

## Natronambulite from the Dohnoiri mine, Kanuma City, Tochigi Prefecture, Japan

Satoshi Matsubara<sup>1</sup>, Akira Kato<sup>1</sup>, Ritsuro Miyawaki<sup>1</sup>, Yoshiro Komuro<sup>2</sup> and  
Yoshio Okada<sup>3</sup>

<sup>1</sup>Department of Geology and Paleontology, National Museum of Nature and Science,  
3–23–1 Hyakunin-cho, Shinjuku, Tokyo 169–0073, Japan

<sup>2</sup>Komuro Hoshoku, No. 102, 2–30–6 Hakusan, Bunkyo, Tokyo 112–0001, Japan

<sup>3</sup>843–3 Yumoto, Hakone-machi, Kanagawa 251–0311, Japan

**Abstract** Natronambulite from the Dohnoiri mine was found as the second occurrence in Japan. It is an essential constituent of bedded manganese ores formed by very weak metamorphism. The other manganese minerals are braunite, rhodochrosite and rhodonite. They occur as minute grain aggregates forming fine bands with or without quartz. After the calculation of Li<sub>2</sub>O and H<sub>2</sub>O contents, EDS analyses are idealized as (Na,Li,Ca)(Mn,Ca,Mg)<sub>4</sub>[Si<sub>5</sub>O<sub>14</sub>(OH,O)], where Na>Li, Mn>Ca, Mg and OH>O, substantiating the original interpretation of essential nature of Ca substituting Mn. Natronambulite and nambulite in Japan have been found in weakly to moderately metamorphosed bedded manganese ore deposits which are principally developed in such a siliceous rock as chert in Jurassic mélange. The ore minerals therefrom include braunite without exception. It is thus very likely that the oxidizing condition might have helped the concentration of lithium. Two natronambulites in Japan were found from a member of low grade siliceous bedded manganese ores, whereas nambulite are found as veinlets cutting low to high grade manganese ores in all the known Japanese localities. These two lithium-manganese silicates might have been confused due to the color with rhodonite or pyroxmangite, especially high iron materials of the former, suggesting the more common occurrences.

**Key words:** natronambulite, Dohnoiri mine, manganese ore.

### Introduction

Natronambulite, (Na,Li)(Mn,Ca)<sub>4</sub>[Si<sub>5</sub>O<sub>14</sub>OH], was first described from the metamorphosed bedded manganese ore deposit of the Tanohata mine, Iwate Prefecture, Japan by Matsubara *et al.* (1985), as the Na-dominant member of nambulite, (Li, Na)Mn<sub>4</sub>[Si<sub>5</sub>O<sub>14</sub>OH], in which Li>Na (Yoshii *et al.*, 1972). However, Matsubara *et al.* (1985) considered the mineral not to be a mere Na-dominant member but pointed out the essential nature of Ca replacing Mn. Prior to the first find of this mineral, the similar material had been found in the Kombat mine, Namibia, by von Knorring *et al.* (1978), who handled it as nambulite due to the reason that the original nambulite was chemically characterized as LiNaMn<sub>8</sub>-[Si<sub>5</sub>O<sub>14</sub>OH]<sub>2</sub> with Li:Na=0.51:0.49 (Yoshii *et*

*al.*, 1972), while the Kombat material has Li:Na=0.40:0.60, and the authors considered the chemical difference between two to be too insignificant to create a new species.

Synthesis of LiMn<sub>4</sub>[Si<sub>5</sub>O<sub>14</sub>OH] was succeeded by Ito (1972) prior to the discovery of nambulite. He also acquired synthetic (Na,Li)Mn<sub>4</sub>-[Si<sub>5</sub>O<sub>14</sub>OH], but failed to obtain synthetic pure Na end member, or NaMn<sub>4</sub>[Si<sub>5</sub>O<sub>14</sub>OH]. According to his personal communication he remarked very slow reaction speed of gel mixture of employed ingredients for NaMn<sub>4</sub>[Si<sub>5</sub>O<sub>14</sub>OH] and possibility of disintegration of product into two, synthetic serandite (NaMn<sub>2</sub>[Si<sub>3</sub>O<sub>8</sub>OH]) and pyroxmangite (Mn<sub>7</sub>[Si<sub>7</sub>O<sub>21</sub>]).

The present natronambulite contains essential Ca in place of Mn as seen in the original analysis, substantiating the interpretation as to the ne-

cessity of larger divalent cation than  $Mn^{2+}$ , facilitating the substitution of Na for Li, i.e., the substitution of larger cation for smaller one.

