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Article

Magnesiohögbomite-6N12S, Mg$_5$Al$_{11}$TiO$_{23}$(OH), a new högbomite-group mineral from the DeWitts Corners, Ontario, Canada

Inna Lykova[1]* , Ralph Rowe[1], Glenn Poirier[1], Gerald Giester[2] and Kate Helwig[3]

[1]Canadian Museum of Nature, PO Box 3443, Station "D", Ottawa, Ontario K1P 6P4, Canada; [2]Institute of Mineralogy and Crystallography, University of Vienna, Vienna A–1090, Austria; and [3]Canadian Conservation Institute, 1030 Innes Road, Ottawa, Ontario K1B 4S7, Canada

Abstract

The new högbomite-group mineral magnesiohögbomite-6N12S, ideally Mg$_5$Al$_{11}$TiO$_{23}$(OH), was found in calcite "vein-dikes" at the DeWitts Corners occurrence, lots 10 and 11, concession 1, Bathurst Township, Ontario, Canada. It forms tabular and short-prismatic crystals up to 5 mm in size. The major forms are pinacoid {0001} and hexagonal pyramid {11$\bar{2}$1}, sometimes modified by hexagonal prism {11$\bar{2}$0}. The associated minerals are magnesiohögbomite-2N3S, spinel, corundum, diopside, magnesio-hastingsite, pargasite, clinochlore and calcite. Magnesiohögbomite-6N12S is dark brown to black with brown streak and vitreous lustre. It has no cleavage and its fracture is uneven. The Mohs hardness is 6½. D_{calc} is 3.87 g/cm^3. The infrared spectrum is reported. The composition (wt.%) is MgO 13.09, ZnO 0.46, FeO 11.91, Fe$_2$O$_3$ 6.84, Al$_2$O$_3$ 62.70, TiO$_2$ 4.44, H$_2$O 0.99, total 100.43. The empirical formula calculated on the basis of 17 cations, excluding H$^+$, is (Mg$_{2.95}$Fe$^{2+}_{1.51}$Al$_{0.49}$Zn$_{0.05}$)$_{\Sigma5}$(Al$_{10.71}$Fe$^{3+}_{0.78}$Ti$_{0.51}$)$_{\Sigma12}$O$_{23}$(OH). The simplified formula is (Mg,Fe)$_5$(Al,Fe, Ti)$_{12}$O$_{23}$(OH). The mineral is trigonal, $R\bar{3}m$, $a = 5.7194(2)$, $c = 83.069(5)$ Å, $V = 2353.3(2)$ Å^3 and $Z = 6$. The strongest reflections of the powder X-ray diffraction pattern [d,Å(I)(hkl)] are: 2.921(26)(0.1.23), 2.863(49)(110), 2.687(29)(0.1.26), 2.547(31)(0.1.$\bar{28}$) and 2.434(100)(1.1.18). The crystal structure was solved and refined from single-crystal X-ray diffraction data to $R_1 = 0.022$. It is composed of alternating spinel (S) and nolanite (N) modules in the sequence 3 × ($NSSNSS$). The sequence of cubic 'c' and hexagonal 'h' closed-packed oxygen layers is 3 × ($cccccchcccch$). It is the first polysome in the högbomite supergroup with such a sequence.

Keywords: magnesiohögbomite-6N12S, new mineral, magnesiohögbomite-2N3S, högbomite group, crystal structure, polysome, Canada

Introduction

The högbomite-supergroup minerals are complex oxides that form a polysomatic series composed of spinel $T_2M_4O_8$ (S) and nolanite TM_4O_7(OH) (N) modules, where T and M represent tetrahedrally and octahedrally coordinated cations, respectively (Armbruster, 1998, 2002; Heiny and Armbruster, 2002). Five groups belonging to the högbomite supergroup are known. The taaffeite group includes minerals with modified nolanite BeTM_4O_8 (N') modules (Armbruster, 2002). The velesite group, the only one known with iron-spinel modules (T_2Fe$_4$O$_8$), currently consists of one parent species zincovelesite-6N6S, Zn$_3$(Fe^{3+},Mn^{3+},Al,Ti)$_8$O$_{15}$(OH) (Chukanov *et al.*, 2018). The remaining three – högbomite, nigerite (Armbruster, 2002) and beltrandoite (Cámara *et al.*, 2018) groups – include minerals with aluminium-spinel modules (T_2Al$_4$O$_8$). They are named based on the combination of the predominant cation at the largest M-centred octahedron in the N module [rootname; Ti – högbomite, Sn – nigerite (Armbruster, 2002) and Fe^{3+} – beltrandoite (Cámara *et al.*, 2018)], the predominant T in the S module [prefix; Mg – magnesio, Fe^{2+} – ferro and Zn – zinco, e.g.

magnesiotaaffeite] and the total number of N and S modules [hyphenated suffix; e.g. zincohögbomite-2N6S, ferronigerite-6N6S and magnesiobeltrandoite-2N3S].

Magnesiohögbomite-6N12S, (Mg,Fe)$_5$(Al,Fe,Ti)$_{12}$O$_{23}$(OH), is a new member of the högbomite group described in this paper. It is named in accordance with the International Mineralogical Association (IMA) nomenclature of the högbomite supergroup (Armbruster, 2002) as a mineral with Ti as the predominant cation in the N module [rootname högbomite], Mg – the predominant T in the S module [prefix magnesio-], and 6 and 12 as the total number of N and S modules, respectively [hyphenated suffix 6N12S]. Both the new mineral and the name have been approved by the Commission on New Minerals, Nomenclature and Classification of the IMA, (IMA2020-029; Lykova *et al.*, 2020). The holotype was deposited in the collection of the Canadian Museum of Nature, Ottawa, Canada. The catalogue number is CMNMC 87484.

