

NAMBULITE AND NATRONAMBULITE OCCURRENCE IN THE MANGANESE BELT, BISTRITA MOUNTAINS, EASTERN CARPATHIANS, ROMANIA

Paulina HÎRTOPANU¹, Nicolae CĂLIN², & Sorin S. UDUBAŞA^{1*}

¹University of Bucharest, Faculty of Geology and Geophysics, Bd. N. Bălcescu, 1, RO-010041, Bucharest, Romania, paulinahirtopanu@hotmail.com, *Corresponding author: sorin.udubasa@gmail.com;

²Geological Institute of România, Caransebeş Str., No. 1, sector 1, RO-012271, Bucharest, Romania, nicolae_cln@yahoo.com.

Abstract: Nambulite, $(\text{Li},\text{Na})\text{Mn}_4\text{Si}_5\text{O}_{14}(\text{OH})$, and natronambulite, $(\text{Na},\text{Li})(\text{Mn},\text{Ca})_4\text{Si}_5\text{O}_{14}(\text{OH})$, occur in many deposits of Manganese Belt (MnB) in Bistrița Mountains, Eastern Carpathians, Romania. The nambulite and natronambulite form small bands which cut the old bands/lens of braunite-bixbyite-hausmannite ore. Nambulite has $\text{Li} > \text{Na}$ and forms a series with natronambulite. The natronambulite has $\text{Na} > \text{Li}$ and $\text{Mn} > \text{Ca}$. The X-ray analyses of MnB nambulite showed that it crystallizes in triclinic system, space group $\text{P}\bar{1}(2)$. Its unit cell parameters are: $a=7.5300 \text{ \AA}$, $b=11.7360 \text{ \AA}$, $c=6.7100 \text{ \AA}$, $Z=2$, $V=565.00 \text{ \AA}^3$, $\alpha=92.97^\circ$, $\beta=95.23^\circ$, and $\gamma=106.27^\circ$. The natronambulite has: $a=7.6200 \text{ \AA}$, $b=11.7620 \text{ \AA}$, $c=6.7370 \text{ \AA}$, $Z=2$, $V=574.436 \text{ \AA}^3$, $\alpha=92.81^\circ$, $\beta=94.55^\circ$, and $\gamma=106.87^\circ$. The cell parameters of natronambulite are very close to those of nambulite. The chemical compositions of nambulite and natronambulite of MnB deposits were determined by SEM and wet chemical analyses. Their Li_2O and Na_2O were determined by AAS and by wet chemical analyses. The wet chemical analyses of nambulite show variation for $\text{Li}_2\text{O}=1.05\text{-}1.34 \text{ wt.}\%$ and $\text{Na}_2\text{O}=1.28\text{-}0.72 \text{ wt.}\%$. The natronambulite has $\text{Li}_2\text{O} < \text{Na}_2\text{O}$, and higher Na_2O and CaO contents than nambulite. In natronambulite the Li_2O content varies between $0.45\text{-}0.65 \text{ wt.}\%$ and that of Na_2O between $1.10\text{-}5.96 \text{ wt.}\%$. The main MnO compound for both minerals has variations between $38.20\text{-}46.01 \text{ wt.}\%$, where Mn cations have minor substitutions with Mg, Ca, Ni and Zn. The mineral textural relations show that the oldest mineral of ore is braunite, closed associated with bixbyite/hausmannite. The braunite is cut/substituted by the new nambulite and natronambulite, which in their turn are substituted by leakeite and holmquistite, respectively. Both minerals are closely associated with aegirine and albite. A wide range of many minerals, some of them unusual and new for Romania, occur as veins through the nambulite/natronambulite associations: jacobsonite-Q, namansilite, lithiomarsturite, serandite, hematophanite, fairfieldite, yoshimuraite, imandrite, and others. Also, many common minerals like magnetite, hematite, spessartine, albite, microcline, barium feldspars, barite, nickelian phlogopite/kinoshitalite, and others occur. The mineralogy, geochemistry, and tectonically setting of Mn deposits showed their hydrothermal submarine origin related to subduction processes. The source of Li was not from external supply.

Key words: Manganese Belt, nambulite, natronambulite, associated minerals, hydrothermal submarine genesis related to subduction.

1. INTRODUCTION

Nambulite has been described as a new mineral in the Funakowa Mine in the Kitakami Mountains of north-eastern Japan (Yoshii et al., 1972). The other 4 nambulite occurrences were found in: the Kombat Mine in the Otavi Mountains of northern Namibia (Von Knorring et al., 1978), Figuerinha Mine, Urucum District, Matto Grosso do Sui, Brazil

(Schneider & Urban, 1983), the Sausar Group of rocks, Central India (Mukhopadhyay et al., 2005), and the Woods mine, New South Wales, Australia (Coombs et al., 2009).

The nambulite with a high sodium content, $\text{Na} > \text{Li}$, was considered enough to allow the creation of a new Na-dominant analogue, under the name natronambulite (Matsubara et al., 1985). The mineral and its name, as a new mineral, have been approved

by the Commission on New Minerals and Mineral Names of IMA. The natronambulite is physically and optically hard to distinguish from nambulite unless analysed. The IMA formula of natronambulite is $(\text{Na},\text{Li})(\text{Mn},\text{Ca})_4\text{Si}_5\text{O}_{14}$. It forms a series with nambulite. The Li and Na distribution in the nambulite and natronambulite structure is random, because of the big difference in size of Na and Li elements, and therefore, a wide range solid solution could be expected of $(\text{Li}, \text{Na})(\text{Mn}_8\text{Si}_{10}\text{O}_{20})$ (Narita et al., 1975).

The nambulite and natronambulite were determined for the first time in România, in Tolovanu deposit of Manganese Belt (MnB) (Hîrtopanu & Scott, 1999). More recently, they were determined in many deposits of MnB in Bistrița Mts. Besides nambulite, natronambulite, Li-amphiboles - holmquistite and Li bearing sodium amphiboles - leakeite were found in the Dadu, Colacu, Tolovanu, Oița, Argeștru, Căprărie, Mândrileni, Sărișor, and Todireni deposits. The Li bearing minerals occur in the oxidized associations of these Mn- deposits, such as the metacherts, quartzites with large alkali pyroxenes and amphiboles, and braunite-nambulite.

2. OCCURRENCE OF NAMBULITE AND NATRONAMBULITE

The Bistrița Mountains of the Eastern Carpathians are petrologically constituted by Cambrian Tulgheș Series rocks (Tg), which is a polymetamorphic retrograde series, metamorphosed initially at amphibolites facies. The relics of biotite, almandine, ilmenite, and others are frequent in the schists lithology dominated by quartz/muscovite/chlorite/calcite/graphite. The thick Tulgheș Series of more than 6,000 m, hosts four mineralized belts with line development, which are oriented NW-SE, from West to East, and from bottom up: the Manganese Belt (MnB) situated in Tg1, the Barium Belt (BaB), situated in Tg2, the Sulfide (SB) situated in Tg3, and the Uranium (UB) situated in Tg4 (Hîrtopanu, 2020). The MnB has a great mineralogical diversity and rarity containing more than 350 minerals and mineral varieties, of which more than 182 are new for Romania, making it one of the most complex deposits in the world (Hîrtopanu, 2019).

The MnB of about 100 km along the Bistrița Valley consists of more than 20 deposits. The ore has lens-like form with medium dimensions, concordant with the foliation of country rocks. The manganese ores/manganiferous rocks have well-developed laminations/bandings, that appeared in hand samples and thin sections, representing distinct lithologies/ petrographic types, named after the predominant

mineral. The following types were established: metacherts, quartzites with large alkali sodium pyroxenes and Li-bearing amphiboles, mangancumingtonite/mangangrunerite, tephroite, Mn-humites, spessartine, pyroxmangite, rhodonite, johannsenite, hydrated Li-Na pyroxenoids and Na-Li/Li alkali amphiboles, pyrosmalites, and vein type (bannisterite, ganophyllite, and stilplomelane). The metacherts show similar, although in low concentrations of trace elements, to the type of large quartzites with alkali sodium pyroxenes and Li-bearing sodium amphibole. The relatively high Li content (3,000 ppm) as trace element in some metacherts banded with quartzites with large alkali sodium pyroxenes and Li-bearing sodium amphiboles, is due to the presence of microscopic aegirine and Li-bearing sodium amphibole in its mineralogical composition, showing their strong genetic link and common evolution (Hîrtopanu, 2023).