### Occurrence

The Dohnoiri mine is located at about N  $36^{\circ}32'36''$  and E  $139^{\circ}38'20''$ , and operated for manganese ore about 50 years ago. Currently some small dumps are left around the collapsed portal. Considering from the contents of dump materials and exposures nearby the portal, the ore deposit consists of ore beds of manganese minerals developed within bedded or massive chert beds. The principal ore-forming minerals are rhodochrosite, rhodonite, hematite, braunite and natronambulite. Gangue minerals are quartz, albite and barite. Besides them minor pyrite grains are involved within low grade manganese ores composed of rhodonite and quartz.

Natronambulite occurs as light orange to brownish yellow very minute grains forming bands composed of aggregates with fine-grained quartz. Their individual grains are of microscopic dimensions (Fig. 1). Natronambulite is easily recognized due to the color. It's light orange to brownish yellow color is discernibly different from light pink color of rhodonite. Aggregates of natronambulite-quartz and rhodonite-quartz are closely accompanied by light brownish hematite-quartz bedded aggregates that develop conchoidal fracture if crashed. This suggests the practical absence of recrystallization, meaning the extremely weak metamorphic effects. Some of ores accompany colorless to gray chert with conchoidal fracture as well as the ores. Also, some ores are intersected by veinlets of colorless barite, which is uniquely coarser-grained, and a light yellow fibrous amphibole developed parallel to veinlets walls attaining a centimeter long.

Under the microscope, natronambulite occurs as a minute grain with quartz and rhodochrosite, though the mineral grains tend to form minute aggregates of less than millimeter size (Fig. 2). Some interstices of quartz grains are filled in albite of similar size. In aggregates of natronambu-

lite and quartz, veins of minute fiber crystals of amphibole are observed (Fig. 3). Although the amphibole resembles Mn-rich richterite, it has been subjected to current study. It is visually distinguishable from natronambulite due to its fibrous nature and less orange or brownish and lighter yellowish color.

### Chemical composition

The electron microprobe analyses were made using Link Systems energy dispersive X-ray spectrometer (QX-2000). The results of the analyses are given in Table 1. All of them have low totals, which are considered to be due to  $Li_2O$  and  $H_2O$ . The basis of calculation taking  $Si=5$  is warranted due to the absence of  $Al_2O_3$ . Since all of them gave slight excess of divalent cations, a part of Ca is transferred to the site for Li and Na, requiring slight deficiency of  $H_2O$  for charge balance. The addition of above components is validated because all summations of analyses are nearly ideal.

The estimated  $Na/(Na+Li)$  ratio situated between the original (0.80) and Kombat material (0.60) serves to confirm the existence of continuous solid solution series within the compositional range of natronambulite, if the appropriate amount of CaO is involved.

Table 1. Chemical composition of natronambulite

	1	2	3
SiO <sub>2</sub>	49.27	48.61	48.50
MgO	1.22	1.07	0.80
MnO	42.51	39.09	39.19
CaO	2.31	4.87	4.96
Na <sub>2</sub> O	2.85	3.66	3.56
Li <sub>2</sub> O*	0.86	0.40	0.47
H <sub>2</sub> O*	1.36	1.30	1.32
Total	100.38	99.00	98.80
Si	5	5	5
Mg	0.185	0.164	0.123
Mn	3.654	3.405	3.422
Ca	0.251	0.536	0.548
Na	0.561	0.730	0.712
Li	0.349	0.165	0.195
H	0.910	0.895	0.907

\*: calculation



Fig. 1. The banded structure of natronambulite (orange), rhodonite (pink) and quartz (white). Specimen is approximately 12 cm wide.