Occurrence and general appearance

The mineral was found at the DeWitts Corners occurrence, lots 10 and 11, concession 1, Bathurst Township, Lanark County, Ontario, Canada (44°49′47″N, 76°21′05″W). Magnesiohögbomite-6N12S occurs, together with magnesiohögbomite-2N3S, Mg$_4$Al$_9$TiO$_{19}$(OH), black spinel, corundum, diopside, magnesio-hastingsite, pargasite and clinochlore, in calcite "vein-dikes". The

*Author for correspondence: Inna Lykova, Email: ilykova@nature.ca

Fig. 1. Tabular magnesiohögbomite-6*N*12*S* crystal and prismatic magnesiohögbomite-2*N*3*S* crystal on spinel. Field of view = 2 mm. Specimen CMNMC 88160. Photo: Paul Sokoloff and Inna Lykova.

host rocks are marble of the Central Metasedimentary Belt of the Precambrian Grenville Geological Province (Wynne-Edwards, 1972). The "vein-dikes" were exposed in two adjacent shallow pits separated by a road, and thus located at different lots. The holotype of magnesiohögbomite-6*N*12*S* originates from the pit located at the lot 11; however, the new mineral was found in pits at both lot 10 and lot 11.

The origin of calcite "vein-dikes" has long been a subject of debates. However, in a recent study Martin and Schumann (2019) argued that at least some of the "vein-dikes" were formed as a result of melting of Grenville marble.

Magnesiohögbomite-6*N*12*S* occurs as thin tabular to short-prismatic crystals up to 5 mm in size (Fig. 1). The major forms are pinacoid {0001} and hexagonal pyramid {11$\bar{2}$1}, often striated. Some crystals also show a striated hexagonal prism {11$\bar{2}$0}. Most often magnesiohögbomite-6*N*12*S* forms tabular crystals as epitaxial overgrowths on spinel. The {0001} faces of magnesiohögbomite-6*N*12*S* and the {111} faces of spinel are parallel. Free standing crystals are rare and can be found on, or in, spinel and, sometimes, corundum pseudomorphs after spinel. Short-prismatic crystals with striated pyramid and prism faces have a barrel shape. Magnesiohögbomite-6*N*12*S* occurs together with visually indistinguishable magnesiohögbomite-2*N*3*S* (Fig. 1). No preference for a particular habit or association was found for either of the polysomes, and the two minerals are roughly equally abundant at the occurrence.

Physical and optical properties

Magnesiohögbomite-6*N*12*S* is dark brown to black with brown streak and vitreous lustre. It has no cleavage or parting. The Mohs hardness is 6½. The fracture is uneven. The mineral is non-fluorescent under ultraviolet light. The density calculated using the empirical formula and unit-cell volume refined from the single-crystal XRD data is 3.87 g/cm^3.

Magnesiohögbomite-6*N*12*S* is optically uniaxial (–). The refractive indices were not measured due to the lack of available high refractive index (> 1.8) immersion fluids. The mean refractive index obtained from the Gladstone–Dale relationship (Mandarino, 1981) is 1.857. Pleochroism is weak; the absorption scheme is as follows: O = brown and E = pale brown.

Experimental methods

Chemical data for magnesiohögbomite-6*N*12*S* and magnesiohögbomite-2*N*3*S* were obtained using a JEOL 8230 SuperProbe electron microscope equipped with five WDS spectrometers (University of Ottawa – Canadian Museum of Nature MicroAnalysis Laboratory, Canada) with an acceleration voltage of 20 kV, a beam current of 40 nA and a beam diameter of 5 μm. The following reference materials were used: chromite (Mg*K*α and Al*K*α), hematite (Fe*K*α), gahnite (Zn*K*α) and rutile (Ti*K*α). Raw intensities were converted to concentrations using the default φρZ corrections of the *Probe for EMPA* software package (Armstrong, 1988). Water contents were calculated from stoichiometry and included in the matrix correction.

The Fourier transform infrared (FTIR) spectrum of magnesiohögbomite-6*N*12*S* was obtained at the Canadian Conservation Institute, Canada using a Bruker Hyperion 2000 microscope interfaced to a Tensor 27 spectrometer with a wide-band mercury cadmium telluride (MCT) detector. A small fragment of magnesiohögbomite-6*N*12*S* was mounted on a low-pressure diamond anvil microsample cell and analysed in transmission mode. The spectrum was collected between 400–4000 cm^{-1} with the co-addition of 150 scans at a 4 cm^{-1} resolution.

Powder X-ray diffraction data were collected at the Canadian Museum of Nature, Canada using a Bruker D8 Discover micro-diffractometer equipped with a DECTRIS EIGER2 R 500K detector and IμS microfocus X-ray source (λCu*K*α = 1.54184 Å). The instrument was calibrated at a sample-to-detector distance of 175 mm using a statistical calibration method (Rowe, 2009). A powder ball 200 μm in diameter, mounted on a fibre pin mount, was analysed with continuous Phi rotation and 10° rocking motion along the Psi axis of the Centric Eulerian Cradle stage.

Single-crystal X-ray studies were carried out at *T* = 296 K using a Bruker Kappa X8 APEX diffractometer equipped with a CCD detector and with an Incoatec Microfocus Source IμS (30 W, multi-layer mirror, Mo*K*α) at the Institute of Mineralogy and Crystallography, University of Vienna, Austria. Eighteen sets of phi and omega scans with 0.75° scanwidth were measured up to 80°2θ (full sphere) at a crystal-detector distance of 50 mm. The absorption was corrected by evaluation of multi-scans (Krause *et al.* 2015).

