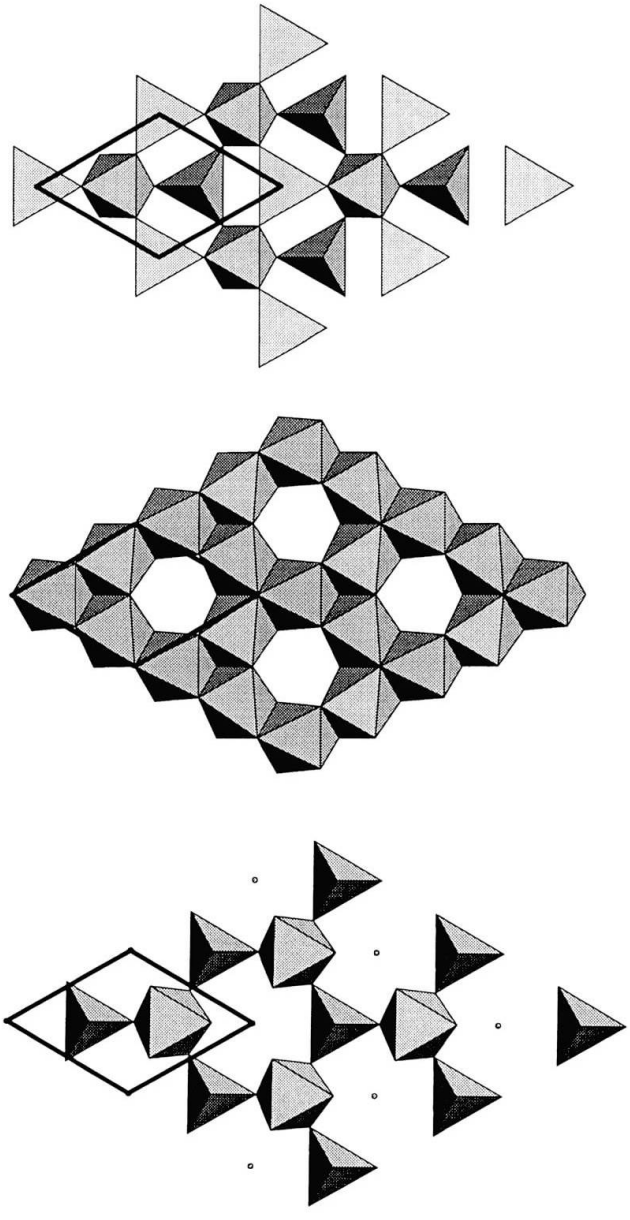

Fig. 3 Polyhedral model with unit-cell outlines of $\mathbf{T_1}$ (bottom), **O** (middle), and $\mathbf{T_2}$ (top) layers found in högbomite related structures. **O** and either $\mathbf{T_1}$ or $\mathbf{T_2}$ layers alternate parallel to the stacking direction. $\mathbf{T_1}$ layers with tetrahedral vacancies (small dots) occur only on a '*hc*' interface and are characteristic of a nolanite-like unit. An alternation of **O** and $\mathbf{T_2}$ layers is characteristic of spinel building blocks.

Tab. 5 Schematic representation of cation and oxygen stacking in zincohögbomite-16*H*, nomenclature explained in the text.

A	c	O1, O5		
			O	M10
B	c	O9, O13		
			$\mathbf{T_2}$	T2, T3, M15
C	c	O2, O3		
			O	M13
A	c	O10, O14		
			$\mathbf{T_2}$	T6, T7, M12
B	c	O4, O6		
			O	M9
C	h	O12, O15		
			$\mathbf{T_1}$	T1, M8
B	c	O7, O11		
			O	M14
A	c	O8, O16		
			$\mathbf{T_2}$	T4, T5, M11
C	c	O1, O5		
			O	M10
B	c	O9, O13		
			$\mathbf{T_2}$	T2, T3, M15
A	c	O2, O3		
			O	M13
C	c	O10, O14		
			$\mathbf{T_2}$	T6, T7, M12
B	c	O4, O6		
			O	M9
A	h	O12, O15		
			$\mathbf{T_1}$	T1, M8
B	c	O7, O11		
			O	M14
C	c	O8, O16		
			$\mathbf{T_2}$	T4, T5, M11

Tab. 6 Selected interatomic distances (Å) for zincohögbomite-16*H*.