The braunite-bixbyite-hausmannite/nambulite bands are in direct contact with rhodonite. The fibrous pinkish natronambulite band of a few cm is banded with acmite-aegirine-namansilite association (Figure 1 right). The nambulite/natronambulite bands cut the old braunite rich bands (Figure 2 left and Figure 6 left and right).

3. PHYSICAL PROPERTIES OF NAMBULITE AND NATRONAMBULITE

Nambulite and natronambulite form bands/veins of coarser-grained/crystals aggregates of dm across. The crystals of nambulite and natronambulite are prismatic, sometimes fibrous prismatic. The maximum single grain/crystal size of nambulite/natronambulite reaches 2 cm and more (Figure 1 left). The colour of nambulite in hand sample is orange, yellow/orange, reddish yellow with orange tint and with vitreous luster (Figure 1 left and Figure 2 left). The natronambulite is apparently indistinguishable from nambulite. In hand sample it has a yellow orange pinkish colour and a vitreous luster (Figure 1 right, Figure 2 right, and Figure 3 left), which can show similar colour with the nambulite. Its streak is nearly white with a very faintly orange tint. Instead, the nambulite has a very pale-yellow streak. In Figure 1 right the natronambulite is banded by aegirine rich bands, in Figure 2 right is intergrown with holmquistite, and in Figure 3 left, it is associated with celsian and holmquistite. In Figure 2 left the nambulite cuts the braunite rich band and is associated with brown leakeite.



Figure 1. Coarse orange nambulite crystals of 2 cm long, leakeite (greenish yellow, middle top), braunite-bixbyite (black, small, bottom, left), sample BT250, 12x6x6 cm, Tolovanu mine (left); Large yellow pinkish natronambulite (centre) banded with rich acmite-aegirine (violet brown), sample BT1001, 14x10x8 cm (right). Photos by Ana Tudor.



Figure 2. Nambulite veins (orange) cuts braunite-bixbyite (black), leakeite (small, yellow brown, bottom right), sample BT259, 5x3x2 cm (left); natronambulite (light yellow) intergrown with holmquistite (greenish black), sample BT64, 5x4x3 cm (right), Tolovanu mine. Photos by Ana Tudor.



Figure 3. Natronambulite (pinkish orange), celsian (centre and left bottom, white), Li-amphibole (greenish black, left middle) sample BTm420, 6x6x3 cm (left); Rhodonite (light rose), banded by aegirine –acmite /serandite/ ardennite association (top, yellow-brown), sample BT258R, 5x3x4 cm (right), Tolovanu mine. Photos by Ana Tudor.

4. OPTICAL PROPERTIES OF NAMBULITE AND NATRONAMBULITE

The nambulite and natronambulite are almost transparent in thin sections. The nambulite is very faint light yellow, yellow (Figure 4 left), or could be nearly colourless in thin sections. The pleochroism is very slight for both minerals. Nambulite has a perfect

cleavage on (001) (Figure 4 right), and distinct on (010) and (100), and natronambulite has perfect cleavages along (100) and (001) (Figure 8 left). The natronambulite is very light yellow (Figure 5 left) or colourless (Figure 8 right) in transmitted light (TL). Both minerals are optically biaxial and positive, with small $2V(+)$ of about 30° for nambulite, and 45° for natronambulite. The two minerals have

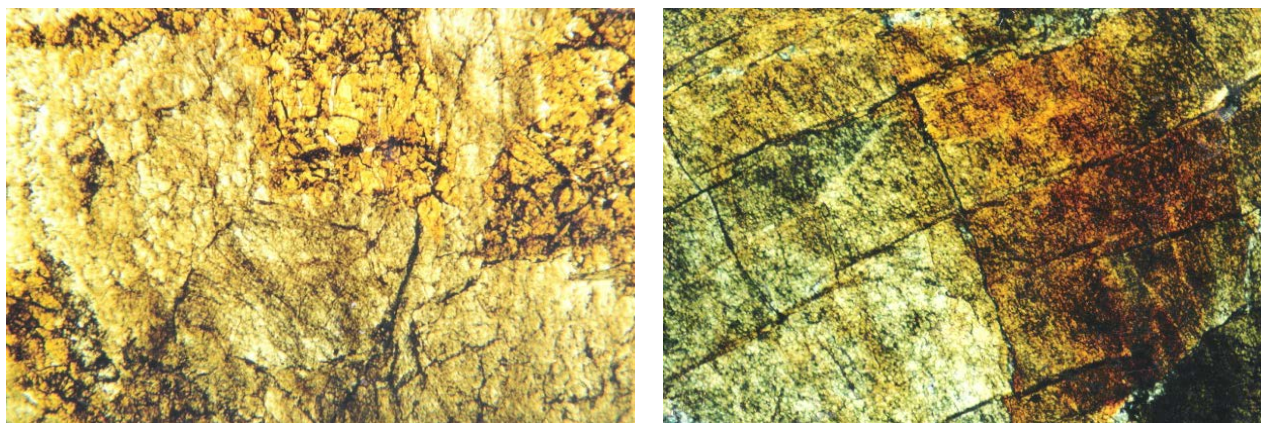


Figure 4. Nambulite (large light yellow), aegirine (yellow), TL, NII, x20, sample BT258 (left); nambulite with distinct cleavages on (010), medium/high birefringence, TL, N+, x20, sample BT250 (right), Tolovanu mine.

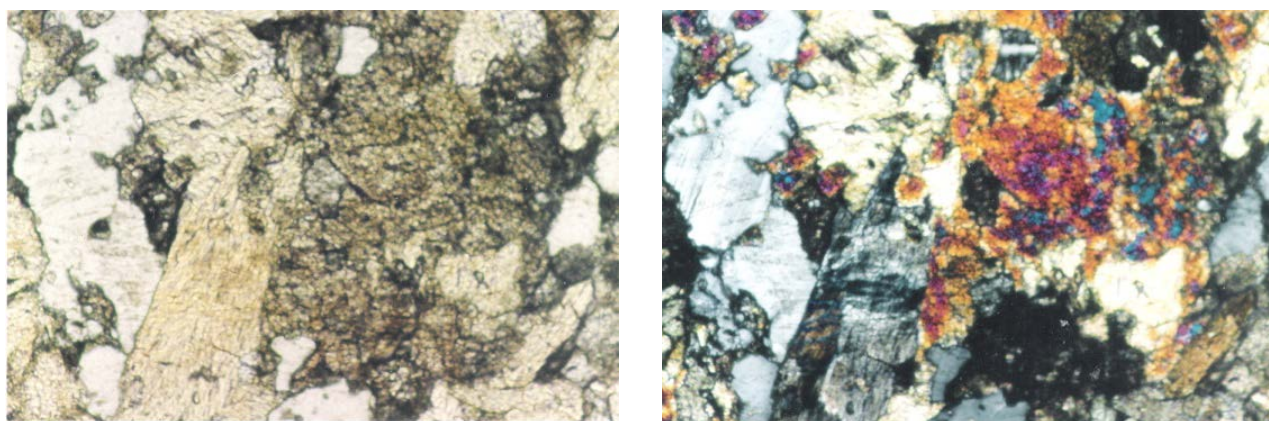


Figure 5. Natronambulite (light yellow, high refringence and birefringence), leakeite (large prism and cross section, light yellow, low birefringence), and albite (white, light grey), TL, NII (left) and N+ (right), x30, sample BT1002F, Tolovanu mine.

medium to high birefringence colours, as can be seen in Figure 4 right for nambulite and in Figure 5 right for natronambulite. The nambulite has sometimes zoned birefringence, especially when it is associated with leakeite (Figure 7 right). The faint yellowish colour of natronambulite in NII (Figure 5 left) distinguishes it from rhodonite, pyroxmangite, and johannsenite, all of which are colourless in thin sections and have the same cleavages, the same positive optic sign, and the same relatively small 2V. Under the microscope the substitution of rhodonite by nambulite or natronambulite has not been observed, instead the braunite rich association to which the two belong is banded by rhodonite.