Results

Chemical data

Chemical data for magnesiohögbomite-6*N*12*S* and magnesiohögbomite-2*N*3*S* are given in Table 1. The data on the holotype of magnesiohögbomite-6*N*12*S* (6 analyses) were collected on a crystal later used for the crystal-structure study. The empirical formula calculated on the basis of 17 cations, excluding H$^+$, is $(Mg_{2.95}Fe^{2+}_{1.51}Al_{0.49}Zn_{0.05})_{\Sigma5}(Al_{10.71}Fe^{3+}_{0.78}Ti_{0.51})_{\Sigma12}O_{23}(OH)$. The Fe^{2+}/Fe^{3+} ratio was calculated by the charge balance. For comparison, the formula calculated based on an average of 25 analyses of six crystals from different specimens is $(Mg_{3.01}Fe^{2+}_{1.46}Al_{0.49}Zn_{0.04})_{\Sigma5}(Al_{10.66}Fe^{3+}_{0.83}Ti_{0.51})_{\Sigma12}O_{23}(OH)$. The data show that the mineral is homogeneous. The empirical formula of magnesiohögbomite-2*N*3*S* based on an average of 31 analyses of six crystals and calculated on the basis of 14 cations, excluding H$^+$, is $(Mg_{2.36}Fe^{2+}_{1.08}Al_{0.52}Zn_{0.04})_{\Sigma4}(Al_{8.69}Fe^{3+}_{0.83}Ti_{0.48})_{\Sigma10}O_{19}(OH)$.

The simplified formula of magnesiohögbomite-6*N*12*S* is $(Mg,Fe)_5(Al,Fe,Ti)_{12}O_{23}(OH)$. The end-member formula is $Mg_5Al_{11}TiO_{23}(OH)$, which requires MgO 23.68, Al$_2$O$_3$ 65.88, TiO$_2$ 9,38, H$_2$O 1.06, total 100 wt.%.

Table 1. Chemical data (wt.%) for magnesiohögbomite-6*N*12*S* and magnesiohögbomite-2*N*3*S* from the DeWitts Corners.

| | Magnesiohögbomite-6*N*12*S* | | | | Magnesiohögbomite-2*N*3*S* | |
| | holotype, average of 6 analyses | | average of 25 analyses of 6 crystals | | average of 31 analyses of 6 crystals | |
Constituent	Mean	Range	Mean	Range	Mean	Range
MgO	13.09	12.86–13.36	13.30	11.96–13.88	12.60	12.22–13.15
ZnO	0.46	0.43–0.48	0.40	0.30–0.63	0.38	0.30–0.73
[FeO(total)]	[18.05]	17.72–18.32	[17.99]	17.38–20.16	[18.20]	17.43–18.91
FeO*	11.91		11.49		10.28	
Fe₂O₃*	6.84		7.26		8.78	
Al₂O₃	62.70	61.54–63.75	62.27	61.54–63.75	62.17	61.27–63.22
TiO₂	4.44	4.37–4.48	4.49	4.09–4.80	5.11	4.44–5.61
H₂O**	0.99		0.99		1.19	
Total	100.43		100.20		100.51	
Atoms per formula unit (based on 17 cations, excluding H⁺ for magnesiohögbomite-6*N*12*S* and 14 cations for magnesiohögbomite-2*N*3*S*)						
Mg	2.95		3.01		2.36	
Zn	0.05		0.04		0.04	
Fe²⁺	1.51		1.46		1.08	
Fe³⁺	0.78		0.83		0.83	
Al	11.20		11.15		9.21	
Ti	0.51		0.51		0.48	
H	1.00		1.00		1.00	

*Fe^{2+}/Fe^{3+} ratio was calculated based on the charge balance.
**Calculated from the stoichiometry.

Magnesiohögbomite-6*N*12*S* does not react with a diluted aqueous HCl solution at room temperature.

Infrared spectroscopy

The IR spectrum of magnesiohögbomite-6*N*12*S* (Fig. 2) shows IR bands of O–H-stretching (at 3365 cm⁻¹) vibrations and *M*–O-stretching (in the range from 440 to 680 cm⁻¹) vibrations where *M* = Mg, Fe, Al, Ti and Zn. The band assignment was made in accordance with Chukanov and Chervonnyi (2016).

Characteristic bands of H–O–H bending vibrations of H_2O molecules (in the range 1550–1750 cm⁻¹) and CO_3^{2-} anions (in the range 1350–1550 cm⁻¹) are absent in the IR spectrum of magnesiohögbomite-6*N*12*S*.

X-ray diffraction data

The indexed powder X-ray diffraction data are given in Table 2. Parameters of the trigonal unit cell refined from the powder data are as follows: $a = 5.7262(1)$, $c = 83.1262(6)$ Å and $V = 2360.51(2)$ Å³.