T1	O7	1.921(5) 3x	M9	O15	1.900(5)
T1	O15	1.926(8)	M9	O4	1.913(5)
average		1.922	M9	O12	1.935(3) 2x
			M9	O6	1.963(3) 2x
T2	O3	1.958(6) 3x	average		1.935
T2	O13	1.965(8)			
average		1.960	M10	O9	1.915(3) 2x
			M10	O13	1.911(5)
T3	O9	1.944(5) 3x	M10	O5	1.915(3) 2x
T3	O2	1.921(9)	M10	O1	1.934(5)
average		1.938	average		1.918
T4	O5	1.949(5) 3x	M11	O5	1.911(6) 3x
T4	O16	1.969(9)	M11	O8	1.925(5) 3x
average		1.954	average		1.918
T5	O8	1.954(5) 3x	M12	O6	1.888(6) 3x
T5	O1	1.927(9)	M12	O10	1.928(7) 3x
average		1.947	average		1.908
T6	O6	1.938(5) 3x	M13	O14	1.909(5)
T6	O14	1.988(9)	M13	O10	1.915(3) 2x
average		1.951	M13	O3	1.918(3) 2x
			M13	O2	1.930(5)
T7	O10	1.944(6) 3x	average		1.918
T7	O4	1.967(9)			
average		1.942	M14	O16	1.887(5)
			M14	O7	1.905(3) 2x
M8	O12	1.894(6) 3x	M14	O8	1.913(3) 2x
M8	O7	2.105(5) 3x	M14	O11	1.969(4)
average		2.000	average		1.915
			M15	O3	1.898(6) 3x
			M15	O9	1.935(5) 3x
			average		1.917

Discussion

Zincohögbomite-16*H*, $Zn_{14}(Fe^{3+},Al,Ti,Mg)_8Al_{24}O_{62}(OH)_2$, from the marbles at Nezilovo has a quite different color (orange-yellow) compared to the deep brown to dark crystals from Samos or Turkey (OCKENGA et al., 1998). This lighter color is probably due to the very low content of Fe, Ni, and Co and due to the clear, transparent, and well developed crystals with only very few and minute solid inclusions.

The crystal structure of zincohögbomite-16*H* is the first description of a 16*H* sequence for högbomites in general. The new member of the group has sixteen oxygen layers stacked in the sequence ABCABCBACBACBABC (Tab. 5). The 14 tetrahedral sites per formula unit (p.f.u.) are occupied by 13 Zn p.f.u. with additional minor Mg and Al indicating that this högbomite possesses nearly end-member composition. The fundamental rules of stacking sequences in högbomites related minerals were disclosed by GREY and GATEHOUSE (1979). The latter authors recognized that this family of structures is characterized by the predominance of spinel-like cubic stacking of oxygen layers. In cubic spinels two types of cation layers (Fig. 3) alternate perpendicular to (111): (a) the octahedral layers, designated **O**, where 3/4 of the octahedral vacancies are occupied and (b) the mixed octahedral-tetrahedral layers, designated $\mathbf{T_2}$, where 1/4 of the octahedral and 1/4 of the tetrahedral voids are occupied (there are twice as many tetrahedral than octahedral voids). If the stacking sequence of oxygen layers locally changes from cubic to hexagonal close packing, the mixed octahedral-tetrahedral layer has for electrostatic reasons additional tetrahedral vacancies and only 1/8 of the tetrahedral voids are occupied (Fig. 3). Such a layer, designated $\mathbf{T_1}$, occurs *e.g.*, in the nolanite-type structure (GATEHOUSE et al., 1983). An alternative description of the ABCABCBACBACBABC stacking sequence, found

for zincohögbomite-16*H*, is the *cccchcccccchcc* nomenclature where '*c*' indicates that a specific oxygen layer is neighbored by layers stacked in the cubic close packed fashion. Correspondingly, '*h*' stands for a layer where the above and below layer are of the same stacking type (*e.g.*, BCB or BAB in the above stacking sequence). This latter nomenclature is very helpful to indicate the predominance of cubic close packed sequences and to assign the $\mathbf{T_1}$ cation layers which are between '*ch*' type sequences. In addition, the number of '*h*' layers and correspondingly the number of $\mathbf{T_1}$ layers is responsible for the ratio of octahedral/tetrahedral sites in structures related to högbomite.

