

# Crystal chemistry of the polysome ferrohögbomite-2*N*2*S*, a long-known but newly defined mineral species

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**Abstract:** Ferrohögbomite-2*N*2*S* is a polysomatic högbomite-group mineral composed of two nolanite modules (*N*) and two spinel modules (*S*) where the spinel modules have ideally hercynite composition. Ferrohögbomite has been described in the literature for a long time but was not distinguished from magnesiohögbomite and simply named högbomite. The revised nomenclature of högbomite minerals required definition of ferrohögbomite polysomes as new mineral species.

The sample from Aïn Taïba, northwestern edge of Grand Erg Oriental in the Algerian Sahara, has the simplified composition  ${}^{\text{IV}}(\text{Fe}^{2+}_3\text{ZnMgAl})_{\Sigma=6}{}^{\text{VI}}(\text{Al}_{14}\text{Fe}^{3+}\text{Ti}^{4+})_{\Sigma=16}\text{O}_{30}(\text{OH})_2$ . The crystal structure was refined from single-crystal X-ray data. The mineral crystallizes in the acentric space group  $P6_3mc$  with  $a = 5.712(1)$ ,  $c = 18.317(7)$  Å, and shows twinning by merohedry with the inversion centre as twinning operation. This ferrohögbomite-2*N*2*S* is associated with ilmenite, hematite, minor magnetite, and pseudorutile. Some of the ferrohögbomite-2*N*2*S* grains are rimmed by hercynite,  $\text{Fe}_{0.57}\text{Zn}_{0.26}\text{Mg}_{0.18}\text{Al}_2\text{O}_4$ , which separates them from hematite. The original assemblage probably consisted of ilmenite and Al-bearing magnetite or another Ti-bearing spinel phase. During oxidation ilmenite was replaced by ferrohögbomite on its rims and magnetite was oxidized to hematite. Finally, residual ilmenite was partly transformed along cracks and grain boundaries to pseudorutile. A HRTEM study showed homogeneous ferrohögbomite-2*N*2*S* with minor planar faults increasing towards the grain boundaries. The observed orientation relation between ferrohögbomite-2*N*2*S* and hematite suggests that ferrohögbomite-2*N*2*S* formed topotactically from a primary spinel or magnetite phase that had been subsequently oxidized to hematite.

**Key-words:** ferrohögbomite-2*N*2*S*, polysomatism, crystal structure, HRTEM, new mineral, Algeria.

## Introduction

The högbomite-group minerals form a polysomatic series consisting of interlayered spinel (*S*) and nolanite-like (*N*) modules (Gatehouse & Grey, 1982; Armbruster *et al.*, 1998; Armbruster, 1998, 2002; Hejny & Armbruster, 2002). The nolanite-like module has the simplified composition  $(\text{Fe}^{2+}, \text{Zn}, \text{Mg})\text{Ti}(\text{Al}, \text{Fe}^{3+})_3\text{O}_7(\text{OH})$ . The spinel module is derived from spinel,  $\text{MgAl}_2\text{O}_4$ , hercynite,  $\text{FeAl}_2\text{O}_4$ , or gahnite,  $\text{ZnAl}_2\text{O}_4$ . According to the new nomenclature accepted by the *IMA CNMMN* (Armbruster, 2002) magnesiohögbomite, ferrohögbomite, and zincohögbomite are distinguished according to the dominant divalent cation in the spinel module. For a full characterization of a högbomite-group mineral a hyphenated suffix composed of the total number of nolanite (*N*) and spinel (*S*) modules is attached. From this suffix the approximate lattice parameter *c* and the space group can be derived (Hejny & Armbruster, 2002; Armbruster, 2002). Without knowledge of the type of polysome (ratio of *N* and *S* modules) the formula of a

högbomite-group mineral cannot be calculated if the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio is unknown.

Originally högbomite was described by Gavelin (1916) as an Al-Fe-Mg-Ti oxide from the Routevara magnetite ores, Sweden. Subsequent crystallographic studies on this högbomite (McKie, 1963) and additional knowledge of the crystal structure of högbomite (Gatehouse & Grey, 1982) allowed the type-locality högbomite to be classified as magnesiohögbomite-2*N*2*S* (Armbruster, 2002). Other högbomite minerals belonging to the subgroup of magnesiohögbomite are: magnesiohögbomite-2*N*3*S* (Nel, 1949; McKie, 1963; Teale, 1980; Hejny & Armbruster, 2002), and magnesiohögbomite-6*N*6*S* (Schmetzer & Berger, 1990; Hejny & Armbruster, 2002).

Known members of the zincohögbomite subgroup are zincohögbomite-2*N*2*S* (Ockenga *et al.*, 1998; Armbruster, 1998), and zincohögbomite-2*N*6*S* (Armbruster *et al.*, 1998).

Actually, the first structure solution of a högbomite-group mineral was performed by Gatehouse & Grey (1982) on a specimen that fulfils the criteria of ferrohögbomite-

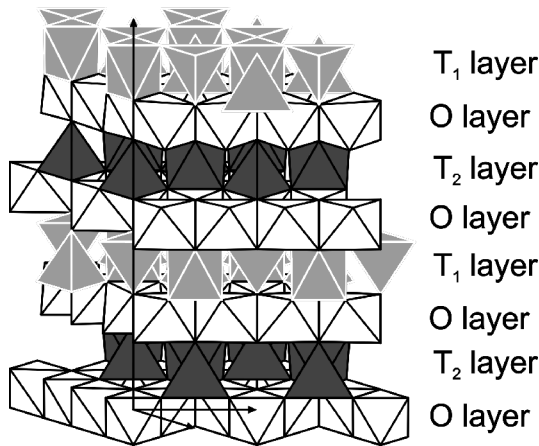


Fig. 1. Polyhedral representation of the ferrohögbomite-2N2S structure. All octahedral layers (O layers) are white with black rims, mixed octahedral-tetrahedral layers of spinel type (T<sub>2</sub> layers) are dark grey with black rims and mixed octahedral-tetrahedral layers of nolanite-type (T<sub>1</sub> layers) are light grey with white rims. Ferrohögbomite-2N2S is composed of two spinel and two nolanite-like modules. The cation-layer sequence in ferrohögbomite-2N2S is O – T<sub>2</sub> – O – T<sub>1</sub> – O – T<sub>2</sub> – O – T<sub>1</sub>.

2N2S. According to the new IMA-CNMMN nomenclature the original högbomite-8H (Gatehouse & Grey, 1982) is now ferrohögbomite-2N2S (Armbruster, 2002). The cation-layer sequence in ferrohögbomite-2N2S (Fig. 1) is O – T<sub>2</sub> – O – T<sub>1</sub> – O – T<sub>2</sub> – O – T<sub>1</sub> (Gatehouse & Grey, 1982), where O – T<sub>1</sub> represents a nolanite-like module (N) and O – T<sub>2</sub> a spinel module (S). The O layer is occupied by only octahedrally coordinated cations (M) yielding the composition M<sub>3</sub>O<sub>4</sub> whereas the T layers have tetrahedrally (T) and octahedrally (M) coordinated cations. The difference between T<sub>1</sub> and T<sub>2</sub> layers is as follows: The T<sub>2</sub> layer carries two tetrahedrally coordinated cations yielding the composition

T<sub>2</sub>MO<sub>4</sub>, and the T<sub>1</sub> layer has one tetrahedrally coordinated cation and an OH site yielding the composition TMO<sub>3</sub>(OH). A nolanite-like module has the composition TM<sub>4</sub>O<sub>7</sub>(OH) whereas a spinel module has the composition T<sub>2</sub>M<sub>4</sub>O<sub>8</sub>. Both modules are ca. 4.6 Å thick and consist of two closest-packed oxygen layers stacked parallel to the hexagonal *c* axis. A -2N2S polysome has thus the composition 2 × T<sub>3</sub>M<sub>8</sub>O<sub>15</sub>(OH). The chemical formula, based on electron-microprobe analyses, of a -2N2S polysome may hence be calculated by normalization to 22 cations and the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio is obtained by the stoichiometric formula with 62 negative charges.