The single-crystal X-ray diffraction data were indexed in the $R\bar{3}m$ space group with the following unit-cell parameters: $a = 5.7194(2)$, $c = 83.069(5)$ Å and $V = 2353.3(2)$ Å³. The structure was solved and refined to $R_1 = 0.022$ on the basis of 1891
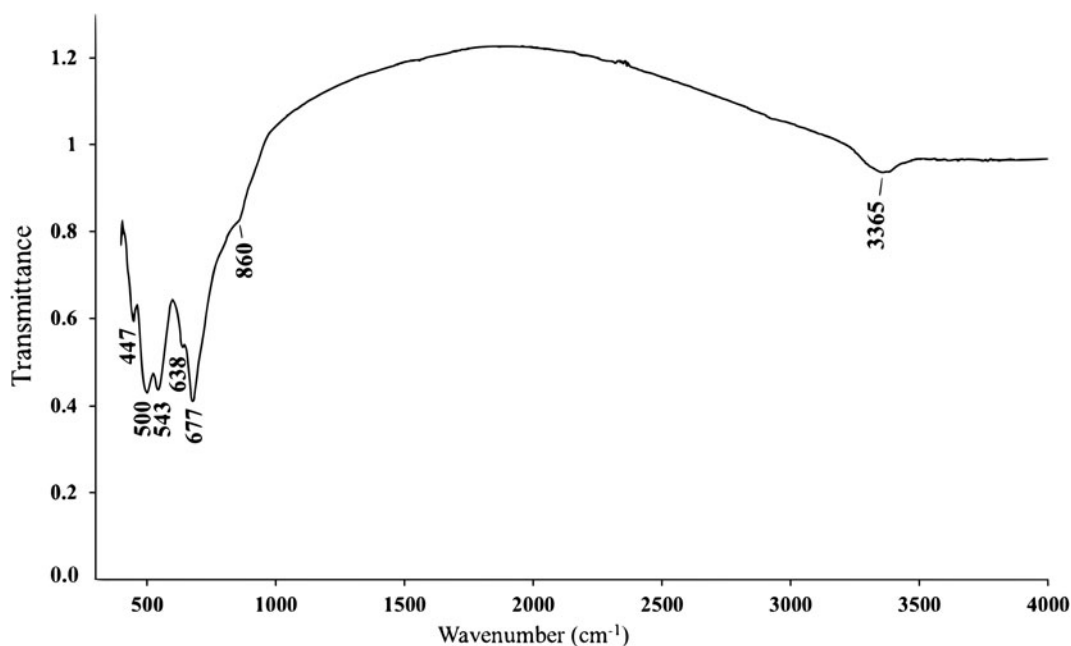

Fig. 2. Infrared spectrum of magnesiohögbomite-6*N*12*S*.

Table 2. Powder X-ray diffraction data (*d* in Å) for magnesiohögbomite-6*N*12*S*. The strongest lines are in bold.

$I_{obs.}$	$I_{calc.}$[a]	$d_{obs.}$	d_{calc}[b]	*hkl*
5	2	27.79	27.69	003
4	3	4.943	4.944	$01\bar{1}$
4	2	4.825	4.818	$01\bar{4}$
10	7	4.620	4.615	0.0.18
16	12	4.575	4.571	$01\bar{7}$
8	5	4.146	4.142	0.1.11
6	4	3.920	3.915	$0.1.\bar{13}$
6	3	3.481	3.479	0.1.17
8	7	3.282	3.278	$0.1.\bar{19}$
7	3	3.005	3.003	$0.1.\bar{22}$
26	23	**2.921**	2.918	0.1.23
49	43	**2.863**	2.860	110
29	26	**2.687**	2.685	0.1.26
31	27	**2.547**	2.545	$0.1.\bar{28}$
19	14	2.482	2.480	0.1.29
7	4	2.462	2.459	024
17	18	2.453	2.450	02-5
100	100	**2.434**	2.431	1.1.18
13	9	2.426	2.424	027
15	14	2.412	2.409	02-8
6	4	2.377	2.373	0.2.10
11	9	2.359	2.357	$0.1.\bar{31}$
4	2	2.301	2.299	0.1.32
8	6	2.289	2.286	$0.2.\bar{14}$
7	4	2.238	2.235	0.2.16
10	7	2.130	2.127	$0.2.\bar{20}$
22	20	**2.073**	2.071	0.2.22
15	12	2.045	2.043	$0.2.\bar{23}$
23	20	**1.9879**	1.9857	0.2.25
8	6	1.9595	1.9574	$0.2.\bar{26}$
4	3	1.8751	1.8734	$0.2.\bar{29}$
3	3	1.6984	1.6966	$0.1.\bar{46}$
11	2, 3, 8	1.6647	1.6646, 1.6634, 1.6621	0.1.47, 0.2.37, 1.2.23
5	6	1.6534	1.6510	030
10	11	1.6174	1.6152	1.2.26
3	2	1.5934	1.5913	0.2.40
15	15	1.5850	1.5832	$1.2.\bar{28}$
21	10, 13	**1.5693**	1.5682, 1.5671	$0.2.\bar{41}$, 1.2.29
22	12, 11	**1.5565**	1.5546, 1.5546	0.3.18, $0.3.\bar{18}$
8	3, 9	1.5365	1.5383, 1.5363	0.0.54, $1.2.\bar{31}$
15	16	1.5029	1.5014	$0.2.\bar{44}$

[a]Calculated from the crystal structure determination, only reflections with intensities >1 are given.
[b]For the unit-cell parameters calculated from single-crystal data.

Table 3. Crystal data, data collection information and structure refinement details for magnesiohögbomite-6*N*12*S*.

Crystal data	
Ideal formula	$Mg_5Al_{11}TiO_{23}(OH)$
Crystal dimensions (mm)	$0.025 \times 0.050 \times 0.070$
Crystal system, space group	Trigonal, $R\bar{3}m$
a, *c* (Å)	5.7194(2), 83.069(5)
V (Å³)	2353.3(2)
Z	6
Calculated density (g cm⁻³)	3.87
μ (mm⁻¹)	3.25
Data collection	
Crystal description	Dark brown tabular crystal
Instrument	Bruker Kappa X8 APEX CCD
Radiation type, wavelength (Å)	Mo*Kα*, 0.71073
Number of frames	2815
θ range (°)	1.47–40.26
Absorption correction	Multi-scan (Krause *et al.*, 2015)
T_{min}, T_{max}	0.683, 0.748
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	51020, 2011, 1891
R_{int}	0.0252
Data completeness to 33.39°θ (%)	99.95
Indices range of *h*, *k*, *l*	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-150 \leq l \leq 150$
Refinement	
Refinement	Full-matrix least-squares on F^2
Number of reflections, parameters, restraints	2011, 113, 7
R_1 [$I > 2\sigma I$], R_1(all)	0.022, 0.023
wR_2 [$I > 2\sigma I$], wR_2(all)	0.054, 0.055
GoF	1.021
No. of refined parameters	113
$\Delta\rho_{max} / \Delta\rho_{min}$ ($e^- Å^{-3}$)	0.59 / −1.00

independent reflections with $I > 2\sigma(I)$ using the *SHELXL-2018/3* program package (Sheldrick, 2015). Crystal data, data collection and structure refinement details are given in Table 3, atom coordinates, equivalent displacement parameters, site occupancy factors in Table 4, selected interatomic distances in Table 5 and bond valence sums (BVS) in Table 6.