The nambulite and natronambulite are substituted by leakeite (Figure 4 right) such as with the substitution of the old augite-jadeite-omphacite by aegirine and the old mangancummingtonite/grunerite by some Li-bearing sodium arfvedsonite and magnesioriebeckite in the quartzites with large alkali pyroxenes and amphiboles type. These quartzite type ore/rocks (band) with large alkali pyroxenes and amphiboles seem not to have nambulite or natronambulite in their mineralogical

composition, maybe because they have an oxidation grade less than that of braunite-nambulite association. Therefore, the Li is an important constituent/trace element in the three-type ore: rich braunite-nambulite, quartzites with large alkali pyroxenes /Na-Li-amphiboles/Li-amphiboles (as constituent), and metacherts (as trace element). It is absent in more reduced or reduced associations, like tephroite, manganese humites, and pyroxmangite type ore.

5. X-RAY DIFFRACTION STUDY OF NAMBULITE AND NATRONAMBULITE

The X-ray analyses of nambulite showed that it crystallizes in triclinic system, space group $P\bar{1}(2)$. Its unit cell dimensions and the strongest lines X-ray diffraction (1) are similar with that of the Gozaisho mine, Fukushima Prefecture (Matsubara, 1985) (2) and with that of Funakozawa mine, Iwate Prefecture (Yoshii et al., 1972) (3) as can be seen comparatively: (1) $a=7.53 \text{ \AA}$, $b=11.736 \text{ \AA}$, $c=6.71 \text{ \AA}$, $\alpha=92.97^\circ$, $\beta=95.23^\circ$, $\gamma=106.27^\circ$, this study; (2) $a=7.571 \text{ \AA}$, $b=11.733 \text{ \AA}$, $c=6.698 \text{ \AA}$, $\alpha=93.20^\circ$, $\beta=94.91^\circ$, $\gamma=105.77^\circ$, (Matsubara et al., 1985) ;

(3) $a=7.621 \text{ \AA}$, $b=11.762 \text{ \AA}$, $c=6.737 \text{ \AA}$ $\alpha=92.810^\circ$, $\beta=94.55^\circ$, $\gamma=106.87^\circ$, (Yoshii et al., 1972).

Also, the main strongest X-ray diffraction lines in the powder pattern of nambulite from Tolovanu mine (Table 1A) (1) are very similar with that original from Funakozawa mine, Iwate Prefecture, Japan (Yoshii et al., 1972) (2), the first nambulite occurrence as new mineral:

(1) 2.96(100); 2.92(70); 3.17(65); 3.07(60); 3.09 (55); 3.14(45); 3.34(40), Tolovanu mine;

(2) 2.96(100), 2.92(70); 3.17(65); 3.07(60); 3.09 (55); 3.01(30); 3.34 (40), Funakozawa mine.

The X-ray analyses of MnB natronambulite showed that it crystallizes in triclinic system, space group $P\bar{1}(2)$. Its unitcell parameters have values very similar with that of original natronambulite from Tanohata mine, Iwate Prefecture, the first natronambulite in the world, as new mineral:

$a=7.62 \text{ \AA}$, $b=11.762 \text{ \AA}$, $c=6.737 \text{ \AA}$, $Z=2$, $V=574.36 \text{ \AA}^3$, $\alpha=92.81^\circ$, $\beta=94.55^\circ$, $\gamma=106.87^\circ$ (Matsubara et al., 1985) ;

$a=7.62 \text{ \AA}$, $b=11.762 \text{ \AA}$, $c=6.737 \text{ \AA}$, $Z=2$, $V=574.36 \text{ \AA}^3$, $\alpha=92.81^\circ$, $\beta=94.55^\circ$, $\gamma=106.87^\circ$ (this study).

Also, the cell edges of MnB natronambulite are close to those of the original nambulite (Yoshii et al., 1972). However, the cell edges of nambulite are discernibly smaller than those of natronambulite. The strongest X-ray diffraction lines in the powder pattern for MnB natronambulite can be seen in Table 2B.

They are very similar with the original Japanese natronambulite of Tanohata mine (Matsubara et al., 1985) as can be seen comparatively, for their strongest lines (d in \AA) and relative intensities:

Tolovanu: 7.13, (47); 6.70, (44); 3.559, (100); 3.348, (40); 3.164, (20); 3.078, (45); 2.972, (34); 2.506, (38); 2.198, (23);

Tanohata: 7.13, (47); 6.70, (44); 3.559, (100); 3.348, (40); 3.160 (20); 3.078, (45); 2.972, (34); 2.506, (38), 2.198, (23).

The crystal structure of nambulite/natronambulite is considered to be more similar to those of rhodonite and /or babingtonite. Rhodonite and babingtonite are known to have five Si-O tetrahedra in their chains, pyroxmangite has seven, and pectolite has three tetrahedra. The IR absorption study of Tolovanu nambulite suggests that the structure of nambulite contains five Si-O tetrahedra as a "structural unit" of its chain, like rhodonite. Because of the same type of structure, the nambulite was considered to be an alkaline analogue of rhodonite (Yoshii et al., 1972).

6. CHEMICAL COMPOSITION OF NAMBULITE AND NATRONAMBULITE

The qualitative values for Li_2O were first determined by AAS (absorption atomic spectrography) (Table 2A and 2B) in the Camborne

Table 1. X-ray powder diffraction pattern of nambulite (A) and natronambulite (B).
A. Sample BT258R.

2 θ	d meas.	I/I ₀ %	(hkl)
18.587	4.77000	7.0 %	1,-1,1
25.000	3.55900	100.0 %	-2,2,0
26.603	3.34800	40.0 %	1,-3,1
28.181	3.16400	20.0 %	-1,0,2
28.986	3.07800	45.0 %	2,-2,1
29.686	3.00700	2.0 %	1,1,-2
30.044	2.97200	34.0 %	0,-2,2
30.624	2.91700	5.0 %	-1,4,0
33.040	2.70900	15.0 %	1,1,2
34.223	2.61800	15.0 %	-2,1,2
35.803	2.50600	38.0 %	-2,2,2
37.884	2.37300	15.0 %	2,-2,2
40.587	2.22100	6.0 %	0,-1,3
41.030	2.19800	23.0 %	3,0,1
48.958	1.85900	6.0 %	1,2,3
49.991	1.82300	4.0 %	2,0,3
54.830	1.67300	20.0 %	-4,3,2
56.141	1.63700	4.0 %	-4,5,1
58.155	1.58500	10.0 %	4,-3,2
59.812	1.54500	3.0 %	-2,2,4
61.121	1.51500	4.0 %	4,2,1
62.823	1.47800	3.0 %	1,-4,4
65.547	1.42300	15.0 %	-2,-5,3

B. Sample BTm420.

2 θ	d meas.	I/I ₀ %	(hkl)
12,439	7.11000	25.0 %	1,-1,0
13,204	6.70000	25.0 %	0,0,1
25,136	3.54000	35.0 %	-1,-2,1
26,668	3.34000	40.0 %	2,0,1
28,127	3.17000	65.0 %	1,0,2
28,401	3.14000	45.0 %	0,1,2
28,871	3.09000	55.0 %	-1,1,2
29,063	3.07000	60.0 %	2,-2,1
29,655	3.01000	30.0 %	-2,-1,1
30,064	2.97000	80.0 %	0,-2,2
30,168	2.96000	100.0 %	1,-1,2
30,591	2.92000	70.0 %	1,0,2
33,027	2.71000	35.0 %	1,1,2
34,196	2.62000	40.0 %	-2,1,2
36,041	2.49000	30.0 %	-1,3,2
40,209	2.24100	20.0 %	1,-4,2
40,587	2.22100	30.0 %	0,-1,3
41,030	2.19800	45.0 %	3,0,1
49,298	1.84700	35.0 %	2,-6,1
53,956	1.69800	25.0 %	4,-4,1
54,060	1.69500	25.0 %	2,-4,3
54,937	1.67000	35.0 %	-3,-3,2
66,017	1.41400	25.0 %	3,2,3

School laboratory, Cornwall. The representative chemical composition of MnB nambulite and natronambulite have been determined by SEM (scanning electron microscope), also in Cornwall (Table 3), and by wet chemical analyses (Table 4) in the laboratory of the Geological Institute of Romania.