The major focus of this study is the definition of ferrohögbomite-2N2S as new mineral species and to describe its occurrence. This becomes necessary due to the introduction of a new nomenclature (Armbruster, 2002). In the past ferrohögbomite minerals have been analysed but were simply classified as högbomite. The mineral species and name ferrohögbomite-2N2S have been approved (2001-048) by the IMA Commission on New Minerals and Mineral Names and the type material from Aïn Taïjba, Algeria, has been deposited at the Museum of Natural History Bern (NMBe-36156).

## Ferrohögbomite-2N2S

### Occurrence and sample description

An isolated rock, originally considered as a meteorite, was found by Serge Guillod at Aïn Taïjba, 30° 16.44' N, 5° 48.94' E, 227 m elevation, which is situated at the north-western edge of Grand Erg Oriental in the Algerian Sahara. Due to the arid climate the surface of the 2 cm sized magnetic rock is covered by a shiny desert varnish. Microscopic and electron-microprobe investigations showed that the rock is an iron ore composed of hematite, ilmenite and högbomite, pseudorutile, magnetite, and hercynite.

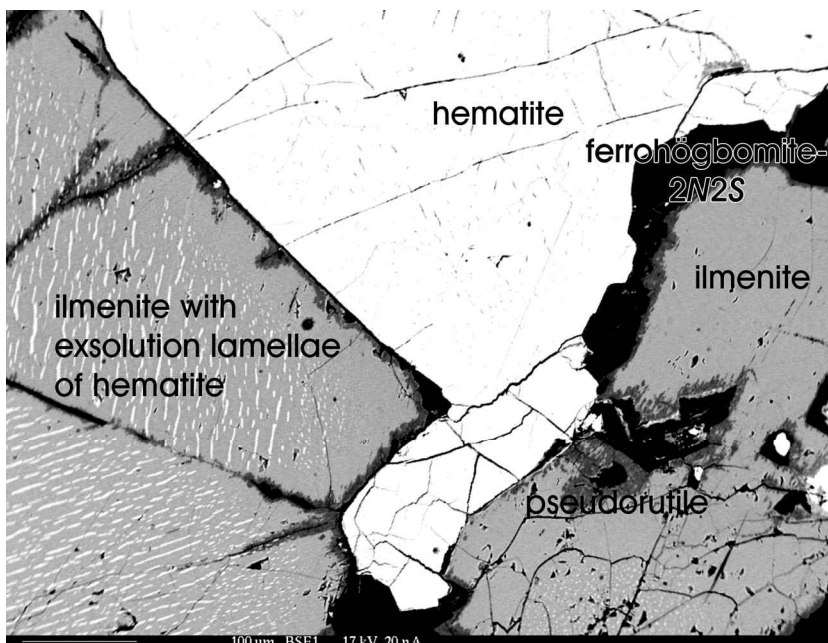


Fig. 2. Back-scattered electron image of the ferrohögbomite-2N2S bearing sample from Aïn Taïjba. Hematite appears white, ferrohögbomite-2N2S black, ilmenite light grey, pseudorutile dark grey. Ferrohögbomite-2N2S can be found on the boundaries between ilmenite and hematite and in pseudorutile-coated fissures within ilmenite. Ilmenite shows exsolution lamellae of hematite and replacement of pseudorutile along margins and fissures.

In hand specimen ferrohögbohmite-2N2S from Aĵn Taĵba is translucent and has reddish brown colour with brownish streak and adamantine lustre. The Mohs hardness is 6 to 7, the cleavage is pronounced parallel to {001}. In thin section ferrohögbohmite-2N2S from Aĵn Taĵba appears yellow to light orange. It is uniaxial negative and shows pleochroism from orange-brown to yellow and shows no UV fluorescence. The mineral is brittle and has conchoidal fracture; its density is calculated to be 4.04 g/cm<sup>3</sup>. Density was not measured because ferrohögbohmite is generally intergrown with other minerals and shows exsolution.

Ferrohögbohmite-2N2S forms euhedral grains up to 0.3 mm in size along grain boundaries and in fissures within ilmenite, pseudorutile, and hematite (Fig. 2). Often the euhedral grains are hexagonally contoured. Some of the ferrohögbohmite-2N2S grains are closely associated with green spinel (hercynite), where spinel is usually found between ferrohögbohmite-2N2S and hematite.

Hematite and ilmenite form euhedral to subhedral grains. Ilmenite shows exsolution lamellae of hematite and less frequently of ferrohögbohmite-2N2S, and is altered to pseudorutile along grain margins. Pseudorutile is considered as weathering product of ilmenite (Fig. 2). Magnetite is largely replaced by hematite, so that only patches of magnetite are left within hematite. At the hematite-magnetite boundary oriented hematite replacement is visible where the closest-packed oxygen array remains preserved [(001)<sub>hem</sub> || (111)<sub>mag</sub>] resulting in a dentate oxidation front between the two minerals. Occasionally single grains of FeOOH can be found within hematite. The Fe<sub>2</sub>O<sub>3</sub> phase replacing magnetite in the sample is definitely hematite and not maghemite. However, we cannot exclude a two-step transformation where maghemite occurred as an intermediate phase.

The isolated occurrence of the rock in the desert without surrounding metamorphic rocks does not allow estimates of metamorphic conditions. The primary assemblage probably consisted of ilmenite and Al-bearing magnetite or another Ti-bearing spinel phase. During an oxidation event ilmenite reacted with magnetite to form ferrohögbohmite, and the original magnetite oxidized to hematite, whereas hercynite formed between hematite and ferrohögbohmite. At a later stage (possibly weathering at surface conditions), pseudorutile formed on the grain boundaries and cracks of ilmenite (Fig. 2).

### Earlier descriptions of ferrohögbohmite minerals

According to the revised nomenclature of högbohmite-group minerals (Armbruster, 2002) several samples described in the literature are ferrohögbohmite-2N2S (Table 1). The type of polysome was identified either from X-ray powder/single-crystal diffraction data given by the authors of the original study or by subsequent single-crystal X-ray study (Strangways Range sample: Gatehouse & Grey (1982); Prince Olav Coast sample: this study).

(1) Högbohmite from Lusaka, Zambia, (Čech *et al.* 1976) formed under amphibolite-facies condition. At this locality ferrohögbohmite-2N2S occurs associated with cabaltoan magnetite, quartz, cobaltoan staurolite (lusaki-

Table 1. Chemical analyses (wt.%) and formulas of literature data on ferrohögbohmite-2N2S.

Refer- ence	(1)	(2)	(3)	(4)	(5)	(5)
sample				81-49	81021401B NIPR	704A NIPR
TiO <sub>2</sub>	6.07	5.37	6.26	4.44	5.17	5.14
SnO <sub>2</sub>		0.06				
SiO <sub>2</sub>	0.40	0.65				
Al <sub>2</sub> O <sub>3</sub>	57.80	59.69	58.57	61.66	59.75	59.25
Cr <sub>2</sub> O <sub>3</sub>					0.04	0.04
Ga <sub>2</sub> O <sub>3</sub>		0.23	0.18			
Fe <sub>2</sub> O <sub>3</sub>	8.65*	5.24	9.03*	9.48*	8.12*	9.41*
FeO	12.28	17.52	16.04	18.07	13.37	14.36
MgO	5.08	7.69	4.44	2.81	4.03	5.04
ZnO	0.54	3.08	3.86	3.22	7.02	4.01
MnO	0.09	0.12	0.16	1.06	0.19	0.13
NiO	0.23	0.04			0.06	0.02
CoO	6.52	0.11				
CaO					0.02	0.01
BeO		0.10				
Na <sub>2</sub> O			0.15			
K <sub>2</sub> O	0.01				0.01	0.02
H <sub>2</sub> O**	1.43	1.49	1.43	1.44	1.41	1.42
Sum	99.10	101.39	100.12	102.18	99.19	98.85
Formula normalized to 22 cations						
Ti	0.972	0.823	0.996	0.695	0.830	0.822
Sn		0.005				
Si	0.085	0.133				
Al	14.503	14.341	14.608	15.123	15.031	14.849
Cr					0.007	0.007
Ga		0.030	0.024			
Fe <sup>3+</sup>	1.386	0.804	1.438	1.485	1.305	1.507
Fe <sup>2+</sup>	2.186	2.987	2.839	3.144	2.387	2.553
Mg	1.612	2.337	1.401	0.872	1.282	1.598
Zn	0.085	0.464	0.603	0.495	1.106	0.630
Mn	0.016	0.021	0.029	0.187	0.034	0.023
Ni	0.039	0.007			0.010	0.003
Co	1.113					
Be		0.049				
Ca					0.005	0.002
Na			0.062			
K	0.003				0.003	0.005