The crystallographic information file for magnesiohögbomite-6*N*12*S* has been deposited with the Principal Editor of *Mineralogical Magazine* and is available as Supplementary material (see below). It was also deposited in the Inorganic Crystal Structure Database (ICSD; #CSD 2046917).

Discussion

Crystal structure

Magnesiohögbomite-6*N*12*S*, $6 \times [(Mg,Fe)_5(Al,Fe,Ti)_{12}O_{23}(OH)]$, is a new polysome of the högbomite group formed by alternation of *N* and *S* modules in the sequence $3 \times (NSSNSS)$ leading to general formula $6 \times T_5M_{12}O_{23}(OH)$. The sequence of cubic '*c*' and hexagonal '*h*' closed-packed oxygen layers is $3 \times (cccccchcccch)$. The structure of a potentially new 6*N*12*S* polysome of the högbomite supergroup was predicted to have the sequences $3 \times (NNSSSS)$ and $3 \times (ccccccchchch)$ (Armbruster, 2002). As our study shows 6*N*12*S* polysomes have a different sequence of the *c* and *h* layers that has not been observed in the högbomite supergroup minerals before.

There are five independent *T* sites and seven independent *M* sites in the structure. Mg, Fe^{2+}, Fe^{3+}, Al and Ti are distributed among these sites based on the microprobe data and refined site-scattering factors (e_{ref}, in electrons per site) taking into account bond valence sums (BVS) and interatomic distances (Tables 4–6). The smallest tetrahedron $Mg(5)O_4$ with the average <Mg5–O> distance of 1.838 Å and the largest octahedron $Ti(12)O_6$ with the average <Ti12–O> distance of 2.036 Å in the structure belong to the *N* module (Fig. 3). The site occupancy at the Mg5 site was refined, assuming full occupancy, as $Mg_{0.803(4)}Fe_{0.197(4)}$ [$e_{ref} = 14.8$]. In the final refinement cycles the occupancy was fixed as $Mg_{0.43}Al_{0.40}Fe^{3+}_{0.17}$. The Ti12 site is occupied by $0.52Ti + 0.39Fe^{3+} + 0.09Fe^{2+}$. The proposed distribution is supported by the observed bond-valence sums at these sites [2.64 valence units (vu) at the Mg5 site and 3.21 vu at the Ti12 site, Table 6]. The other four *T* sites are Mg/Fe^{2+} mixed-occupancy sites with preferential occupancy of Mg (68, 61, 70 and 62% at the Mg1, Mg2, Mg3 and Mg4 sites, respectively; Table 4). *M* sites Al6, Al7, Al8, Al9 and Al10 are fully occupied by Al atoms, while there is an admixture of Fe^{3+} atoms (8% of the site occupancy) at the Al11 site. The ideal composition for the *N* module is $Mg(Al_3Ti)O_7(OH)$ and for the *S* module is $Mg_2Al_4O_8$.

Table 4. Coordinates and equivalent displacement parameters (U_{eq}, in Å²) of atoms and site occupancies for magnesiohögbomite-6N12S.

Site	W^a	x/a	y/b	z/c	U_{eq}	Site occupancy
Mg1	6c	⅔	⅓	0.35437(2)	0.00471(12)	$Mg_{0.683(4)}Fe^{2+}_{0.317(4)}$
Mg2	6c	0	1	0.36927(2)	0.00505(11)	$Mg_{0.607(4)}Fe^{2+}_{0.393(4)}$
Mg3	6c	1	1	0.47882(2)	0.00482(12)	$Mg_{0.703(4)}Fe^{2+}_{0.297(4)}$
Mg4	6c	⅓	⅔	0.46466(2)	0.00465(11)	$Mg_{0.621(4)}Fe^{2+}_{0.379(3)}$
Mg5	6c	⅓	⅔	0.42368(2)	0.00357(8)	$Mg_{0.43}Al_{0.40}Fe^{3+}_{0.17}$*
Al6	9d	0	½	½	0.00305(7)	Al
Al7	6c	⅔	⅓	0.47192(2)	0.00316(9)	Al
Al8	18h	0.83591(3)	0.67183(6)	0.44381(2)	0.00431(6)	Al
Al9	6c	⅓	⅔	0.36113(2)	0.00360(9)	Al
Al10	9e	⅙	⅓	⅓	0.00322(7)	Al
Al11	18h	0.50228(3)	0.00457(6)	0.38973(2)	0.00446(8)	$Al_{0.916(2)}Fe^{3+}_{0.084(2)}$
Ti12	6c	1	1	0.41203(2)	0.00352(5)	$Ti_{0.52}Fe^{3+}_{0.39}Fe^{2+}_{0.09}$**
O1	6c	⅔	⅓	0.43181(2)	0.0074(2)	O
H1	6c	⅔	⅓	0.4210(5)	0.09(2)^b	H
O2	6c	0	1	0.34563(2)	0.00480(18)	O
O3	6c	⅔	⅓	0.51193(2)	0.00470(18)	O
O4	6c	⅔	⅓	0.37787(2)	0.00559(18)	O
O5	6c	⅓	⅔	0.40153(2)	0.0070(2)	O
O6	6c	1	1	0.45549(2)	0.00642(19)	O
O7	18h	−0.03696(16)	0.48152(8)	0.45722(2)	0.00715(12)	O
O8	18h	0.33719(15)	0.16860(8)	0.40142(2)	0.00632(11)	O
O9	18h	0.81463(7)	0.18537(7)	0.48681(2)	0.00416(10)	O
O10	18h	0.03746(14)	0.51873(7)	0.34630(2)	0.00408(10)	O
O11	18h	0.18570(8)	0.37140(17)	0.37557(2)	0.00761(12)	O
O12	18h	0.68630(17)	0.84315(9)	0.43047(2)	0.00851(12)	O