In the synthetic spinel gahnite, $ZnAl_2O_4$, tetrahedral Zn–O distances are 1.950 Å whereas octahedral Al–O distances are 1.914 Å (FISCHER, 1967). These distances are very similar to the average values found for tetrahedral Zn (1.938–1.960 Å) and octahedral Al (1.908–1.918 Å) in the spinel related $\mathbf{T_2}$ and **O** cation layers of zincohögbomite-16*H*. The Zn tetrahedron T1 exhibits the shortest average Zn–O distance of 1.922 Å but this site participates together with the Fe octahedron M8 in a nolanite type $\mathbf{T_1}$ layer. Due to the similar scattering power of Mg and Al minor concentrations of these elements on tetrahedral sites can not be distinguished. However, the T1 tetrahedron reveals the shortest T–O distances thus we may assume that Al is enriched on T1 and Mg is distributed among T2–T7. The relatively short average distance M8–O of 2.000 Å determined for the Fe octahedron strongly suggests that Fe is three-valent (SHANNON, 1976). In addition, M8 exhibits a strong trigonal distortion with three long Fe^{3+}–O bonds of 2.105 Å and three short ones of 1.894 Å. The short bonds are to the three-coordinated, non-hydroxylated, O12 discussed above. The Ti-enriched octahedron M9 occurs in an **O** cation layer at the '*ch*' stacking interface. The differences in scattering power between Ti and Fe are significant enough to suggest that M8 is predominantly occupied by the heavier Fe and so Ti must be assigned to M9. Test refinements allowing for Fe and Ti on M8 converged to almost complete occupancy by Fe. Both M8 and M9 bond to non-hydroxylated, three-coordinated O12. Thus both cation sites are favored to attract high valence cations like Ti^{4+}. From a chemical point of view the formula of zincohögbomite-16*H* $Zn_{14}(Fe^{3+},Al,Ti,Mg)_8Al_{24}O_{62}(OH)_2$ may be divided into a gahnite part with the approximate composition $Zn_{12}^{IV}Al_{24}^{VI}O_{48}$ (or for convenience 2 $Zn_6Al_{12}O_{24}$) and a nolanite-like part, formed by the cation sites T1, M8, and M9, with the approximate composition $Zn_2^{IV}(Fe^{3+})_2^{VI}(Al_{0.74}Ti_{0.26})_6^{VI}O_{14}(OH)_2$ (or for convenience 2 $Zn^{IV}Fe^{3+,VI}(Al_{0.74}Ti_{0.26})_3^{VI}O_7(OH)$). This slightly simplified nolanite-like formula exhibits a charge deficit of –0.22 which is overall balanced by additional minor Al substitution in all Zn-rich tetrahedra of the spinel and nolanite units. The chemically different domains are also structurally separated. If the spinel structure (gahnite) is transformed to rhombohedral symmetry with hexagonal axes, a six layer structure with $a = 5.73$, $c = 14.04$ Å and the composition $Zn_6Al_{12}O_{24}$ results. Thus the structure of zincohögbomite-16*H* may be interpreted as a polysome assembled of an ordered intergrowth, parallel to *c*, of one complete spinel unit ($c = 14.04$ Å, corresponding to six oxygen layers) and one half nolanite-like unit ($c = 9.4/2$ Å, corresponding to two oxygen layers). These units are repeated due to the 6_3 symmetry operation.

Zincohögbomite-16*H* and Zn-rich phlogopite, which are oriented intergrown, display regular and constant cation partitionings (Fe_{tot}/Mg phlogopite ≈ 0.05 versus 4.35 for zincohögbomite-16*H*; Fe_{tot}/Zn phlogopite ≈ 0.39 versus 0.16 for zincohögbomite-16*H*), thus Fe and Zn are strongly attracted to zincohögbomite-16*H* and Mg to phlogopite. It had previously been suggested that zincohögbomite could be formed at the expense of spinel (gahnite) while Ti could be supplied by rutile (FEENSTRA, 1997). In accordance with these findings we suggest that at Nezilovo zincohögbomite-16*H* was at least partly formed at the expense of gahnite, hematite (or the ferric component of gahnite) and rutile. The latter minerals are present as solid inclusions in mica flakes which are intergrown with zincohögbomite-16*H*. Unfortunately, no detailed petrological studies are available for the metamorphic rocks in the Nezilova area (mainly phlogopite bearing gneisses with epidote, piemontite, and spessartine). According to the observed metamorphic paragenesis it seems likely that zincohögbomite-16*H* is formed by a reaction among the minerals:

$$\begin{aligned} &13\ \text{gahnite} + \ \text{rutile} + 2\ \text{hercynite} + H_2O + \\ &13\ ZnAl_2O_4 + TiO_2 + \ 2\ FeAl_2O_4 + \ H_2O + \end{aligned}$$

$$\begin{aligned} &\text{oxygen} \rightarrow \text{zincohögbomite-16}H \\ &{}^1/_2\ O_2 \rightarrow \ Zn_{13}Al_{30}Fe_2TiO_{62}(OH)_2 \end{aligned}$$