\*Fe<sub>2</sub>O<sub>3</sub> and FeO calculated from total FeO to obtain a charge balanced formula

\*\*H<sub>2</sub>O calculated to yield 2H pfu

(1) Čech *et al.* (1976), (2) Wilson (1977), (3) Gatehouse & Grey (1982), (4) Petersen *et al.* (1989), (5) Grew *et al.* (1990)

- te), ilmenite, kyanite, hematite, cordierite, Mg-chlorite, sillimanite, rutile, linnaeite, and pentlandite.
- (2) Ferrohögbohmite-2N2S from Strangways Range (Central Australia) formed by hydrous alteration of (mainly) spinel and biotite under medium to high amphibolite-facies conditions (Wilson, 1977). At this locality ferrohögbohmite-2N2S is associated with phlogopite, green spinel, corundum, chlorite, biotite, opaque oxides, and rutile.
- (3) Ferrohögbohmite-2N2S from Benson Mine, Adirondack Mountains, New York, formed at *ca.* 730°C and 7.5 kbar

Table 2. Chemical analyses (wt.%) of Fe-rich h ogbomite-group minerals lacking information about type of polysome.

Reference	(1)	(2)	(3)	(3)	(3)	(4)	(4)	(4)	(4)	(5)	(5)	(6)
Sample	ZC-6.2					PS84-20	PS84-130	PS84-130	PS84-132	0206B-matr1	0206B-matr2	T50-1 core
TiO <sub>2</sub>	5.12	3.11	3.00	4.50	6.31	5.41	5.17	6.38	3.64	5.30	5.55	7.01
SiO <sub>2</sub>		0.08			0.23					0.0	0.05	
Al <sub>2</sub> O <sub>3</sub>	62.34	61.45	61.22	61.33	61.18	60.25	57.88	57.81	57.00	61.20	60.74	60.51
Cr <sub>2</sub> O <sub>3</sub>		0.06								0.25	0.20	0.15
FeO	22.41	26.30	21.59	21.57	21.32	27.65	26.85	26.07	24.95	24.26	25.30	25.52
MgO	6.11	6.23	10.04	9.47	7.49	2.51	1.26	2.66	3.47	5.97	5.47	5.05
ZnO	1.23	0.65	3.56	2.66	2.42	3.46	7.70	6.15	10.47	1.35	0.83	0.55
MnO	0.20	0.15				0.10	0.14	0.13	0.42	0.25	0.34	0.63
NiO	0.03	0.08										0.30
Sum	97.44	98.11	99.41	99.53	98.95	99.38	99.00	99.20	99.95	98.58	98.48	99.72

(1) Coolen (1981), (2) Mancktelow (1981), (3) Angus & Middleton (1985), (4) Spry & Petersen (1989), (5) Grew *et al.* (1989), (6) Razakamanana *et al.* (2000)

(Petersen *et al.*, 1989) and occurs associated with garnet, sillimanite, biotite, quartz, K-feldspar, magnetite, ilmenite, gahnite, corundum, rutile, pyrite, pyrrhotite, chalcopyrite, and apatite.

(4) Ferroh ogbomite-2N2S from Prince Olav Coast, East Antarctica, could have formed by oxidation-exsolution of titaniferous magnetite to ilmenite, whereby a magnetite containing Al, Zn, Mg, and Ti broke down under oxidizing conditions to form ferroh ogbomite-2N2S (Grew *et al.*, 1990). Associated rutile + magnetite and cordierite + corundum assemblages indicate  $T \leq 500^\circ\text{C}$  and  $P(\text{H}_2\text{O}) < P(\text{total})$  for ferroh ogbomite-2N2S formation.

There are various other studies on ferroh ogbomite-subgroup minerals (or Fe-rich h ogbomite minerals) where the chemical composition has been reported (Table 2) but the type of polysome has not been determined (Coolen, 1981; Mancktelow, 1981; Angus & Middleton, 1985; Spry & Petersen, 1989; Grew *et al.*, 1989; Razakamanana *et al.*, 2000). A -6N12S polysome of ferroh ogbomite has been chemically analysed by Nel (1949) and identified by McKie (1963). In addition, Devaraju *et al.* (1981) claimed that the X-ray powder pattern of their ferroh ogbomite is closely comparable to that recorded for the polysome -6N12S by (McKie, 1963). However, the listed powder reflections are not decisive and similar strong reflections also occur for hercynite. In addition, -2N3S polysomes were described by Beukes *et al.* (1986) and Grew *et al.* (1987). However, the above polysomes ('ferroh ogbomite-6N12S' and 'ferroh ogbomite-2N3S') require acceptance as new minerals. In general, ferroh ogbomite polysomes occur as retrograde minerals in Al-rich amphibolite- to granulite-facies metamorphic rocks in which they are commonly associated with spinel, magnetite, ilmenite, hematite, rutile, and corundum.

The colour of ferroh ogbomite has been described as brownish black (Devaraju *et al.*, 1981), chestnut-brown (Wilson, 1977), or sepia brown (Nel, 1949), the streak is very light brown. Ferroh ogbomite has always been found to be uniaxial negative and shows pleochroism from light, yellowish brown, parallel to  $\omega$ , to brown or dark brown, parallel to  $\epsilon$  (Nel, 1949; Beukes *et al.*, 1986). Wilson (1977) reported following refractive indices:  $n_e = 1.827$  (2),  $n_o =$

Table 3. Chemical analyses (wt.%) of different ferroh ogbomite polysomes.

Reference	(1)	(2)	(3)	(4)
Polysome	2N3S	2N3S	6N12S?	6N12S
Sample	WDB 023	3083E		B
TiO <sub>2</sub>	3.76	2.49	6.01	6.75
SiO <sub>2</sub>	0.18			0.82
Al <sub>2</sub> O <sub>3</sub>	61.99	59.70	59.94	56.48
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.62		
V <sub>2</sub> O <sub>3</sub>			0.21	
Fe <sub>2</sub> O <sub>3</sub>				8.79
FeO	25.77	28.55	21.02	17.96
MgO	6.89	6.40	9.66	9.18
ZnO	0.19	1.09	1.06	
MnO	0.17	0.06	0.14	0.10
NiO	0.05			
CaO	0.02			
Na <sub>2</sub> O	0.04			
K <sub>2</sub> O	0.02			
H <sub>2</sub> O*	1.17	1.14	0.73	0.74
Sum	100.26	100.05	99.53	100.43
	Formula normalized to 28 cations		Formula normalized to 102 cations	
Ti	0.731	0.490	4.26	4.811
Si	0.047			0.777
Al	18.881	18.413	66.59	63.077
Cr	0.002	0.128		
V			0.16	
Fe <sup>3+</sup>	1.588	2.479	2.73	6.268
Fe <sup>2+</sup>	3.981	3.769	13.84	14.019
Mg	2.654	2.497	13.57	12.968
Zn	0.036	0.211	0.74	
Mn	0.037	0.013	0.11	0.080
Ni	0.010			
Ca	0.006			
Na	0.020			
K	0.007			

\* H<sub>2</sub>O calculated to obtain 1 OH per nolanite module

(1) Beukes *et al.* (1986), (2) Grew *et al.* (1987),

(3) Devaraju *et al.* (1981), (4) wet chemical analysis by Nel (1949)

Table 4. Calculated X-ray powder pattern for ferrohögbonite-2N2S (Gatehouse & Grey, 1982) and observed power pattern Čech *et al.* (1976).