^{a}Wyckoff site; $^b U_{iso}$.
*The Mg5 site occupancy was refined assuming full occupancy and refining Mg (including the similarly light Al) against Fe, the best agreement was obtained with $Mg_{0.803(4)}Fe_{0.197(4)}$. In the final refinement cycles the occupancy was fixed as $Mg_{0.43}Al_{0.40}Fe_{0.17}$ on the e_{ref} value [14.8], electron microprobe data, interatomic distances and bond valence calculations.
**The Ti12 site was refined as $Ti_{0.519(7)}Fe_{0.481(7)}$.

Table 5. Selected interatomic distances (Å) in the structure of magnesiohögbomite-6N12S.

Mg1–O4	1.952(1)	Mg5–O12	1.837(1) ×3	Al9–O11	1.892(1) ×3
Mg1–O10	1.955(1) ×3	Mg5–O5	1.840(1)	Al9–O10	1.915(1) ×3
<Mg1–O>	1.954	<Mg5–O>	1.838	<Al9–O>	1.904
Mg2–O11	1.913(1) ×3	Al6–O9	1.912(1) ×4	Al10–O10	1.901(1) ×4
Mg2–O2	1.963(1)	Al6–O3	1.926(1) ×2	Al10–O2	1.942(1) ×2
<Mg2–O>	1.926	<Al6–O>	1.916	<Al10–O>	1.915
Mg3–O6	1.938(1)	Al7–O7	1.910(1) ×3	Al11–O8	1.897(1) ×2
Mg3–O9	1.953(1) ×3	Al7–O9	1.918(1) ×3	Al11–O4	1.903(1)
<Mg3–O>	1.949	<Al7–O>	1.914	Al11–O5	1.940(1)
				Al11–O11	1.968(1) ×2
Mg4–O7	1.935(1) ×3	Al8–O6	1.893(1)	<Al11–O>	1.929
Mg4–O3	1.944(1)	Al8–O7	1.936(1) ×2		
<Mg4–O>	1.938	Al8–O12	1.938(1) ×2	Ti12–O8	1.889(1) ×3
		Al8–O1	1.950(1)	Ti12–O12	2.182(1) ×3
		<Al8–O>	1.932	<Ti12–O>	2.036

Table 6. Bond valence calculations* for magnesiohögbomite-6N12S.

	Mg1	Mg2	Mg3	Mg4	Mg5	Al6	Al7	Al8	Al9	Al10	Al11	Ti12	Σ	H bonding	Σ
O1								0.45$^{×3→}$					1.35	−0.13[O8]	1.22
O2		0.50								0.46$^{×2↓×3→}$			1.88		1.88
O3			0.53			0.48$^{×2↓×3→}$							1.97		1.97
O4	0.52										0.52$^{×3→}$		2.08		2.08
O5					0.66						0.47$^{×3→}$		2.07		2.07
O6			0.53					0.52$^{×3→}$					2.09		2.09
O7				0.54$^{×3↓}$			0.50$^{×3↓}$	0.46$^{×2↓×2→}$					1.96		1.96
O8											0.53$^{×2↓×2→}$	0.74$^{×3↓}$	1.80	+0.13[O1]	1.93
O9			0.51$^{×3↓}$			0.49$^{×4↓×2→}$	0.49$^{×3↓}$						1.98		1.98
O10	0.51$^{×3↓}$								0.49$^{×3↓}$	0.51$^{×4↓×2→}$			2.02		2.02
O11		0.58$^{×3↓}$							0.52$^{×3↓}$		0.44$^{×2↓×2→}$		1.98		1.98
O12					0.66$^{×3↓}$			0.46$^{×2↓×2→}$				0.33$^{×3↓}$	1.91		1.91
Σ	2.05	2.24	2.06	2.15	2.64	2.92	2.97	2.81	3.03	2.96	2.93	3.21			