In Table 4 the samples BT258, BT1002, BT268A, and BT268P with $\text{Li}_2\text{O} > \text{Na}_2\text{O}$, are nambulites and the samples BT1002A, BT1002J, BT224, and BT1002N, BT1000, with $\text{Na}_2\text{O} > \text{Li}_2\text{O}$ are natronambulites. As it can be seen in this table, the MnO content in natronambulite is slightly lower than in nambulite, instead the FeO, MgO, and Ca contents

are slightly higher. These analyses of nambulite and natronambulite show that their compositional variations are not given by a substitution of Na for Li, but accompanied by a concomitant substitution of Ca for Mn, according to the increase of Na relative to Li, and also of Mg and Fe for Mn.

Therefore, in the natronambulite the MnO remains higher than CaO. A formulated expression of the ideal natronambulite is thus: $(\text{Na}, \text{Li})(\text{Mn}, \text{Ca})\text{Mn}_3\text{Si}_5\text{O}_{14}\text{OH}$, where $\text{Na} > \text{Li}$ and $\text{Mn} > \text{Ca}$ in the parentheses and without Li (Mathubara et al., 1985). Based on the chemical data, nambulite and natronambulite may be considered as analogues

2. The AAS analyses on nambulite (A) and and natronambulite (B). Analyst: Sharon Uren.

A.			B.		
Sample/oxide	Li_2O	Na_2O	Sample/oxide	Li_2O	Na_2O
BT268p	1.34	0.83	BT1002CR	0.22	1.27
BT1002C	1.05	0.95	BT1002J	0.45	5.96
BT258	1.34	0.83	BMD1	0.50	3.20
BT1002X	1.23	1.00	BT1002	0.65	1.28
BT258P	1.50	0.90	BT100	0.60	1.10

Table 3. Representative SEM analyses of nambulite, sample BT268P. Analyst Antony Ball.

Oxide/Point	Pnt. 1	Pnt.1a	Pnt. 2	Pnt.5	Pnt. 6	Pnt. 8	Pnt. 10
Na ₂ O	0.900	0.612	0.687	0.866	0.994	0.541	0.381
MgO	1.564	2.066	1.858	1.866	1.524	1.846	1.837
SiO ₂	49.067	48.811	48.367	50.201	49.605	49.564	49.753
CaO	1.131	0.954	0.991	0.867	1.389	0.879	0.906
MnO	44.396	43.717	44.110	45.031	46.011	45.245	45.493
FeO	0.413	0.451	0.000	0.006	0.198	0.085	0.131
NiO	0.000	0.081	0.105	0	0	0	0
Al ₂ O ₃	0	0	0	0.064	0	0	0.026
<i>Li₂O determined by AAS is considered to be the same for all points = 1.34</i>							
Total	97.513	96.693	96.253	98.901	99.721	98.541	97.501

The difference until 100 of total are undetermined F and H₂O.

Table 4. The wet chemical analyses of nambulite and natronambulite. Analyst Doina Necşulescu.

Sample / oxide	*BT258	*BT1002	**BT1002A	**BT1000	**COM1B	*BT268A	*BT268P	**BT1002J	**BT1002N
SiO ₂	48.29	49.77	49.48	50.12	47.20	44.98	48.29	48.69	47.67
Al ₂ O ₃	0.40	0.12	0.60	0.36	0.11	0.40	0.40	0.20	0.91
TiO ₂	0.11	0	0.16	0.03	0.19	0.20	0.11	0.02	0.20
FeO	0	0	0.65	0.06	0.18	0	0	0.52	0.30
Fe ₂ O ₃	0.63	0.49	0.65	0.53	0.27	0.30	0.63	0	3.40
MnO	40.90	40.85	38.20	38.92	38.92	43.07	43.90	38.84	35.26
MgO	2.18	2.28	3.47	3.21	2.35	2.27	2.18	3.21	3.83
CaO	1.36	1.50	2.01	1.95	4.27	4.71	1.36	3.95	3.22
Na ₂ O	0.83	0.95	1.28	1.20	2.33	0.10	0.72	3.11	1.78
K ₂ O	0.27	0.05	0.12	0.05	0.03	0.17	0.27	0.07	0.45
P ₂ O ₅	0.10	0.05	0.09	0.13	0.04	0.06	0.10	0	0.02
H ₂ O ⁺	1.23	1.71	1.82	1.96	0.41	0	1.23	1.77	1.56
Li ₂ O	1.34	1.05	1.23	1.02	0.31	1.34	1.25	0.56	0.47
Total	98.14	98.91	97.98	98.42	98.55	96.18	99.43	98.96	98.30

*Nambulite; **Natronambulite. The total of each analysis included the loss on calcination.

of rhodonite, in which Li and Na seem to substitute Ca. Therefore, the ionic radii of Li and Na are too different ($\text{Li}^{+1} = 0.68 \text{ \AA}$ and $\text{Na}^{+1} = 0.97 \text{ \AA}$) to form a solid solution. Because of this difference of ionic radii, Yoshii et al. (1972) considered that the structural positions of Li and Na are different, and the nambulite formula could be $\text{LiNaMn}_8\text{Si}_{10}\text{O}_{28}(\text{OH})_2$.

7. ASSOCIATED MINERALS TO NAMBULITE AND NATRONAMBULITE

The nambulite is associated with braunite, bixbyite, hausmannite, aegirine/acmite, rhodonite, leakeite, jacobsite-Q, albite, microcline, magnetite, hematite, hematophanite, Ba-feldspars, and quartz. The natronambulite has mostly affinity for the minerals which contain more Na in their composition: aegirine, namansilite, albite, leakeite, serandite, ardenite, and imandrite. Also, it is associated with holmquistite crystals (Figure 2 right), lithiarmsturite, microcline, and quartz.

Braunite, $\text{Mn}^{2+}\text{Mn}^{3+}\text{O}_8\text{SiO}_4$. The old braunite rich bands are cut by nambulite/ natronambulite veinlets (Figures 2 left, 6 left). The braunite is a primary mineral, as are the old Mn silicates of the reduced associations, but it has been formed at a high range of oxygen fugacity. The $f(\text{O}_2)$ varied within different parts of the Mn-ore of MnB, just within a small area, like that of braunite-nambulite association. The more oxidized conditions in these bands are originated in some local domains that behaved as closed systems with respect to $f(\text{O}_2)$, being internally banded through the carbonate- silicate tephroite, manganese humite, rhodonite, pyroxmangite bands, which are formed in reduced/or more reduced conditions. This old braunite belongs to the early Ca-poor type. The Ca-richer braunite with up to 20 wt.% of the neltnerite molecule ($\text{CaMn}^{3+}_6\text{SiO}_{12}$) also occurs later.

The X-ray analyses of MnB braunite showed that it crystallizes in tetragonal system, $I4_1/\text{amd}(142)$ class. Its cell dimensions are: $a=9.43200 \text{ \AA}$, $c=18.70300 \text{ \AA}$, $Z=8$, $V=1,66387 \text{ \AA}^3$. The main lines in the X-ray powder diffraction pattern of a selected sample expressed in terms of d spacings (in \AA), relative intensities (I/I_0 , %) and Miller indices (hkl) can be seen in Table 5A.

Bixbyite, $(\text{Mn}^{3+}\text{Fe}^{3+})_2\text{O}_3$, occurs in small quantities in the rich braunite bands/relics in the large nambulite/natronambulite aggregates. It is cubic, space group $Ia3(206)$, and has the unit cell parameters: $a=b=c=9.40910 \text{ \AA}$, $Z=16$, $V=833.00 \text{ \AA}^3$. The main lines in the X-ray powder diffraction pattern of a selected sample expressed in terms of d spacings (in \AA) relative intensities (I/I_0 , %), and

Miller indices (hkl) are: 2.71497, (100), (224); 2.35800, (12.5), (400); 1.6673, (11.2), (440); 1.660, 20, (27.7), (408); and 1.42081, (13.8), (624).