Miller indices			calculated		observed	
h	k	l	d (Å)	I (%)	d (Å)	I (%)
0	0	2	9.1945	1		
0	1	0	4.9658	2		
0	1	1	4.7941	2		
0	0	4	4.5973	3		
0	1	2	4.3693	7	4.360	16
0	1	3	3.8585	3	3.850	6
0	1	4	3.3735	9	3.363	15
0	1	5	2.9555	22	2.948	32
1	1	0	2.8670	38	2.860	53
1	1	2	2.7370	3		
0	1	6	2.6081	66	2.603	88
0	2	0	2.4829	3		
0	2	1	2.4606	23	2.454	29
1	1	4	2.4327	91	2.427	100
0	2	2	2.3970	23	2.392	28
0	1	7	2.3221	12	2.318	15
0	2	3	2.3013	11	2.296	12
0	2	4	2.1846	14	2.180	16
0	2	5	2.0578	34	2.053	34
0	2	6	1.9293	20	1.925	19
1	2	1	1.8672	4		
1	2	2	1.8390	2		
1	2	3	1.7946	2		
1	2	4	1.7377	6		
0	1	10	1.7245	10	1.721	10
0	2	8	1.6868	8	1.684	6
1	2	5	1.6718	12	1.668	8
0	3	0	1.6553	10	1.650	6
1	2	6	1.6006	60	1.597	34
0	2	9	1.5777	18	1.575	11
0	3	4	1.5574	35	1.554	20
1	2	7	1.5272	22	1.528	7
					1.524	12
0	2	10	1.4777	78	1.475	44
2	2	0	1.4335	100	1.430	56
0	2	11	1.3867	36	1.384	19
2	2	4	1.3685	1		
1	3	2	1.3621	2		
1	3	3	1.3438	1		
1	3	4	1.3193	2		
1	2	10	1.3135	8		
0	2	12	1.3040	2		
1	3	5	1.2898	5		
0	1	14	1.2698	6		
1	3	6	1.2562	23		
1	2	11	1.2483	2		
0	4	1	1.2386	5		
0	4	2	1.2303	8		
1	3	7	1.2198	7		
0	4	4	1.1985	1		
0	1	15	1.1902	4		
0	4	5	1.1762	5		
0	2	14	1.1610	2		
0	4	6	1.1506	6		
2	3	2	1.1306	2		
0	1	16	1.1197	4		
2	3	4	1.1058	1		
1	3	10	1.1024	8		

1.852(2) (chemical composition reported in Table 1), whereas the ones reported by Nel (1949) for his most Ferrich sample B are slightly lower:  $n_e = 1.823(3)$ ,  $n_o = 1.848(3)$  (chemical composition reported in Table 3). The refractive indices of Ajn Tajba ferrohögbonite-2N2S, determined by immersion method, are  $n_e = 1.83$ ,  $n_o = 1.85$ , very similar to the data reported above.

A powder pattern of ferrohögbonite-2N2S was calculated from the single-crystal structure data (Gatehouse & Grey, 1982) for CuK $\alpha$  X-radiation and Debye-Scherrer geometry (Table 4). Data were calculated using Pc-Rietveld plus (Fischer *et al.*, 1993). The calculated powder pattern is compared with the recorded powder pattern of ferrohögbonite-2N2S reported by Čech *et al.* (1976).

### Electron-microprobe analyses

Minerals were analysed with a Cameca SX-50 microprobe using beam conditions of 15 kV, 20 nA and wavelength-dispersive spectrometers. Natural and synthetic minerals were used as standards: corundum AlK $\alpha$  (TAP), spinel MgK $\alpha$  (TAP), ilmenite TiK $\alpha$  (PET), almandine FeK $\alpha$  (LiF), gahnite ZnK $\alpha$  (LiF), esolaite CrK $\alpha$  (LiF), tephroite MnK $\alpha$  (LiF), SnS $_2$  SnK $\alpha$  (LiF), NiO NiK $\alpha$  (LiF), HgGa $_2$ S $_4$  GaK $\alpha$  (LiF), anorthite CaK $\alpha$  (PET), phlogopite FK $\alpha$  (TAP), scapolite ClK $\alpha$  (PET). Elements were controlled for potential overlaps. Raw data were processed with the Cameca version of the PAP (Pouchou & Pichoir, 1991) routine.

### Chemical composition

Results from electron-microprobe analyses (and calculated formulas) for spinel and ferrohögbonite-2N2S are listed in Tables 5 and 6. Spinel was normalized to 3 cations and 8 charges, ferrohögbonite-2N2S was normalized to 22 cations, the Fe $^{2+}$ : Fe $^{3+}$  ratio was calculated to balance 62 negative charges. The -2N2S polysome has the general formula T $_6$ M $_{16}$ O $_{30}$ (OH) $_2$  where T are tetrahedrally and M are octahedrally coordinated cations (Gatehouse & Grey, 1982; Armbruster, 2002). Because of bond-valence requirements, hógbonite minerals are OH-bearing, which has been confirmed by IR-spectroscopy (Hejny & Armbruster, 2002).

Magnetite and hematite show trace contents of Al and (Al + Si) respectively. All other elements are below detection. The excess of Fe in ilmenite is interpreted as hematite component. Therefore the measured ilmenite compositions from Ajn Tajba are beneath the theoretical composition of ilmenite in a ternary plot  $\Sigma M^{2+}$  vs.  $\Sigma M^{3+}$  vs.  $\Sigma M^{4+} + H_2O$  (Fig. 3). Notice that the original ilmenite must have been even richer in Fe $_2$ O $_3$  because a substantial amount of hematite has exsolved. In a detailed view of this ternary plot (Fig. 4) the composition of ferrohögbonite-2N2S from Ajn Tajba is compared with other theoretical compositions of hógbonite-group polysomes. In an ideal hógbonite-group polysome each nolanite-like module carries one Ti per nolanite-like module (Hejny & Armbruster, 2002). In most hógbonite-group minerals the octahedral Ti site is not completely occupied by Ti $^{4+}$  but ferric and ferrous iron enter this site by the

Table 5. Average and individual electron-microprobe analyses and calculated formulas of ferrohögbohmite-2N2S and coexisting hercynite from Aïn Tajba. Number of analyses per mineral is given in parentheses.

	Högbohmite (32)					Hercynite (5)			
	average	#14	#31	#72	#81	average	#28	#32	#38
TiO <sub>2</sub>	5.04	5.10	4.21	4.09	5.77	0.50	0.27	0.56	0.74
SnO <sub>2</sub>	0.38	0.17	0.06	1.23	0.61	0.06	0.07	0.01	0.04
SiO <sub>2</sub>	0.04	0.06	0.02	0.03	0.03	0.03	0.03	0.09	0.05
Al <sub>2</sub> O <sub>3</sub>	59.28	59.41	59.08	59.09	59.80	58.39	58.31	58.19	58.94
Cr <sub>2</sub> O <sub>3</sub>	0.09	0.05	0.09	0.11	0.06	0.11	0.05	0.09	0.12
Ga <sub>2</sub> O <sub>3</sub>	0.25	0.33	0.29	0.15	0.24	0.20	0.00	0.11	0.52
Fe <sub>2</sub> O <sub>3</sub>	8.05*	8.05*	11.91*	10.09*	6.01*				
FeO	16.35	23.86	12.55	14.20	17.46	24.04	23.86	24.00	23.95
MgO	3.27	3.12	3.97	3.73	3.10	4.24	4.47	4.25	4.09
MnO	0.25	0.29	0.25	0.25	0.24	0.29	0.32	0.26	0.36
ZnO	5.88	5.67	7.39	6.42	5.34	12.11	12.21	11.81	11.58
NiO	0.05	0.00	0.03	0.00	0.00	0.01	0.00	0.00	0.00
CaO	0.02	0.03	0.05	0.01	0.00	0.02	0.01	0.02	0.00
H <sub>2</sub> O**	1.42	1.41	1.42	1.41	1.41				
Sum	100.37	100.34	101.32	100.81	100.07	100.00	99.60	99.39	100.34
	Formula normalized to 22 cations					Formula normalized to 3 cations			
Ti	0.81	0.82	0.67	0.65	0.93	0.01	0.01	0.01	0.02
Sn	0.03	0.01	0.01	0.10	0.05	0.00	0.00	0.00	0.00
Si	0.01	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00
Al	14.89	14.91	14.70	14.82	15.03	1.97	1.97	1.97	1.97
Cr	0.02	0.01	0.02	0.02	0.01	0.00	0.00	0.00	0.00
Ga	0.03	0.05	0.04	0.02	0.03	0.00	0.00	0.00	0.01
Fe <sup>3+</sup>	1.29	1.35	1.89	1.62	0.96				
Fe <sup>2+</sup>	2.91	2.90	2.22	2.53	3.11	0.57	0.57	0.58	0.57
Mg	1.04	0.99	1.25	1.18	0.98	0.18	0.19	0.18	0.17
Mn	0.05	0.05	0.05	0.05	0.04	0.01	0.01	0.01	0.01
Zn	0.92	0.89	1.15	1.01	0.84	0.26	0.26	0.25	0.24
Ni	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00