The minor Mg content could originate from the spinel phase. It is also possible that minor Mg is distributed among zincohögbomite-16*H* and phlogopite by the reaction:

$$\begin{aligned} &\text{zinc} + \text{phlogopite} \rightarrow \\ &Zn^{2+} + KMg_3(Si_3AlO_{10})(OH)_2 \end{aligned}$$

$$\begin{aligned} &\text{magnesium} + \text{hendricksite} \\ &\rightarrow Mg^{2+} \quad + KZn_3(Si_3AlO_{10})(OH)_2 \end{aligned}$$

Acknowledgements

We highly appreciate the constructive criticism by Anne Feenstra (Potsdam, Germany), Stefano Merlino (Pisa, Italy), and Ian E. Grey (Clayton, Vic., Australia) on an earlier version of this manuscript.

References

ARMBRUSTER, TH. (1998): Zincohögbomite-8*H* from Samos (Greece): crystal structure, polysomatism and polytypism in högbomite related structures. Schweiz. Mineral. Petrogr. Mitt., 78, 461–468.

BERMANEC, V., ARMBRUSTER, TH., OBERHÄNSLI, R. and ZEBEC, V. (1994): Crystal chemistry of Pb- and REE-rich piemontite from Nezilovo, Macedonia. Schweiz. Mineral. Petrogr. Mitt., 74, 321–328.

BERMANEC, V., HOLTSTAM, D., STURMAN, D., CRIDDLE, A., BACK, M. and SCAVNICAR, S. (1996): Nezilovite, a new member of the magnetoplumbite group, and the crystal chemistry of magnetoplumbite and hibonite. Can. Mineral., 34, 1287–1297.

ENRAF NONIUS (1983): Structure determination package (SDP). Enraf Nonius, Delft, Holland.

FEENSTRA, A. (1997): Zincohögbomite and gahnite in a diaspore-bearing metabauxite from eastern Samos (Greece): mineral chemistry, element partitioning and reaction relations. Schweiz. Mineral. Petrogr. Mitt., 77, 73–93.

FISCHER, P. (1967): Neutronenbeugungsuntersuchungen der Strukturen von $MgAl_2O_4$- and $ZnAl_2O_4$-Spinellen, in Abhängigkeit von der Vorgeschichte. Zeitschr. Kristallogr., 124, 275–302.

FLACK, H.D. (1983): On enantiomorph-polarity estimation. Acta Crystallogr., A39, 876–881.

GATEHOUSE, B.M. and GREY, I.E. (1982): The crystal structure of högbomite-8*H*. Amer. Mineral., 67, 373–380.

GATEHOUSE, B.M., GREY, I.E. and NICKEL, E.H. (1983): The crystal chemistry of nolanite, $(V,Fe,Ti,Al)_{10}O_{14}(OH)_2$, from Kalgoorlie, Western Australia. Amer. Mineral., 68, 833–859.

GREY, I.E. and GATEHOUSE, B.M. (1979): The crystal structure of nigerite-24R. Amer. Mineral., 64, 1255–1264.

MCKIE, D. (1963): The högbomite polytypes. Min. Mag., 33, 563–580.

OCKENGA, E., YALÇIN, Ü., MEDENBACH, O. and SCHREYER, W. (1998): Zincohögbomite-8*H*, a new mineral in eastern Aegean metabauxites. Euro. J. Mineral., in press.

PATTERSON, A.L. and KASPER, J.S. (1962): International Tables for X-Ray Crystallography, Vol. 2, pp. 342–355. Kynoch Press, Birmingham.

PEACOR, D.R. (1967): New data on nigerite. Amer. Mineral., 52, 864–866.

PETERSEN, E.U., ESSENE, E.J., PEACOR, D.R. and MARCOTTY, L.A. (1989): The occurrence of högbomite in high-grade metamorphic rocks. Contrib. Mineral. Petrol., 101, 350–360.

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

SHELDRICK, G.M. (1997): SHELXL-97 and SHELXS-97. Programs for crystal structure determination. University of Göttingen, Germany.

YALÇIN, Ü., SCHREYER, W. and MEDENBACH, O. (1993): Zn-rich högbomite formed from gahnite in the metabauxites of the Menderes Massif, SW Turkey. Contrib. Mineral. Petrol, 113, 314–324.

YVON, K., JEITSCHKO, W. and PARTHÉ, E. (1977): LAZY PULVERIX, a computer program, for calculating X-ray and neutron diffraction powder patterns. J. Appl. Cryst., 10, 73–74.

Manuscript received May 12, 1998; revision accepted July 12, 1998.