In the braunite-bixbyite-hausmannite association the Fe^{3+} is incorporated in bixbyite and the stability field of braunite extends inside the stability field of hausmannite (Sivaprakash, 1980), which becomes stable in this association. Also, the appearance of nambulite and natronambulite in this older oxide association lowers the $f(\text{O}_2)$, because these two minerals are unable to host the Fe^{3+} (Sivaprakash, 1980).

Hausmannite, $\text{Mn}^{2+}\text{Mn}^{3+}_2\text{O}_4$, forms black brown "chocolate" granular aggregates (Figure 7 right). It crystallizes tetragonal, space group $I4_1/\text{amd}(141)$. The elementary unit cell parameters of hausmannite are: $a=5.7540 \text{ \AA}$, $c=9.42980 \text{ \AA}$, $Z=4$, $V=312.29 \text{ \AA}^3$, $\alpha=\beta=\gamma=90^\circ$. The main lines in the X-ray powder diffraction pattern of a selected sample expressed in terms of d spacings (in \AA), relative intensities (I/I_0 , %) and Miller indices (hkl) can be seen in Table 5B. The hausmannite forms a series with hetaerolite and is isostructural with tetragonal jacobsite-Q. In reflected light it is grey, has internal reflections of deep blood-red to red brown, and develops fine lamellar twinning.

Magnetite, Fe_3O_4 , occurs in braunite rich association. The parameters of its unit cell are: $a=8.39300 \text{ \AA}$, $Z=8$, $V=591.22 \text{ \AA}^3$. The main lines in the X-ray powder diffraction pattern of a selected sample of magnetite expressed in terms of d spacings (in \AA), relative intensities (I/I_0 , %), and Miller indices (hkl) are: 2.96737, (26.5), (220); 2.53058, (100.0), (311); 2.09825, (31.2), (400); 1.61523, (25.8), (511); and 1.48369, (41.9), (440).

Jacobsite-Q, $\text{Mn}_2(\text{Fe}^{3+}\text{Mn}^{3+})_2\text{O}_4$, has a greenish/black colour. The X-ray data of the jacobsite-Q show that it is tetragonal, having the space group $I4_1/\text{amd}(141)$. The unit cell dimensions are: $a=6.02500 \text{ \AA}$, $c=8.53900 \text{ \AA}$, $Z=4$, $V=309.97 \text{ \AA}^3$. The **jacobsite-Q** occurs in saturated associations such as in nambulite association, while **the jacobsite** is present in the reduced, free of quartz associations, such as in the tephroite and Mn-humites. The main lines in the X-ray powder diffraction pattern of a selected sample of jacobsite-Q expressed in terms of d spacings (in \AA), relative intensities (I/I_0 , %), and Miller indices (hkl) are: 4.92292, (19.5), (101); 3.01574, (35.1), (200); 3.01574, (35.1), (112); 2.56957, (100), (211); 2.56957, (100), (103); 2.13016, (19.7), (220).

Leakeite, $\text{NaNa}_2(\text{Mg}_2\text{Fe}^{3+}_2\text{Li})\text{Si}_8\text{O}_{22}(\text{OH},\text{F})$, crystallizes in monoclinic system, space group $C2/m(12)$. The colour of leakeite is green yellowish (Figure 1 left) or yellow brown in hand sample

Table 5. Xray powder diffraction pattern of braunite (A) sample BT268H and hausmannite (B), sample BT262.

A.				B.			
Θ	dValue	I/I ₀	(hkl)	Θ	dValue	I/I ₀	(hkl)
18.026	4.91704	23.3 %	1,0,1	18.044	4.91229	22.6 %	1,0,1
28.927	3.08417	37.3 %	1,1,2	28.961	3.08058	37.7 %	1,1,2
31.036	2.87920	15.7 %	2,0,0	32.429	2.75860	76.0 %	1,0,3
32.376	2.76300	75.7 %	1,0,3	36.149	2.48282	100.0 %	2,1,1
36.122	2.48459	100.0 %	2,1,1	44.504	2.03417	19.3 %	2,2,0
36.519	2.45852	14.3 %	2,0,2	50.912	1.79217	22.4 %	1,0,5
38.069	2.36190	18.6 %	0,0,4	58.613	1.57371	27.9 %	3,2,1
44.464	2.03590	20.3 %	2,2,0	60.013	1.54029	49.9 %	2,2,4
50.815	1.79534	22.3 %	1,0,5	60.027	1.53998	48.1 %	2,2,4
58.570	1.57475	28.1 %	3,2,1	64.761	1.43837	17.3 %	4,0,0
59.937	1.54208	50.2 %	2,2,4	74.312	1.27536	8.0 %	4,1,3
64.699	1.43960	18.1 %	4,0,0	86.744	1.12169	5.3 %	4,1,5

(Figure 2 left), and in thin sections is yellow/light yellow (Figure 5 left). Frequently it is zoned, due to the variation of its composition: the core of leakeite is yellow light, and the rim is yellow (Figure 7 left). In transmitted light leakeite has low birefringence (Figures 5 right and 7 right), and can be seen how it grown on nambulite. In the Figure 7 right the nambulite is cut by zoned yellow leakeite with very variable birefringence in the same crystal.

The dimensions of unit cell of MnB leakeite (1) are similar with that of leakeite from Madhya Pradesh, India (Hawthorne et al., 1992) (2) and that of ferri-fluor-leakeite from Bratthagen, Norway (Oberti et al., 2014) (3):

(1) $a=9.7897 \text{ \AA}$, $b=17.8478 \text{ \AA}$, $c=5.2867 \text{ \AA}$, $Z=2$, $V=895.88 \text{ \AA}^3$, $\beta=104.103^\circ$;

(2) $a=9.8223 \text{ \AA}$, $b=17.8366 \text{ \AA}$, $c=5.2862 \text{ \AA}$, $Z=2$, $V=897.15 \text{ \AA}^3$, $\beta=104.373^\circ$;

(3) $a=9.7879 \text{ \AA}$, $b=17.8263 \text{ \AA}$, $c=5.2822 \text{ \AA}$, $Z=2$, $V=893.5 \text{ \AA}^3$, $\beta=104.195^\circ$

The first occurrence of leakeite as a new amphibole is the Kajlidongri manganese mine, Jhabua district, Madhya Pradesh, India (Hawthorne et al., 1992), where it occurs in amphibolites-braunite-bixbyite-rocks. In MnB the leakeite occurs in the same braunite rich rocks, but has the nambulite in association, on which it seems to grow (Figures 1 left, 2 left, and 7). The second occurrence of ferri-fluoro-leakeite, with a different origin than MnB leakeite has been identified in the Bratthagen nepheline syenite pegmatite, Vestfold County, Norway (Oberti et al., 2014).

Holmquistite, $\text{Li}_2(\text{Mg}_3\text{Fe}^{2+})_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$.

The holmquistite group comprises orthorhombic amphiboles of the lithium amphibole subgroup. The mineral holmquistite is defined with $\text{Mg} > \text{Fe}^{2+}$ and Al^{3+} in the C position. The colour in hand sample is black, grey, bluish-grey, black grey (Figure 2 right). It is vitreous and glassy. In MnB the holmquistite

forms large grains/crystals associated with natronambulite (Figure 2 right). The optical and physical properties are similar to those of other holmquistites cited in the literature. The main lines in the X-ray powder diffraction pattern of a selected holmquistite sample expressed in terms of d spacings (in \AA) and relative intensities (I/I₀, %) are very similar with that of the Barraute occurrence, Canada (Nickel et al., 1960) as can be seen below:

MnB, Romania: 8.107 (100), 3.00 (90), 4.427 (70), 3.339 (60), 3.612 (50), 2.538 (50), 2.797 (40);

Barraute, Canada: 8.107 (100), 3.00 (90), 4.430 (70), 3.340 (60), 3.610 (50), 2.538 (50), 2.797 (40).