\* Fe<sub>2</sub>O<sub>3</sub> calculated from total FeO to obtain a charge balanced formula

\*\* calculated corresponding to 2 OH

Table 6. Representative individual electron-microprobe analyses of ilmenite, hematite, magnetite, and pseudorutile coexisting with högbohmite-2N2S from Aïn Tajba. Number of analyses per mineral is given in brackets.

	Ilmenite (18)					Hematite (10)				Magnetite (2)		Pseudorutile (25)				
	#43	#65	#75	#76	#91	#48	#23	#40	#70	#71	#84	#11	#13	#44	#74	#78
TiO <sub>2</sub>	49.188	49.310	49.136	49.370	48.549	0.033	0.123	0.048	0.087	0.047	0.020	64.566	56.671	66.891	56.559	58.382
SnO <sub>2</sub>	0.013	0.000	0.000	0.080	0.032	0.033	0.000	0.014	0.000	0.027	0.000	0.034	0.013	0.023	0.000	0.018
SiO <sub>2</sub>	0.011	0.013	0.030	0.013	0.013	0.364	0.445	0.556	0.389	0.009	0.019	0.558	1.731	0.695	1.615	0.066
Al <sub>2</sub> O <sub>3</sub>	0.000	0.000	0.000	0.000	0.000	0.351	0.563	0.246	0.478	0.280	0.302	0.113	0.501	0.370	0.786	0.000
Cr <sub>2</sub> O <sub>3</sub>	0.042	0.048	0.000	0.009	0.006	0.054	0.061	0.061	0.121	0.099	0.126	0.000	0.000	0.000	0.000	0.009
Ga <sub>2</sub> O <sub>3</sub>	0.000	0.000	0.445	0.144	0.000	0.371	0.153	0.000	0.051	0.000	0.000	0.000	0.000	0.159	0.000	0.000
FeO	47.236	47.399	47.592	47.618	47.784	88.563	87.692	88.490	87.995	92.903	93.024	27.558	32.834	24.962	31.279	35.189
MgO	0.297	0.365	0.356	0.315	0.240	0.053	0.030	0.055	0.063	0.020	0.048	0.095	0.109	0.043	0.081	0.068
MnO	1.449	1.432	1.398	1.303	1.382	0.000	0.000	0.050	0.107	0.035	0.000	0.031	0.303	0.006	0.124	0.164
ZnO	0.047	0.002	0.047	0.000	0.000	0.000	0.000	0.000	0.017	0.073	0.061	0.000	0.057	0.123	0.116	0.154
NiO	0.010	0.000	0.000	0.000	0.000	0.080	0.109	0.005	0.024	0.009	0.000	0.000	0.019	0.102	0.010	0.014
CaO	0.064	0.043	0.042	0.028	0.050	0.095	0.087	0.091	0.048	0.024	0.039	0.112	0.273	0.199	0.319	0.067
Sum	98.357	98.613	99.047	98.879	98.056	89.997	89.264	89.617	89.381	93.525	93.640	93.067	92.511	93.573	90.890	94.132

All Fe analysed as FeO

coupled substitution  $\text{Fe}^{3+}_{1-2x}\text{Fe}^{2+}_x\text{Ti}^{4+}_x$  (Hejny & Armbruster, 2002). This type of substitution has also been found for ferrohögbohmite-2N2S from Aïn Tajba and will be discussed below.

The chemical analyses of pseudorutile show a wide compositional range. This is in accordance with other occurrences, where pseudorutile of variable composition and highly disordered structure (Grey *et al.*, 1983; Frost *et al.*,

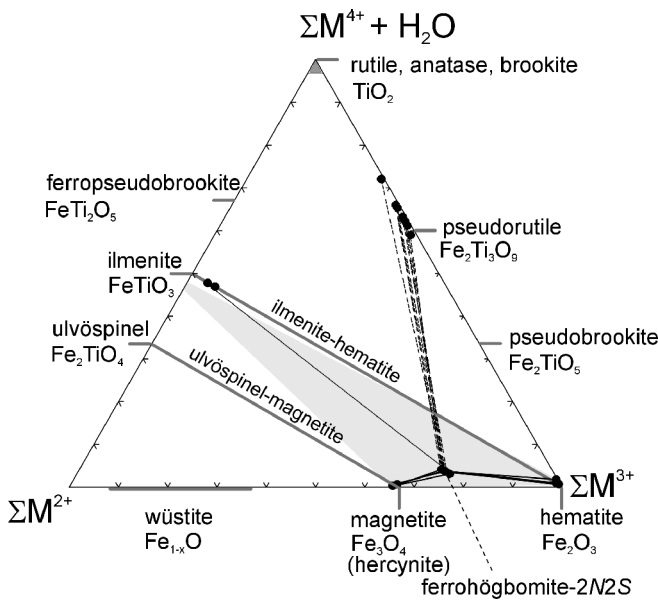


Fig. 3. Ternary  $\Sigma M^{2+} : \Sigma M^{3+} : \Sigma M^{4+} + H_2O$  plot showing the composition of ilmenite, spinel, ferrohögbohmite-2N2S, hematite, and pseudorutile in the Aĭn Tajĭba sample. Thin tie lines connect mineral grains in contact. Tie lines between ferrohögbohmite-2N2S and pseudorutile are dotted because pseudorutile is interpreted as alteration phase. Well-known phases of the system FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> are indicated for comparison and their solid solutions are shown by broad tie lines.

1986; Grey *et al.*, 1994) has been described as intermediate alteration product of ilmenite. The formula Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub> for pseudorutile is only an approximation, and calculation of a mean formula for the 25 spot analyses of pseudorutile from Aĭn Tajĭba was not attempted.

### HRTEM experiments

TEM samples were prepared from double-side polished thin sections of the ferrohögbohmite-2N2S bearing specimen. The

ion-thinned and carbon-coated discs were analysed with a Philips CM20 transmission electron microscope operated at 200 eV (point resolution of 0.27 nm) equipped with a twin objective lens (theoretical resolution 0.27 nm), a TV-Camera GATAN 622 with Image Intensifier and energy-dispersive X-ray (EDX) spectrometer. Image simulations were performed with the software package EMS (Stadelmann, 1987).