*Bond-valence parameters were taken from Brese and O'Keeffe (1991) and, for H bonding, Ferraris and Ivaldi (1988). Bond-valence sums were calculated taking into account site occupancies.
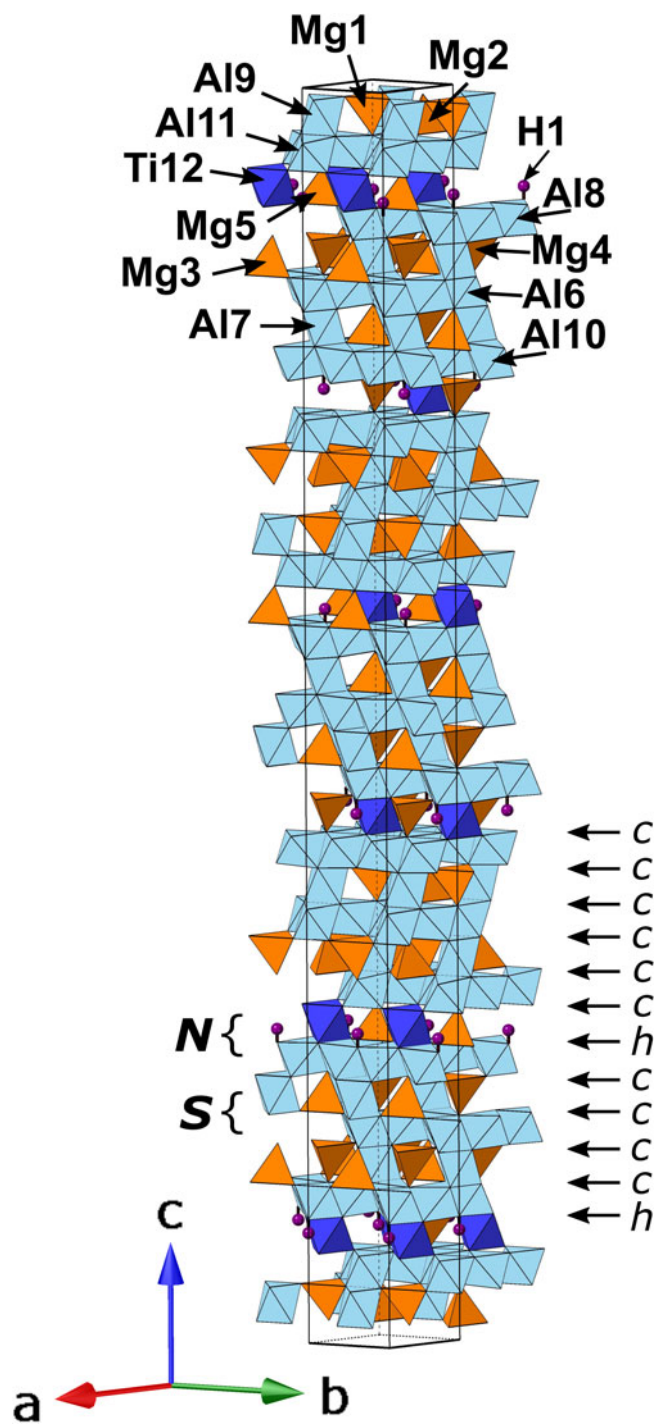
Fig. 3. General view of the crystal structure of magnesiohögbomite-6N12S. Al-centred octahedra are light blue, Ti-centred octahedra are dark blue, Mg-centred tetrahedra are orange and small purple spheres are H. The sequence of cubic 'c' and hexagonal 'h' closed-packed oxygen layers is shown. S: spinel $T_2M_4O_8$ module; N: nolanite $TM_4O_7(OH)$ module. The unit cell is outlined.

the N module. Their data are in a good agreement with the proposed cation distribution in magnesiohögbomite-6N12S.

The BVS at the O1 site (1.22 vu) indicates that it is occupied by OH$^-$ groups. H atoms were localised in the structure; the O1–H1 distance is 0.89 Å, the H1···O8 distance is 2.31 Å and the O1···O8 distance is 3.01 Å. The remaining 11 anion sites are occupied by O^{2-} anions. The band at 3365 cm^{-1} in the IR spectrum of magnesiohögbomite-6N12S confirms the presence of hydroxyl groups (Fig. 2). Both BVS and IR data indicate the absence of H$_2$O^0 in magnesiohögbomite-6N12S.

The proton position was not very reliably determined, so we used the correlation of O–H stretching frequencies with O···O and H···O bond lengths, established by Libowitzky (1999), to extract more information about the actual distances. The O···O bond length was estimated as 2.78 Å and the H···O bond length as 1.89 Å.

The resulting structural formula of magnesiohögbomite-6N12S $(Mg_{3.04}^{2+}Fe_{1.39}^{2+}Al_{0.40}Fe_{0.17}^{3+})_{\Sigma5.00}(Al_{10.76}Fe_{0.63}^{3+}Ti_{0.52}Fe_{0.09}^{2+})_{\Sigma12.00}O_{23}(OH)$ is in a good agreement with its empirical formula $(Mg_{2.95}Fe_{1.51}^{2+}Al_{0.49}Zn_{0.05})_{\Sigma5.00}(Al_{10.71}Fe_{0.78}^{3+}Ti_{0.51})_{\Sigma12.00}O_{23}(OH)$.

Relationships with other högbomite-supergroup minerals

Magnesiohögbomite-6N12S is a member of the magnesiohögbomite subgroup composed of högbomite-group minerals with Mg as the predominant tetrahedrally coordinated cation in the S module. Four polysomatic members of the subgroup were known prior to this study: magnesiohögbomite-2N2S, magnesiohögbomite-2N3S, magnesiohögbomite-6N6S (Armbruster, 2002) and magnesiohögbomite-2N4S (Shimura et al., 2012; Table 7). The reasons for the crystallisation of a specific polysome are still not known. Heiny and Armbruster (2002) reviewed available chemical data on different polysomes and concluded that there is no correlation between Ti content and type of polysome. Our data corroborate their findings. There is no substantial difference in the content of Ti between magnesiohögbomite-6N12S (0.51 atoms per formula unit (apfu); Table 1) and magnesiohögbomite-2N3S (0.48 apfu). Moreover, the observed small differences in their chemistry (Table 1) seem to reflect the differences in the $N:S$, and thus $T:M$ ratio, only. Magnesiohögbomite-2N3S ($T:M = 4:10$) is characterised by slightly lower contents of Mg and Fe^{2+}, predominantly concentrated at the T sites, than magnesiohögbomite-6N12S ($T:M = 5:12$). It means that both polysomes used very similar combinations of ions to build N and S modules but followed one of the two stacking patterns with no apparent preference. Out of 23 analysed magnesiohögbomite crystals from the DeWitts Corners, 12 turned out to be magnesiohögbomite-2N3S, nine are magnesiohögbomite-6N12S and two showed the presence of both polysomes. No correlation between crystal habits and/or associations and type of polysome was observed. It is probable that both stacking periodicities are formed under similar conditions and either one or the other is realised randomly during crystallisation, which would explain their equal abundance at the DeWitts Corners occurrence. Why magnesiohögbomite-6N12S was formed and not its hexagonal polymorph magnesiohögbomite-2N4S (Table 7) is unclear.