Based on the X-ray data the holmquistite from MnB (1) was refined as orthorhombic, space group Pnma(62), and has the following unit cell parameters, which are also very similar with that of (2) Barraute holmquistite, as can be seen below:

(1) $a=18.300 \text{ \AA}$, $b=17.6900 \text{ \AA}$, $c=5.3000 \text{ \AA}$, $Z=4$, $V=1715.75 \text{ \AA}^3$ (this study);

(2) $a=18.300 \text{ \AA}$, $b=17.6900 \text{ \AA}$, $c=5.3000 \text{ \AA}$, $Z=4$, $V=1715.75 \text{ \AA}^3$ (Nickel et al., 1960).

These similarities exist between the two holmquistites, in spite of their different genesis. The Barraute holmquistite occurs at/or near the contact of spodumen pegmatite and hornblende -rich rock (Nickel et al., 1960), and Tolovanu holmquistite occurs secondary in the nambulite/natronambulite association of MnB.

Aegirine-acmite, $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$, alkali pyroxene is widespread in the natronambulite/nambulite, alkali quartzite, and metachert associations.

Aegirine has a strong affinity to nambulite (Figures 4 left, 8 left) and natronambulite (Figure 8 right). The Na-pyroxene belongs to aegirine-augite, with great compositional variations, reflected by the frequently marginal and sectorial zonations (Figure 8 left). The (2V) values indicate two minerals: manganaegirine, on the rim, and manganoan aegirine-



Figure 6. Braunite rich band (black) cut by natronambulite (light orange) veinlets, sample BT1002C, 6x3x2 cm (left); Hausmannite (brown “chocolate”) relics in nambulite ore (orange) and cut by very small nambulite veins, sample BT262, 3x3x2 cm dimensions (left). Photos by Ana Tudor.

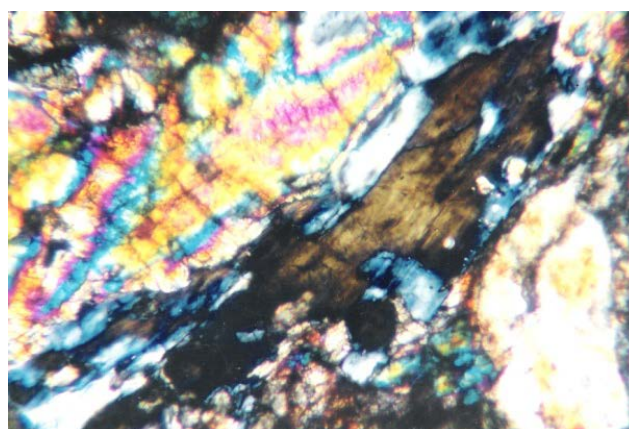
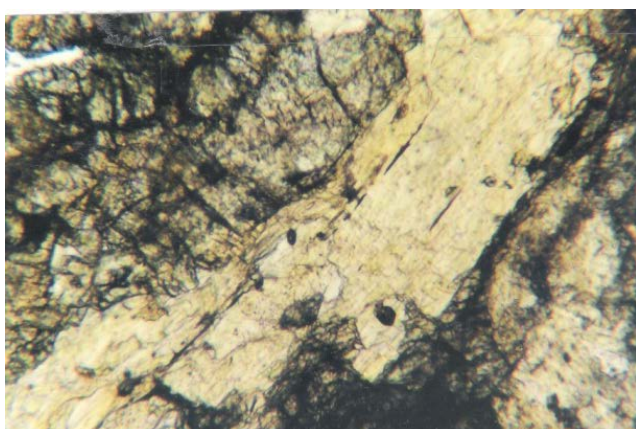


Figure 7. Zoned leakeite (large crystal, light yellow centre and yellow rim) with variable birefringence (right), cuts the nambulite (white yellowish, high refringence and birefringence), TL, NII (left) and N+ (right), x30, sample BT258P.

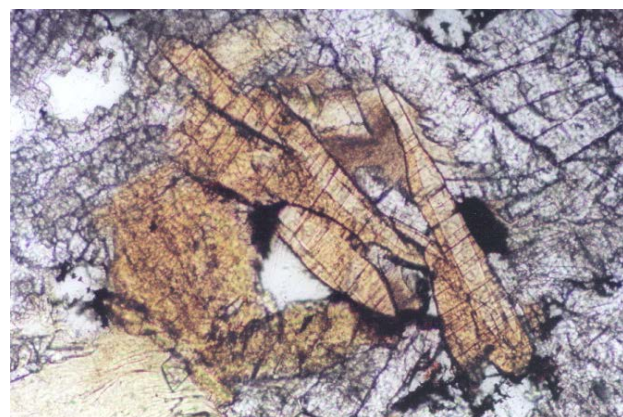
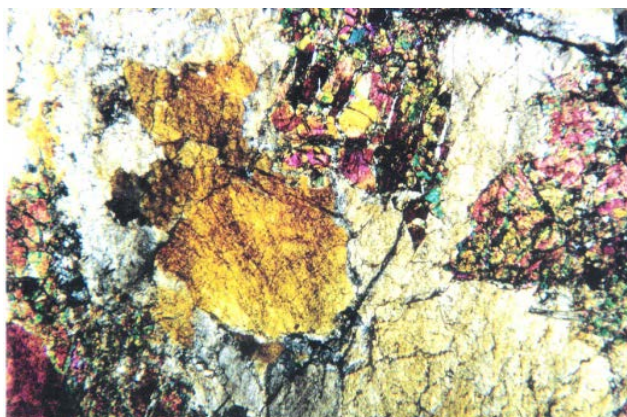


Figure 8. Aegirine-acmite (high birefringence, fine twinned, coloured), nambulite (yellow, light yellow, orange), TL, N+, x30, sample BT258 (left); Zonings of manganoan aegirine-augite (yellow light brown), natronambulite (white, cleavage), leakeite (light yellow, bottom left corner), TL, NII, x35, sample BT1007A (right), Tolovanu mine.

augite, in the core of the crystal. The compositional zoning shows that the new alkali pyroxenes could crystallize from the old hedenbergite-jadeite-johannsenite type composition. The manganoaegirine is an acmite variety. It occurs as a small band of aggregates of brownish violet colour in hand sample

(Figure 3 right) where it is associated with serandite, ardennite, and is banded with rhodonite. It is yellow in transmitted light (Figure 4 left) or light brown (Figure 8 right) and has low content of FeO, TiO₂, MnO, and CaO, and higher content of Fe₂O₃ than that of the green black aegirine variety. The aegirine-

augite crystallizes in monoclinic system, space group C2/c(15), and has the following parameters of unit cell: $a=9.657 \text{ \AA}$, $b=8.8010 \text{ \AA}$, $c=5.2910 \text{ \AA}$, $\beta=107.40^\circ$, $V=429.11 \text{ \AA}^3$, $Z=4$.

Namansilite, $\text{NaMn}^{3+}\text{Si}_2\text{O}_6$, forms mm veinlets of stout prismatic crystals up to 2-3 mm long which cut the hausmannite ore. The X-ray powder diffraction for namansilite given the cell dimensions which are essentially identical with that determined by Kawachi & Coombs (1993) for the namansilite at the Woods mine, New South Wales, Australia:

$a=9.500 \text{ \AA}$, $b=8.611 \text{ \AA}$, $c=5.3560 \text{ \AA}$, $z=4$, $V=423.22 \text{ \AA}^3$, $\beta=105.00^\circ$, Tolovanu mine;

$a=9.500 \text{ \AA}$, $b=8.611 \text{ \AA}$, $c=5.3561 \text{ \AA}$, $z=4$, $V=423.14 \text{ \AA}^3$, $\beta=105.00^\circ$, Woods mine.

The namansilite belongs to highly oxidized nambulite/ natronambulite-braunite-hausmannite associations. The presence of associated acmite, imandrite, and serandite, are further evidence of availability of Na. The namansilite occurrence which is the Mn analogue of aegirine, in associations with other minerals with Mn^{3+} and Fe^{3+} , is specific to subduction zones, which is the tectonic-structural setting of the Manganese Belt.