The analysed ferrohögbohmite-2N2S crystals are intergrown with corundum, rutile (both of submicroscopic size), and pseudorutile and embedded in large hematite crystals. SAED patterns and high-resolution TEM images (Fig. 5) of the crystal interior are compatible with the 2N2S-polysome obtained from the single-crystal analysis. The following topotactic relationships between the ferrohögbohmite-2N2S and hematite crystals is observed:  $[100]_{hög} \parallel [-1-21]_{hem}$ ;  $c_{hög} \parallel [101]_{hem}$  (Fig. 6). The interfaces  $(001)_{hög} \parallel (101)_{hem}$  are coherent and flat, whereas the faces perpendicular to  $c_{hög}$  are irregular and have frequent steps. Ferrohögbohmite-2N2S crystals pseudomorphic after spinel have their  $c$  axis parallel to  $[111]$  of the primary spinel. Thus their closest-packed oxygen layers are parallel to each other. The cubic closest-packing in the spinel structure causes four closest-packed  $\{111\}$  layers cutting each other under  $109.45^\circ$ . In hematite  $\{101\}$  cuts  $\{001\}$  under approximately  $107^\circ$  (close to  $109.45^\circ$ ) and  $\{101\}$  faces cut each other under *ca.*  $111^\circ$  (close to  $109.45^\circ$ ). Thus  $\{101\}_{hem}$  parallel to  $\{111\}_{spinel}$  would be an expected orientation relation for a spinel-hematite transformation where one closest-packed  $\{111\}$  layer of spinel is parallel to  $\{001\}_{hem}$ . The observed topotactic relationship between hematite and ferrohögbohmite-2N2S is explained if one assumes that hematite was formed from a primary spinel phase that was already partially transformed to högbohmite. The orientation is dictated by stress minimization. Planar faults parallel to  $(001)$  of ferrohögbohmite are present in the interior of the grains, but their concentration increases towards the grain boundaries (Fig. 6). Corresponding defects have been shown in other högbohmite-2N2S samples (Bovin, 1981). In addition, Bovin (1981) noticed that some högbohmite samples are disordered by non-

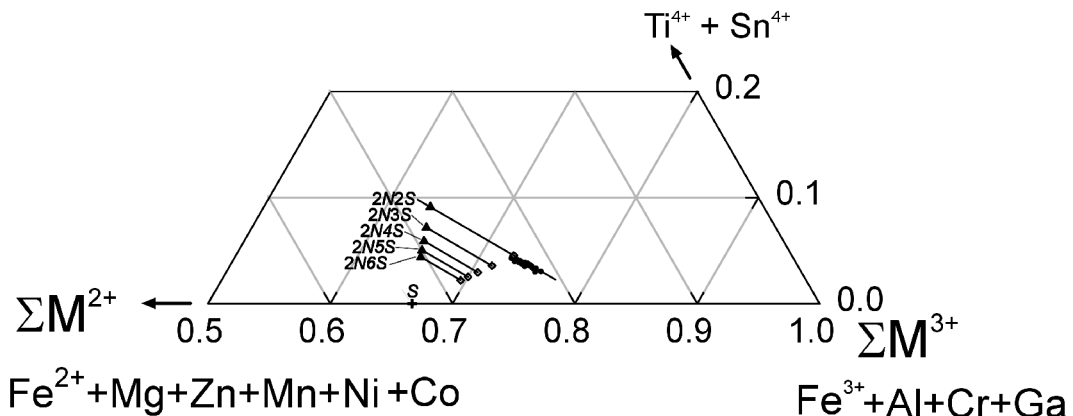


Fig. 4. Detailed view of the ternary  $\Sigma M^{2+} : \Sigma M^{3+} : \Sigma M^{4+} + H_2O$  plot showing the composition of ferrohögbohmite-2N2S from Aĭn Tajĭba as black circles. Black triangles are theoretical compositions for polysomes with all tetrahedral positions occupied with M<sup>2+</sup>, each nolanite module carrying one Ti on an octahedral position and all other octahedral positions occupied with M<sup>3+</sup> (Hejny & Armbruster, 2002). Each black triangle is connected with a tie line to an open diamond representing the same polysome with one Ti replaced according to the exchange  $Ti^{4+} + M^{2+} \leftrightarrow 2 M^{3+}$ . The symbol 'S' on the horizontal bottom line represents the composition of a spinel module (e.g., hercynite).

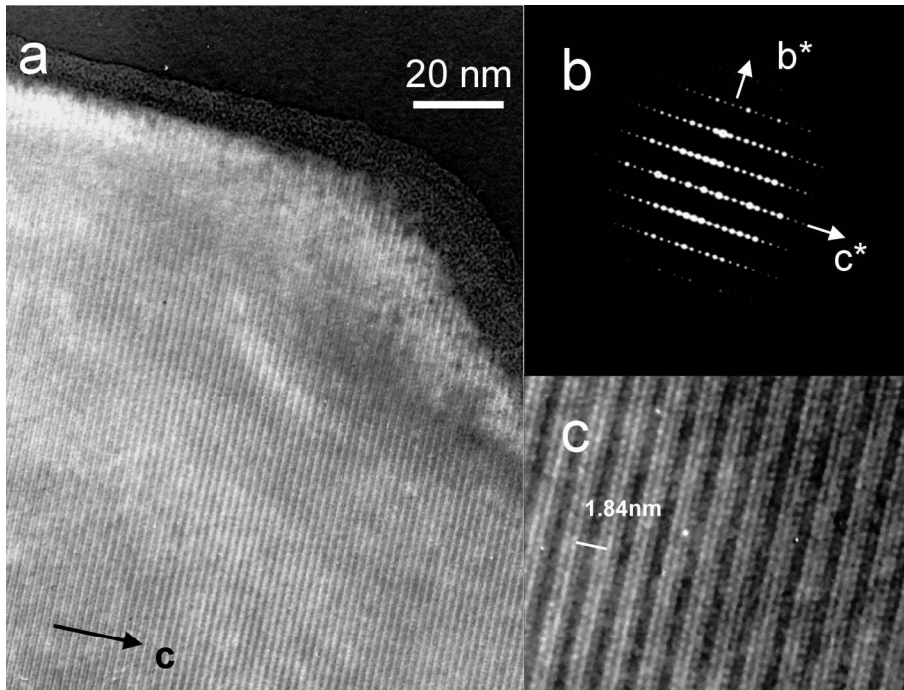


Fig. 5. a) [100] HRTEM image of a regular fault-free högbomite crystal; b) corresponding SAED pattern; c) details of the HRTEM image.

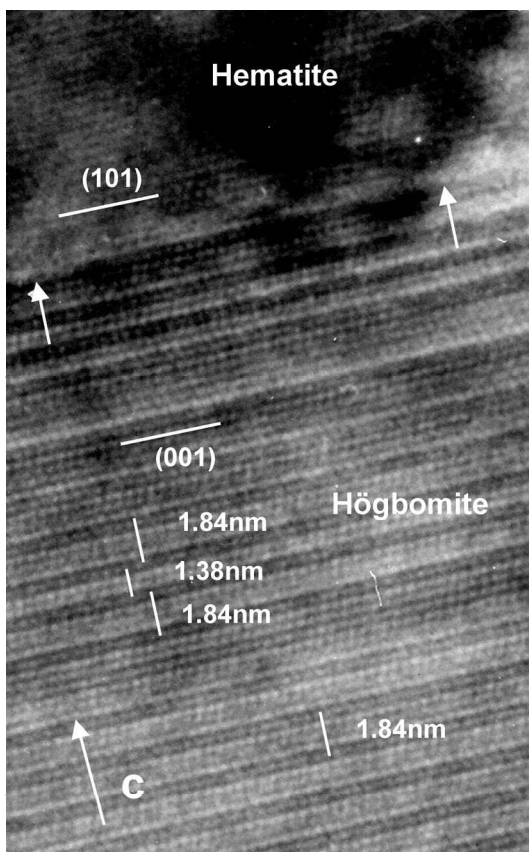


Fig. 6. [100] HRTEM image of högbomite taken close to a grain boundary with hematite. The area close to the boundary is faulted, and sequences with a 1.38 nm period can be observed. This periodicity is characteristic of a  $-2N1S$  polysome which has not yet been described for högbomite-group minerals but is a common polysome for nigerite-group minerals (Armbruster, 2002).

regular intergrowth of slabs of various thickness and should hence be classified as two-dimensional crystals. This is not the case for ferrohögbomite- $2N2S$  from Aïn Taïba which displays large structurally homogeneous volumes.