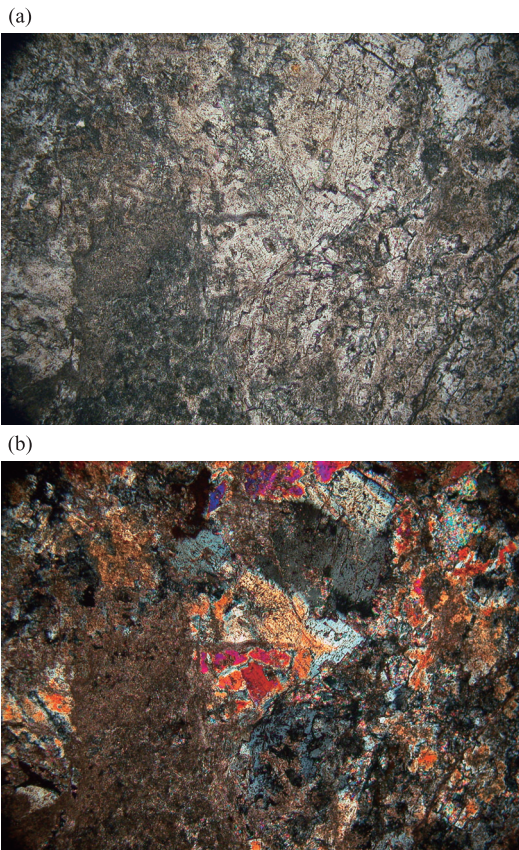


Fig. 2. Photomicrographs of natronambulite. a: one polar, b: crossed polars. Field view is approximately 1 mm wide.

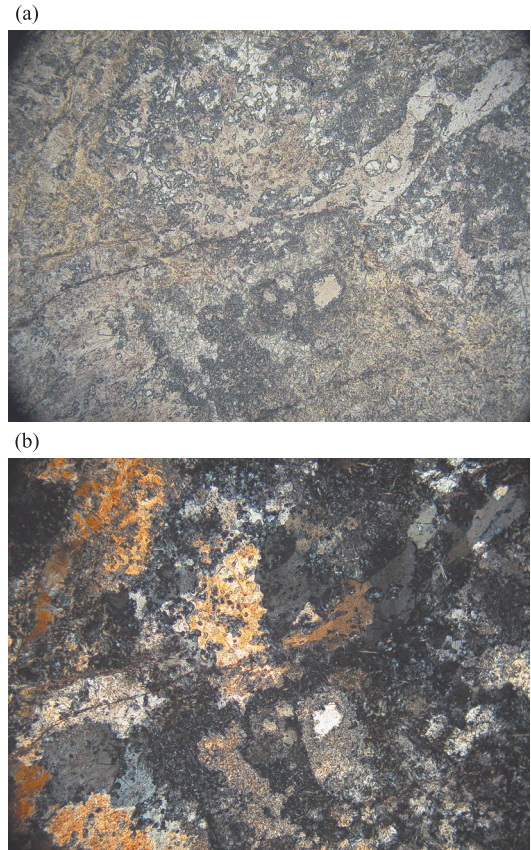


Fig. 3. Photomicrographs of minute prismatic crystals of Mn-bearing amphibole including in natronambulite. a: one polar, b: crossed polars. Field view is approximately 1 mm wide.

Table 2. The powder X-ray diffraction pattern for natronambulite.

Dohnoiri				Tanohata		
dobs.	dcalc.	I	hkl	dobs.	I	hkl
7.11	7.09	13	$\bar{1}10$	7.13	47	$\bar{1}10$
6.70	6.69	15	001	6.70	44	001
4.76	4.75	9	$1\bar{1}1$	5.21	1	$\bar{1}20, \bar{1}01$
				4.77	7	$1\bar{1}1$
				4.15	1	$021, \bar{1}21$
				3.94	2	$120$
				3.80	2	$\bar{2}10$
3.56	3.54	6	$\bar{2}20$	3.359	100	$\bar{2}20, 12\bar{1}$
3.35	3.35	16	002	3.348	40	$1\bar{3}1, 002$
				3.280	1	$0\bar{1}2$
3.17	3.17	28	$\bar{1}02$	3.164	20	$\bar{1}02, 031$
3.09	3.09	14	$\bar{1}12$	3.078	45	$221$
3.07	3.07	17	$2\bar{3}0, 2\bar{2}1$			
3.00	3.01	21	$11\bar{2}$	3.007	2	$11\bar{2}$
2.97	2.97	64	$0\bar{2}2, 1\bar{1}2$	2.972	34	$0\bar{2}2, 1\bar{1}2$
2.91	2.88	100	$\bar{1}40$	2.917	5	$\bar{1}40, 102$
				2.829	1	$122, \bar{1}22$
				2.778	1	$022$
2.71	2.71	73	$2\bar{2}0$	2.709	15	$112, 220$
2.64	2.64	13	$041$			
2.62	{2.62	11	$\bar{2}12, 2\bar{2}\bar{1}$	2.618	15	$\bar{2}12, 2\bar{2}\bar{1}$
	{2.61		$\bar{1}41$			
2.50	2.50	10	$\bar{3}20$	2.506	38	$\bar{2}22, \bar{3}20$
2.42	2.42	14	$122$	2.435	1	$\bar{3}11$
				2.402	1	$\bar{3}21$
2.33	{2.35	2	$\bar{2}02$	2.373	15	$222, \bar{3}30$
	{2.32		$\bar{1}50$			
2.23	2.24	13	$310$	2.245	1	$1\bar{4}2, 23\bar{1}$
				2.230	1	$310$
2.22	2.22	16	$04\bar{2}$	2.221	6	$0\bar{1}3$
2.20	2.20	17	$\bar{2}50, 10\bar{3}$	2.198	23	$301, \bar{1}03$
				2.169	3	$\bar{1}13$
2.11	2.10	11	$\bar{2}51$			
2.06	2.06	12	$311$	2.081	2	$\bar{3}22$
				1.995	4	$\bar{2}13, \bar{2}03$
				1.931	3	
				1.889	2	
				1.879	2	
				1.859	6	
				1.823	4	
				1.777	2	
				1.763	5	
				1.740	1	
1.695	1.691	22	$\bar{2}43$	1.697	2	
1.689	{1.686	10	$\bar{3}52$			
	{1.683		$160$			
1.674	{1.675	15	$3\bar{6}1$	1.673	20	
	{1.674		$014$			