Rhodonite, $\text{CaMn}_3\text{MnSiO}_4$. The former simplified MnSiO_3 formula of rhodonite no longer represents the overall rhodonite group. Structural studies and the recognition of new species in the rhodonite group indicate a pure Mn-dominant rhodonite expressed as $\text{Mn}^{2+}\text{Mn}^{2+}_3\text{Mn}^{2+}[\text{Si}_5\text{O}_{15}]$. This composition was recognized as the new mineral, named **vittinkiite**. It is isostructural with rhodonite. The vittinkiite is a Ca free rhodonite. The end-member formulae of approved rhodonite-group minerals are as follow: **rhodonite** $\text{CaMn}_3\text{Mn}[\text{Si}_5\text{O}_{15}]$ **ferrorhodonite**, $\text{CaMn}_3\text{Fe}[\text{Si}_5\text{O}_{15}]$ (Shchipalkina et al., 2017), and **vittinkiite** $\text{MnMn}_3\text{Mn}[\text{Si}_5\text{O}_{15}]$ (Shchipalkina et al., 2020). In manganese deposits of MnB were found the rhodonite and ferrorhodonite. The rhodonite represents the primary mineral of old type ore, while the ferrorhodonite occurs secondary, formed on old johannsenite (Hirtopan, 2019). The X-ray data of rhodonite (Table 6) show that it is triclinic, space group $\text{C}\bar{1}(2)$, and has the unit cell data: $a=9.87930 \text{ \AA}$, $b=10.52980 \text{ \AA}$, $c=12.22570 \text{ \AA}$, $\alpha=108.744^\circ$, $\beta=103.752^\circ$, $\gamma=82.03^\circ$, $Z=4$, $V=583.57 \text{ \AA}^3$.

Hematophanite, $\text{Pb}_4\text{Fe}_3\text{O}_8(\text{OH},\text{Cl})$, is member of perovskite group. In transmitted light it has a red brown colour, very good micaceous cleavages, and is uniax (-). Hematophanite crystallizes tetragonal system, space group $\text{P}4\text{mm}$. Its unit cell dimensions are: $a=3.9200 \text{ \AA}$, $c=15.3100 \text{ \AA}$, $Z=1$, $V=235.26 \text{ \AA}^3$, and $\alpha=\beta=\gamma=90^\circ$. The unit cell dimensions and the main lines in the X-ray powder diffraction pattern of a selected sample expressed in

terms of d spacings (in \AA), relative intensities (I/I_0 , %), and Miller indices (hkl) are very similar with Långban (Sweden) hematophanite (Rouse, 1973). The MnB hematophanite occurs in the hausmannite oxidized association.

Table 6. X-ray powder diffraction pattern of rhodonite (Sample BTM420).

Θ	d Value	I/I_0	(hkl)
18.520	4.78704	21.8 %	2,0,0
18.520	4.78704	21.8 %	-2,0,1
28.446	3.13514	41.3 %	-3,-1,2
28.446	3.13514	41.3 %	1,-3,1
29.954	2.98071	57.9 %	-3,1,0
29.954	2.98071	57.9 %	1,-3,2
30.563	2.92269	78.5 %	1,1,3
32.261	2.77256	100.0 %	-2,-2,4
34.497	2.59785	22.6 %	0,-4,1
40.636	2.21841	22.7 %	4,2,0
40.636	2.21841	22.7 %	2,2,3
41.422	2.17814	28.9 %	2,-4,1

Serandite, $\text{NaMnSi}_3\text{O}_8(\text{OH})$, is the manganese analogue of pectolite, $\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$, and the sodium analogue of tanohataite, $\text{LiMn}_2\text{Si}_3\text{O}_8(\text{OH})$. It forms a series with schizolite, $\text{NaCaMn}(\text{Si}_3\text{O}_8)$, and pectolite. The serandite prismatic acicular grains have light orange/salmon red/yellow colour or colourless in transmitted light. The crystals have perfect cleavages on (001) and (100), and they are twinned. It is biaxial positive with $2V=40^\circ$ and has high birefringence. The serandite occurs in association with aegirine-acmite and ardennite, as narrow/small veins in natronambulite or rhodonite (Figure 3 right).

Ardennite-(As),

$\text{Mn}_2\text{Al}_4(\text{AlMg})(\text{AsO}_4)(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})(\text{OH})_6$, occurs as fibrous, silky, elongated yellow green/pinkish white crystals. It has two perfect cleavages on (001) and (100), and parting on (001). In transmitted light it has weak pleochroism, is biaxial positive with $2V$ around 30° , and has moderated to low birefringence. The X-ray data show for MnB ardennite: orthorhombic system, space group Pnmm , unit cell dimensions $a=8.7670 \text{ \AA}$, $b=5.8460 \text{ \AA}$, $c=18.613 \text{ \AA}$, $V=953.95 \text{ \AA}^3$, $Z=2$, and $\alpha=\beta=\gamma=90^\circ$. The main lines in the X-ray powder diffraction pattern of a selected sample expressed in terms of d spacings (\AA), relative intensities (I/I_0 , %), and Miller indices (hkl) are: 3.19071, (35.5), (204); 2.95614, (89.8), (115); 2.923, (51.3), (300); 2.9230, (51.3), (020); 2.61393, (100), (310); 2.61393, (100), (116); 2.47517, (33.6), (304); 2.47517, (33.6) (024); 2.03596, (31.6) (225), 1.5863 (32.6) (505), and 1.58635 (32.6) (425).

The ardennite is associated with aegirine-

acmite and serandite which banded the rhodonite (Figure 3 right).

Phlogopite

nickelian,

$\text{K}(\text{Ni,Mn,Mg})_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{F,OH})_2$, contains up to 3% NiO and up to 6-7% MnO. It is associated to manganoan aegirine-acmite/namansilite, hematite, albite, and quartz. The sulfides are absent. This association belongs to highly oxidized one, where F_{S_2} is sufficiently low for Ni sulfides to be unstable. The Ni substitutes Mg in octahedral sites in phlogopite, the way Cu substitutes Mg in the highly oxidized Mineoka siliceous schists from Kamogawa, Bosso Peninsula, central Japan (Hiroi et al., 1992).

Imandrite, $\text{Na}_{12}\text{Ca}_3\text{Fe}^{3+}_2\text{Si}_{12}\text{O}_{36}$, belongs to the lovozerite group. This very rare mineral was determined in Tolovanu deposit, in association with natronambulite, aegirine, and leakeite. The imandrite was found for the first time in Khibiny massif, Russia, in apatite-bearing alkali pegmatite, in a differentiated alkali massif. There it is associated with eudialyte, aegirine, pectolite, and alkali amphiboles (Khomyakov et al., 1979). The imandrite of MnB seems to be the second occurrence in the world and first in the metamorphic manganese deposits. Its occurrence here is very different from that of Khibiny alkaline massif, however their X-ray data are very similar. In transmitted light it has characteristic honey/kaki colour and a very low dark grey blue birefringence. Imandrite crystallizes in orthorhombic system, space group Pmn(58). Its unit cell parameters and unit cell volume are very similar with that of Khibiny imandrite, as can be seen below:

$a=7.4260 \text{ \AA}$, $b=10.5460 \text{ \AA}$, $c=10.3310 \text{ \AA}$, $Z=2$, and $V=809.07 \text{ \AA}^3$, $\alpha=90^\circ$, $\beta=90^\circ$, and $\gamma=90^\circ$: Tolovanu;
 $a=7.4260 \text{ \AA}$, $b=10.5460 \text{ \AA}$, $c=10.3310 \text{ \AA}$, $Z=2$, and $V=809.07 \text{ \AA}^3$, $\alpha=90^\circ$, $\beta=90^\circ$, and $\gamma=90^\circ$: Khibiny.

The main lines in the X-ray powder diffraction pattern of a selected sample expressed in terms of d spacings (\AA), relative intensities (I/I_0 , %), and Miller indices (hkl) are: 3.93435, (23.7), (211); 3.68998, (21.3), (220); 3.31686, (23.6), (112); 2.63650, (26.7), (040); 2.61731, (100), (222); 2.58275, (25.2), (400); and 1.84499, (29.5), (440).

Other minerals associated to nambulite are celsian, hematite, rhodochrosite, quartz, and to natronambulite are: lithiomarsturite, albite, barite, microcline, hyalophane, hematite, and quartz.