### X-ray experiments

A single crystal of ferrohögbomite- $2N2S$ , ca.  $30 \times 170 \times 220 \mu\text{m}^3$  in size, was handpicked from a crushed ore sample and analysed on an ENRAF NONIUS CAD4 diffractometer (MoK $\alpha$  X-radiation). Hexagonal cell parameters of  $a = 5.712(1)$   $c = 18.317(7)$  Å, obtained from 25 reflections with  $7.84 < \theta < 27.69$ , led to the identification of the  $-2N2S$  polysome. The single-crystal diffraction pattern did not show evidence of admixed phases, e.g., other polysomes. Diffraction data were collected with graphite-monochromated MoK $\alpha$  radiation up to  $\theta = 30^\circ$ , yielding 2069 reflections of which 348 were unique and 279 had  $F > 4\sigma(F)$ . Data reduction, including background and Lorentz polarization correction, was carried out with the SDP program system (Enraf Nonius, 1983). Experimental details of data collection and structure refinement are summarized in Table 7.

Using the space group  $P6_3mc$  and the coordinates from the refinement of Gatehouse & Grey (1982), the measured data were refined with the program SHELXL-97 (Sheldrick, 1997), applying the scattering factors for neutral atoms. In order to assign cations to tetrahedrally and octahedrally coordinated sites the following strategy was used: In test refinements  $U_{\text{iso}}$  of octahedrally coordinated sites was fixed at  $0.004 \text{ \AA}^2$  and Al scattering curves were assigned to M1, M2, and M4 but a Ti scattering curve was chosen for M2.  $U_{\text{iso}}$  of tetrahedrally coordinated sites (Fe scattering curves) and of oxygen atoms was fixed at  $0.005 \text{ \AA}^2$  and



Table 7. Details of X-ray data collection of ferrohögbonite-2N2S from Aĭn Tajba.

space group	$P6_3mc$ (No. 186)
$a, c$ (Å)	5.712 (1), 18.317 (7)
$V$ (Å <sup>3</sup> )	517.6 (4)
diffractometer	Enraf Nonius CAD4
X-ray radiation	MoK $\alpha$
X-ray power	55 kV, 40 mA
temperature	293 K
crystal size	30 × 170 × 220 $\mu\text{m}^3$
upper $\theta$ limit	30°
$h, k, l$ limit	$-8 \leq h \leq 7, -1 \leq k \leq 8, -1 \leq l \leq 25$
$\mu$ (mm <sup>-1</sup> )	5.40
reflections measured	2069
unique reflections	348
reflections > 4 $\sigma(F)$	279
absorption correction	not applied
$R$ (int)	8.79
$R$ ( $\sigma$ )	4.69
Number of least square parameters	42
GooF	0.779
$R1, F_o > 4\sigma(F_o)$	2.96
$R1, \text{all data}$	4.39
$wR$ (on $F^2$ )	10.39

0.007 Å<sup>2</sup>, respectively. In subsequent refinements the cation population of each site was refined separately. In cases where the site population differed significantly from 1.0, a second cation species was introduced accordingly. It was found that the octahedrally coordinated sites of both **O** layers and the octahedral position of the **T**<sub>2</sub> layer are Al positions, as presumed from the beginning. This in accordance with cation assignment (Table 8) in zincohögbonite-2N2S (Armbruster, 1998) and ferrohögbonite-2N2S (Gatehouse & Grey, 1982), although the latter report minor amounts of Fe on the M4 position. The octahedral position (M2) of the **T**<sub>1</sub> layer is shared by approximately equal amounts of Ti and Fe. The Ti content was subsequently fixed at 0.4 (equivalent to 0.8 apfu) according to the Ti concentration determined by electron-microprobe analyses. The tetrahedral positions of the **T**<sub>1</sub> and **T**<sub>2</sub> layers are occupied with (Fe, Zn) and (Mg, Al) in different ratios. After correct assignment of the cation species, the total occupancy was fixed at 1.0 and isotropic displacement parameters were refined for all atoms. The

Flack  $x$  parameter (Flack, 1983) indicated that partial 'polarity twinning' had to be assumed. This twinning by merohedry (Catti & Ferraris, 1976) has the inversion centre as twinning operation. A subsequent twin refinement yielded that the crystal is composed of two twin components, one with volume 0.25 and the second with volume 0.75. This is in analogy to zincohögbonite-2N2S (Armbruster, 1998), which showed the same kind of twinning.

The final cation assignment found for ferrohögbonite-2N2S from Aĭn Tajba is given in Table 8 together with the cation assignment of ferrohögbonite-2N2S from Strangways Range (Gatehouse & Grey, 1982) and zincohögbonite-2N2S (Armbruster, 1998). Due to similar ionic radii and X-ray scattering power Fe and Zn cannot be distinguished in this refinement and therefore the Fe scattering curve was used to model Fe and Zn. In addition, Mg and Al have similar X-ray scattering power which must be considered when interpreting X-ray results and comparing them with chemical compositions obtained from electron-microprobe analyses. Final least-squares refinement converged at  $R1 = 2.96\%$  for 279 observations > 4 $\sigma(F_o)$  and 42 parameters. Highest and lowest peaks (0.61 and -0.72 e/Å<sup>3</sup>) in the difference-Fourier map were close to O4. The quality of the collected diffraction data was not sufficient to resolve a difference-Fourier peak that could be interpreted as an H atom. The cation and oxygen numbering schema is the same as used by Gatehouse & Grey (1982) and Armbruster (1998). Atomic coordinates and isotropic displacement parameters for ferrohögbonite-2N2S are given in Table 9. Table 10 shows selected interatomic distances of ferrohögbonite-2N2S from Aĭn Tajba compared to corresponding distances in other -2N2S polytypes (Gatehouse & Grey, 1982; Armbruster, 1998). The consistency of interatomic distances in the three structures is very good and the difference is max. 0.02 Å (T6 – O).

### Crystal chemistry

The formula refined from X-ray data is (Fe,Zn)<sub>5.17</sub> Ti<sub>0.80</sub> [Mg<sub>2.03</sub>Al<sub>14.00</sub>] <sub>$\Sigma=16.03$</sub>  O<sub>32</sub>(OH)<sub>2</sub>. The agreement with the one obtained from electron-microprobe analyses, [Fe<sub>4.20</sub>Zn<sub>0.92</sub>(Mn,Ni,Ca)<sub>0.06</sub>] <sub>$\Sigma=5.18$</sub>  Ti<sub>0.81</sub> [Al<sub>14.89</sub> Mg<sub>1.04</sub>] <sub>$\Sigma=15.93$</sub>  (Cr,Ga,Sn,Si)<sub>0.09</sub> O<sub>32</sub>(OH)<sub>2</sub>, is excellent if considering that transition metals (mainly Fe and Zn) have been refined together with the scattering curve of Fe. In addition, Mg and Al are difficult to distinguish due to their similar scattering

Table 8. Cation assignment for ferrohögbonite-2N2S (this study), ferrohögbonite-2N2S (Gatehouse &amp; Grey, 1982) and zincohögbonite-2N2S (Armbruster, 1998).

	this study	Gatehouse & Grey, 1982	Armbruster, 1998
M1	1 Al	1 Al	1 Al
M2	0.60 Fe + 0.40 Ti	0.50 Ti + 0.50 Fe	0.60 (1) Ti + 0.40 Fe
T3	0.57 (1) Al, Mg + 0.43 Fe, Zn	0.35 Al + 0.40 Fe + 0.25 Mg	0.69 (1) Fe + 0.31 Al
M4	1 Al	0.93 Al + 0.07 Fe	1 Al
M5	1 Al	1 Al	1 Al
T6	0.89 (2) Fe, Zn + 0.11 Mg, Al	0.60 Fe + 0.20 Mg + 0.15 Zn + 0.05 Al	0.84 (1) Zn + 0.16 Al
T7	0.68 (2) Fe, Zn + 0.32 Mg, Al	0.50 Fe + 0.25 Mg + 0.15 Zn + 0.10 Al	0.75 (1) Zn + 0.25 Al