Magnesiohögbomite-6N12S is the first 6N12S polysome of the högbomite supergroup studied in detail. A högbomite-group mineral with 6N12S as the total number of N and S (also known as a polytype 36R) was previously found at the Dentz Farm, Gravelotte, Murchison Range, Limpopo, South Africa (Nel, 1949; McKie, 1963). It was included in the revised nomenclature of the högbomite-group minerals as a potentially new mineral

Cámara et al. (2018) who studied Fe^{2+}/Fe^{3+} distribution between T and M sites in magnesiobeltrandoite-2N3S, Mg$_3$Al$_{10}$Fe^{3+}O$_{19}$(OH), showed that, although Fe^{2+} is mostly ordered at the T sites, whereas Fe^{3+} is at the M sites, some Fe^{3+} atoms are present at the tetrahedral site of the N module and some Fe^{2+} atoms are observed at the largest octahedron of

Table 7. Comparative data for magnesiohögbomite-6N12S and other members of the magnesiohögbomite subgroup.

Mineral	Magnesiohögbomite-2N2S*	Magnesiohögbomite-2N3S**	Magnesiohögbomite-2N4S	Magnesiohögbomite-6N6S*	Magnesiohögbomite-6N12S
Idea formula	$Mg_3Al_7TiO_{15}(OH)$	$Mg_4Al_9TiO_{19}(OH)$	$Mg_5Al_{11}TiO_{23}(OH)$	$Mg_3Al_7TiO_{15}(OH)$	$Mg_5Al_{11}TiO_{23}(OH)$
Theoretical composition[1]	$2 \times T_3M_8O_{15}(OH)$	$2 \times T_4M_{10}O_{19}(OH)$	$2 \times T_5M_{12}O_{23}(OH)$	$6 \times T_3M_8O_{15}(OH)$	$6 \times T_5M_{12}O_{23}(OH)$
N and S modules sequence[2]	NSNS	NSSNS	NSSNSS	3 × (NNSS)	3 × (NSSNSS)
Crystal system	Hexagonal	Trigonal	Hexagonal	Trigonal	Trigonal
Space group	$P6_3mc$	$P\bar{3}m$	$P6_3mc$	$R\bar{3}m$	$R\bar{3}m$
a (Å)	5.734	5.722	5.7105	5.7145	5.7194
c (Å)	18.389	23.026	27.6760	55.056	83.069
V (Å³)	523.61	652.9	781.60	1557.0	2353.3
D, g/cm³	4.04 (calc.)	4.06 (calc.)	3.70 (calc.)	3.77 (calc.)	3.87 (calc.)
Strongest reflections of the PXRD pattern: d, Å (*I*)	2.956 (30)	2.860 (69)	2.856 (37)	2.857 (37)	2.921 (26)
	2.867 (51)	2.739 (50)	2.612 (39)	2.825 (67)	2.863 (49)
	2.601 (78)	2.488 (42)	2.428 (100)	2.435 (49)	2.687 (29)
	2.461 (25)	2.429 (100)	2.416 (39)	2.425 (100)	2.547 (31)
	2.433 (100)	2.421 (39)	2.012 (50)	2.009 (31)	2.434 (100)
	2.397 (24)	2.081 (48)	1.549 (35)	1.547 (25)	2.073 (22)
	2.058 (29)	1.979 (40)		1.539 (31)	1.988 (23)
	1.601 (43)	1.569 (24)			1.569 (21)
	1.557 (25)				1.557 (22)
References	Hejny and Armbruster (2002); Armbruster (2002)	Hejny and Armbruster (2002); Armbruster (2002); our data	Shimura *et al.* (2012)	Hejny and Armbruster (2002); Armbruster (2002)	This work

*Powder X-ray diffraction patterns calculated from the crystal structure data by Hejny and Armbruster (2002). **Powder X-ray diffraction pattern obtained on magnesiohögbomite-2N3S from the DeWitts Corners locality, our data.
[1]M: Mg, Fe, Al; T: Al, Fe, Ti; [2] S: spinel $T_2M_4O_8$ module; N: nolanite $TM_4O_7(OH)$ module.

'ferrohögbomite-6N12S' (Armbruster, 2002), but never properly examined. The Dentz Farm, where cores of spinel are rimmed by chlorite, corundum and hogbomite in aluminous lenses in serpentines, is one of the type localities of magnesiohögbomite-2N3S (Nel, 1949; McKie, 1963, Armbruster, 2002), and so, possibly, the second locality where both 2N3S and 6N12S polysomes occur together. While more work is required on the prospective 6N12S polysome to confirm this conjecture, such an occurrence would support the idea that magnesiohögbomite-6N12S and magnesiohögbomite-2N3S are formed under the same conditions.

Both magnesiohögbomite-6N12S and magnesiohögbomite-2N3S from the DeWitts Corners are characterised by a relatively low Ti content (0.51 and 0.48 apfu, respectively; Table 1). However, because Fe^{2+} atoms are distributed between both the T sites and the Ti site (see above), both Fe^{3+} and Fe^{2+} atoms are present at the Ti site, and so Ti atoms are the predominant component at the site, not Fe^{3+}, even when the total Fe occupancy slightly exceeds the Ti occupancy. Thus, both minerals belong to the högbomite group with the Ti dominant N module, not to the beltrandoite group with the Fe^{3+} dominant N module.

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