8. GENETICAL CONSIDERATIONS

Schneider (1987) considered that the nambulite occurs under low T and P conditions, in hydrothermal system related to contact metamorphism and no external supply of elements is necessary, all components for its formation can be derived from the

surrounding ore. The manganese orebodies in the Kitakami Mountains, Japan and that of Figuerinha Mine, Brazil are considered to be of the contact-metamorphosed origin. The ore of nambulite and natronambulite from Tanohata mine, Iwate Prefecture, Japan, was formed at the contact of Jurassic chert which was recrystallized by the intrusion of Cretaceous granodiorite body. The grade of contact metamorphism estimated from the metamorphic minerals is slightly lower than amphibolite facies (Matsubara et al., 1985). The nambulite of Kombat manganese ore from Namibia is considered to be related/associated with widespread intrusions of granitoids (Schneider, 1987). In agreement with this genesis of nambulite and natronambulite it is likely that in the depth of Bistrița Mountains there are some granitic plutons, which are common in many regions with similar manganese deposits in the world. No granitic plutons have been yet discovered in the depth of Bistrița Mountains.

In the MnB a wide range of prograde amphibolites facies silicate and manganese-rich oxide mineral assemblages are found, including those rich in grünerite/Mn-grünerite, cummingtonite/mangancummingtonite, tephroite, manganese humite +jacobsonite, spessartine, pyroxmangite, rhodonite, johannsenite, ferrorhodonite, and braunite/bixbyite/hausmannite/magnetite. A retrograde metamorphic and metasomatic overprint, possibly related to the Variscan orogeny, has produced assemblages with Mn-aegirine, Mn-rich sodium alkali amphiboles, many Li minerals such as nambulite, natronambulite, Li-Na amphiboles, and Li-amphiboles. The presence of fine microscopic exsolutions inside alkali pyroxenes and amphiboles by cooling, indicates that they are formed at the expense of older chemically homogenous minerals of higher T and P. It can suggest that this old initial paragenesis was the hedenbergite/ omphacite /jadeite /johannsenite-glaucophane. The Na source could be the augite-jadeite and glaucophane which was probably formed in the first metamorphic phase. The Li minerals formed at this phase may have disappeared through the metamorphism. The rhodonite which was formed in this metamorphic phase has very rare Li as trace element, but doesn't show microscopic substitution by nambulite. It can be assumed that the Li source has been probably the hydrothermal jaspers/silica, which accompanied the mafic gabbroic/basaltic rocks, and probably some Li minerals, like todorokite and buserite, typically manganese hydrothermal minerals, whose crystal tunnel structure hosts Li, Ba, and Mg. Both minerals occur in the modern submarine hydrothermal manganese deposits (Cann et al., 1977). The polymetamorphism of hydrothermal submarine

deposits has been probably accompanied by insitu metasomatic processes, especially with Na and Li, and by hydrothermal metamorphic activity, when the nambulite/natronambulite were formed only in the association with very high oxidizing grade, such as the old braunite rich association. Later, at the expense of nambulite/natronambulite, leakeite, holmquistite, lithiomastrurite occur in the very high oxidized conditions.

The metacherts, the quartzites with large alkali pyroxenes and Li-bearing sodium amphiboles /Li-amphiboles, and the braunite/natronambulite /nambulite type ore, have Li concentrations as trace/content element. The three oxidated lithologies are formed under different $f(\text{O}_2)$ conditions: metacherts were formed at high fugacity, the quartzites were formed at higher fugacity, and the braunite-nambulite association was formed at very high fugacity. Some metacherts (c-metachert, Hirtopanu, 2023) have a diluted composition like those of the quartzite with large alkali pyroxenes and Li-bearing sodium amphiboles. In terms of absolute concentrations, the (c)-metachert has relatively high Na, K, and Li contents. The thin bands of this (c)-metachert type are banded with quartzites with large alkali pyroxenes and amphiboles. The three lithologies types are contemporaneous with Mn ore types which were formed under reduced/more reduced conditions, which has not Li as trace element/content. Therefore, the old primary minerals, Mn silicates and Mn oxides of the manganese ore were formed at a high range of oxygen fugacity. The $f(\text{O}_2)$ varied within different parts of the Mn-ore of MnB, just within a small area, like that of braunite rich/nambulite association. The varying oxygen fugacity was not externally imposed, but was internally inherited and the mobility of oxygen was restricted during metamorphism (Sivaprakash, 1980). Internally inherited variations $f(\text{O}_2)$ has produced local variations in primary mineralogy and mineral compositions. Strong internally buffering of $f(\text{O}_2)$ by mineral reactions during prograde metamorphism produced such diverse assemblages in closely spaced units (Sivaprakash, 1980), such is the braunite rich nambulite association. The more oxidized conditions in this band originated in some local small domains that behaved as closed systems with respect to $f(\text{O}_2)$, being internally banded through the silicate-carbonate lens such as are tephroite, manganese humite, pyroxmangite bands, which are formed in reduced /or more reduced conditions.

The ore of MnB could be a **fossil hydrothermal submarine manganese deposit** (the term belongs to Glasby, 1988) formed as a result of

subduction-related processes. The tectonic setting at the time of formation of the Mn deposits was an intraplate area. The recent geological setting of the MnB is a result of its long structural evolution through many tectogeneses cycles – between the Eurasia Plate in East and Central European Plate in West. The association of Barium, Sulfide, and Uranium Belts to the Manganese Belt, formed in the same subduction zone, hosted by the same very thick Tulgheş Series, such as in Bistriţa Mountains, is known in the world in similar deposits, which are well characterized tectonically and geochemically (Glasby, 1988).

9. CONCLUSIONS

The nambulite and natronambulite vein type ore cut the old oxidized braunite rich association which occurs as small bands inside the ore of MnB, near/inside the rhodonite type band.

The nambulite has $\text{Li} > \text{Na}$ and the natronambulite has $\text{Na} > \text{Li}$. Their ideal formulas are: nambulite $(\text{Li}, \text{Na})\text{Mn}_4\text{Si}_5\text{O}_{14}(\text{OH})$, unless any substitutions for Mn takes place, and $(\text{Na}, \text{Li})(\text{Mn}, \text{Ca})\text{Mn}_3\text{Si}_5\text{O}_{14}(\text{OH})$ natronambulite, in which the substitution of Na for Li is accompanied by a concomitant substitution of Ca for Mn (Matsubara et al., 1985).

The nambulite is associated with braunite, bixbyite, hausmannite, aegirine/acmite, rhodonite, leakeite, albite, microcline, magnetite, kutnohorite, hematite, hematophanite, Ba-feldspars, and others. The associated minerals to natronambulite are the silicates with Na as essential element.

The X-ray powder diffraction pattern and the cell edges of Manganese Belt nambulite and natronambulite are very close, and they are similar with that of others occurrences of the world.

The cross-cutting veins system occurrence of nambulite and natronambulite in old braunite rich ores, proves the presence of a late metamorphic hydrothermal activity in close connection with the metamorphism. The nambulite and natronambulite are hydrothermal minerals, being the result of the insitu metasomatic and metamorphic hydrothermal process related to subduction. The Li source was not from an external supply, it was probably present in the original hydrothermal submarine deposits.

The Li minerals are present in the metacherts, in the quartzites with large alkali pyroxenes and amphiboles, and in braunite rich –natroambulite/nambulite associations, all three are highly oxidized. Also, the Li as trace/content element are present only in these three associations. According to the trace element concentrations of manganese ore types from

the MnB, the banded manganiferrous rock/ manganese ore types have been formed by submarine hydrothermal activity (Hirtopanu, 2019).

The intraplate area tectonic setting at the time of MnB deposits formation, their complex mineralogy and geochemical features, proved their hydrothermal submarine origin related to subduction zone. The associated Ba, Sulfide, and U belts, all hosted by Tulgheș Series, are now the terrestrial fossil hydrothermal submarine deposits, formed as a result of subduction-related processes.

It has been established that the metamorphic evolution of the MnB ore was achieved through repeated and superimposed metamorphic events, a fact explaining its complex mineralogy. The MnB has a great mineralogical diversity and rarity containing more than 350 minerals and mineral varieties, of which the Li-minerals have the largest presence, being one of the most complex deposits in the world.

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