Table 9. Atomic positional parameters and  $U_{\text{iso}}$  values, with standard deviations in parentheses, for ferrohögbomite-2N2S from Ajn Taiba. MW is site multiplicity and Wyckoff letter.

atom	layer	MW	$x/a$	$y/b$	$z/c$	$U_{\text{iso}}$
M1	O	6c	0.6711 (5)	0.8355 (3)	0.9410 (2)	0.0071 (5)
M2	T <sub>1</sub>	2a	0	0	0.7970 (2)	0.0071 (6)
T3	T <sub>1</sub>	2b	2/3	1/3	0.8506 (2)	0.0023 (8)
M4	O	6c	0.0055 (5)	0.5028 (3)	0.6965 (2)	0.0044 (5)
M5	T <sub>2</sub>	2b	2/3	1/3	0.5660 (3)	0.0062 (8)
T6	T <sub>2</sub>	2b	1/3	-1/3	0.5361 (2)	0.0081 (7)
T7	T <sub>2</sub>	2a	0	0	0.6041 (2)	0.0037 (7)
O1		2a	0	0	0.9956 (6)	0.009 (2)
O2		6c	0.038 (1)	0.519 (6)	0.9983 (3)	0.006 (1)
O3		2b	1/3	-1/3	0.8844 (5)	0.004 (2)
O4		6c	0.8475 (6)	0.695 (1)	0.8811 (3)	0.011 (1)
O5		2b	-1/3	-2/3	0.7472 (6)	0.010 (2)
O6		6c	0.663 (1)	0.8313 (6)	0.7489 (3)	0.006 (1)
O7		2b	1/3	2/3	0.6416 (6)	0.011 (2)
O8		6c	0.8114 (6)	0.623 (1)	0.6328 (4)	0.011 (1)

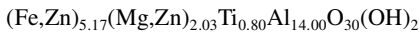


Table 10. Interatomic distances (Å) for ferrohögbomite-2N2S (this study), ferrohögbomite-2N2S (Gatehouse & Grey, 1982) and zincohögbomite-2N2S (Armbruster, 1998).

			this study	Gatehouse & Grey, 1982	Armbruster, 1998	
M1	O2	2 ×	1.895 (4)	1.907	1.902 (2)	
		O1	1 ×	1.910 (7)	1.915	1.905 (3)
		O4	2 ×	1.916 (4)	1.915	1.902 (2)
		O3	1 ×	1.967 (6)	1.963	1.962 (2)
average			1.917	1.920	1.913	
M2	O6	3 ×	1.887 (6)	1.896	1.892 (3)	
		O4	3 ×	2.156 (7)	2.184	2.171 (3)
average			2.022	2.040	2.031	
T3	O4	3 ×	1.873 (6)	1.872	1.881 (3)	
		O5	1 ×	1.90 (1)	1.876	1.869 (5)
average			1.880	1.873	1.878	
M4	O6	2 ×	1.887 (4)	1.900	1.896 (2)	
		O7	1 ×	1.908 (6)	1.904	1.903 (3)
		O5	1 ×	1.916 (6)	1.935	1.922 (2)
		O8	2 ×	1.954 (4)	1.965	1.949 (2)
average			1.918	1.928	1.919	
M5	O8	3 ×	1.883 (8)	1.920	1.884 (3)	
		O2	3 ×	1.916 (7)	1.885	1.919 (3)
average			1.900	1.903	1.901	
T6	O7	1 ×	1.93 (1)	1.966	1.955 (5)	
		O2	3 ×	1.963 (6)	1.978	1.960 (3)
average			1.955	1.975	1.958	
T7	O8	3 ×	1.939 (6)	1.933	1.930 (3)	
		O1	1 ×	1.99 (1)	1.995	1.983
average			1.951	1.948	1.944	

power and for this reason the refined sum (Mg + Al) should be compared with the analytical results. Notice that in the above-refined formula Al was only assigned to the octahedral sites M1, M4, and M5 whereas Mg was assigned to tetrahedral sites. However, this cation assignment is not completely correct and will be discussed below.

The M2-O distance (2.022 Å) within the nolanite module is shorter than the one (2.040 Å) in ferrohögbomite-2N2S studied by Gatehouse & Grey (1982) and also shorter than the one (2.031 Å) determined for zincohögbomite-2N2S (Armbruster, 1998). As found in the other two structure refinements (Gatehouse & Grey, 1982; Armbruster, 1998) the remaining occupancy on the Ti position (M2) is Fe. To explain the bond distance of 2.022 Å, Fe<sup>2+</sup> and Fe<sup>3+</sup> have to be assumed in addition to 0.4 Ti<sup>4+</sup>. The Al-O distances range from 1.900 to 1.918 Å and Al on the octahedral positions M1, M4, and M5 sums up to 14 Al pfu, which is 0.89 apfu less than found by electron-microprobe analyses. The remaining 0.89 apfu Al are hence expected to occupy tetrahedral positions. T3 (in the nolanite module) has a significantly smaller cation-oxygen distance of 1.880 Å than T6 (1.955 Å), and T7 (1.951 Å). It is likely that at least some of the remaining Al can be assigned to T3, which has been refined to 0.57 Mg and/or Al and 0.43 Fe. Assigning all 0.89 apfu Al to T3 (adjusted occupancy: 0.445 Al, 0.125 Mg, 0.43 Fe<sup>2+</sup>) this occupation yields an average T3-O distance of 1.867 Å (Brown, 1996). If 0.43 Fe<sup>3+</sup> are considered instead of 0.43 Fe<sup>2+</sup>, the average T3-O bond length becomes 1.814 Å (Brown, 1996). Both calculated values are still smaller than the observed value of 1.880 Å. It may hence be concluded that not all of the 0.89 Al pfu are positioned on T3 and minor Al may be distributed over T6 and T7. A cation assignment based on scattering power and analyses of bond lengths is given in Table 8.

Comparison of TiO<sub>2</sub> concentrations in Tables 1 and 3 for the various polysomes could mislead to the presumption that -2N3S polysomes have lower TiO<sub>2</sub> concentrations than -2N2S polysomes. However, Hejny & Armbruster (2002), comparing chemical analyses of magnesiohögbomite-2N3S, showed in detail that the Ti content in -2N3S polysomes varies between 0.5 and 1.66 Ti pfu and the data in Table 3 just represent the lower limit of this range. Furthermore, the theoretical formula of a nolanite module may also be expressed without Ti<sup>4+</sup> by the composition Fe<sup>3+</sup><sub>5</sub>O<sub>7</sub>OH. Thus in highly oxidized rocks, as is the case for the Ajn Taiba sample, ferric iron may partially replace Ti<sup>4+</sup> and Fe<sup>2+</sup>. Average formula calculation based on electron-microprobe analyses according to the theoretical composition T<sub>6</sub>M<sub>16</sub>O<sub>30</sub>(OH)<sub>2</sub> yields 1.29 Fe<sup>3+</sup> pfu which is concentrated on T3 and M2 (nolanite-like module). Notice that analyses with the lowest molar concentration of Ti + Sn (#31 and #72 in Table 5) yield the highest calculated Fe<sup>3+</sup> values whereas the analysis with the highest Ti + Sn concentration (#81) yields the lowest Fe<sup>3+</sup> value. Therefore, the TiO<sub>2</sub> concentration does not provide a tool for determining the polysome which can be done only by diffraction methods and HRTEM imaging. Petrologists are highly encouraged to supplement electron-microprobe analyses with these experimental techniques. Only a combination of P-T estimates, chemical composition, and polysome data will provide better understanding of högbomite-polysome stability. Furthermore, högbomite-group minerals must be considered as hydrous minerals where the number of OH groups depends on the number of nolanite modules (Hejny & Armbruster, 2002). Electron-microprobe analyses of högbomite minerals must also include determination of V, Cr, Ni, Co, Ga, and Sn in

addition to the major constituents Mg, Fe, Mn, Zn, Al, and Ti. Only complete analyses allow the calculation of the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio for various polysomes.

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