Dohnoiri: present study

Tanohata: Matsubara *et al.* (1985)



### X-ray crystallography

The powder X-ray diffraction pattern was obtained using a Gandolfi camera, 114.6 mm in diameter, employing Cr  $K\alpha$  radiation (Table 2). The unit cell parameters are:  $a=7.624(5)$ ,  $b=11.605(9)$ ,  $c=6.738(3)$  Å,  $\alpha=92.96(6)^\circ$ ,  $\beta=94.75(5)^\circ$ ,  $\gamma=106.26(6)^\circ$ ,  $V=568.7(6)$  Å<sup>3</sup>. Though the pattern is apparently similar to that of rhodonite or pyroxmangite, it corresponds well to that of the original one (Matsubara *et al.*, 1985). As the compositional variation of natronambulite yields minor variation in powder X-ray diffraction pattern, it is very likely that the similarity to rhodonite or pyroxmangite has induced the confusion with this mineral.

### Consideration

In addition to the retained bedded texture, fine grain size of natronambulite as well as the associated quartz suggests the lesser degree of influence of metamorphism. It is highly likely that all the component of natronambulite had been concentrated prior to its formation.

The Na : Li ratio in the original natronambulite is 0.82 : 0.18. Matsubara *et al.* (1985) have considered that the entrance of Na in place of Li necessitates that of larger cation in place of Mn such as Ca on the basis of the unique original analysis in which the quantitative determination was made by wet method. The chemical analyses of the present material substantiate this conclu-

sion; higher CaO content than the original one and no mutual correlation between Li<sub>2</sub>O and CaO contents.

Natronambulite and nambulite are apparently characterized by orange to brownish yellow color. However, they have been miss-identified as rhodonite or pyroxmangite to date, since some of high iron-bearing rhodonite has orange brown color similar to those of natronambulite and nambulite. This evidence may lead to the new find of these Li-bearing pyroxenoids in lower grade siliceous manganese ores from weakly to highly metamorphosed bedded manganese deposits.

### Acknowledgements

We thank Mrs. M. Shigeoka for her assistance in EPMA analysis.

### References

- Ito, J., 1972. Synthesis and crystal chemistry of Li-hydro-pyroxenoids. *Mineralogical Journal*, **7**: 45–65.
- Matsubara, S., A. Kato & T. Tiba, 1985. Natronambulite, (Na,Li)(Mn,Ca)<sub>4</sub>Si<sub>5</sub>O<sub>14</sub>OH, a new mineral from the Tanohata mine, Iwate Prefecture, Japan. *Mineralogical Journal*, **12**: 332–340.
- Von Knorring, O., Th. G. Sahama & R. Törnroos, 1978. Second find of nambulite. *Neues Jahrbuch für Mineralogie, Monatshefte*, 346–348.
- Yoshii, M., Y. Aoki & K. Maeda, 1972. Nambulite, a new lithium- and sodium-bearing manganese silicate, from the Funakozawa mine, northeastern Japan. *Mineralogical Journal*, **7**: 29–44.