Natronambulite, $(Na, Li)(Mn, Ca)_4Si_5O_{14}OH$, a new mineral from the Tanohata mine, Iwate Prefecture, Japan

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Abstract

Natronambulite, $(Na, Li)(Mn, Ca)_4Si_5O_{14}OH(Na > Li; Mn > Ca)$ is triclinic, P1 or P$\bar{1}$, $a = 7.620$, $b = 11.762$, $c = 6.737$Å, $\alpha = 92.81°$, $\beta = 94.55°$, $\gamma = 106.87°$, $Z = 2$. The electron microporbe and wet chemical analyses gave SiO_2 50.39, TiO_2 0.03, FeO 0.31, MnO 38.94, MgO 1.24, CaO 3.66, Na_2O 3.55, Li_2O 0.43, H_2O^+ 1.46, H_2O^- 0.54, total 100.55%, yielding the empirical formula $(Na_{0.69}Li_{0.17})_{\Sigma 0.86}(Mn_{3.32}Ca_{0.39}Mg_{0.19}Fe_{0.03})_{\Sigma 3.93}Si_{5.07}O_{14.02}(OH)_{0.98}$ (basis O = 15), or ideally $(Na, Li)(Mn, Ca)_4Si_5O_{14}OH$ $(Na > Li; Mn > Ca)$.

It is pinkish orange in colour with a vitreous luster and nearly white streak. H.(Mohs) = 5½ – 6. Density (g/cm³) 3.51 (meas.), 3.50 (calc. using the empirical formula). Cleavage [100] and [1̄00], perfect. Optically it is biaxial and positive, $2V \approx 45°$, r > v, moderate. Refractive indices are: $\alpha = 1.706(2)$, $\beta = 1.710(2)$, $\gamma = 1.730(5)$. It is nearly colourless in thin section.

It occurs in a low grade manganese ore from the thermally metamorphosed manganese ore deposit of the Tanohata mine, Iwate Prefecture, Japan, in association with manganoan aegirine, manganoan arfvedsonite, quartz and rhodonite, or with albite, microcline, quartz and serandite.

Introduction

Nambulite of the original and subsequent descriptions have compositionally covered the variation range between $NaLiMn_8Si_{10}O_{28}(OH)_2$ and $Li_2Mn_8Si_{10}O_{28}(OH)_2$ unless minor substitutions of such octahedral cations as Mg and Ca for Mn are considered, and this was experimentally supported by Ito (1972), who synthetically determined the variation range of $(Li, Na)Mn_4Si_5O_{14}OH$ to be from $Li_{100}Na_0$ to $Li_{70}Na_{30}$ unless any substitution for Mn takes place. However, the chemical composition of nambulite from Namibia described by von Knorring et al. (1978) has Na:Li = 3:2 and higher CaO content that has never been reported in any nambulite analyses. The appearance of such a high sodium material had brought about the necessity of qualitative examination of nambulites accompanied by silicates with essential sodium. Consequently, the materials from the Tanohata mine, Iwate Prefecture, attracted our attention due to the co-existence with serandite. The subsequent studies on them have proved that some of them also have Na_2O contents high enough to allow the creation of a new Na-dominant analogue of nambulite under the name natronambulite

to indicate the relation. The mineral and name have been approved by the Commission on New Minerals and Mineral Names, I.M.A., prior to the publication. Type material has been deposited in Department of Geology, National Science Museum, Tokyo, Japan.

Occurrence

The ore deposits of the Tanohata mine, Iwate Prefecture are composed of four discrete orebodies, which are described by Nambu et al. (1969). All of them are contact metamorphosed bedded manganese ore deposits developed in upper Jurassic chert recrystallized by the intrusion of older Cretaceous granodiorite body called Tanohata body. The grade of contact metamorphism estimated from the metamorphic minerals is slightly lower than amphibolite facies. The nearest exposure of granodiorite
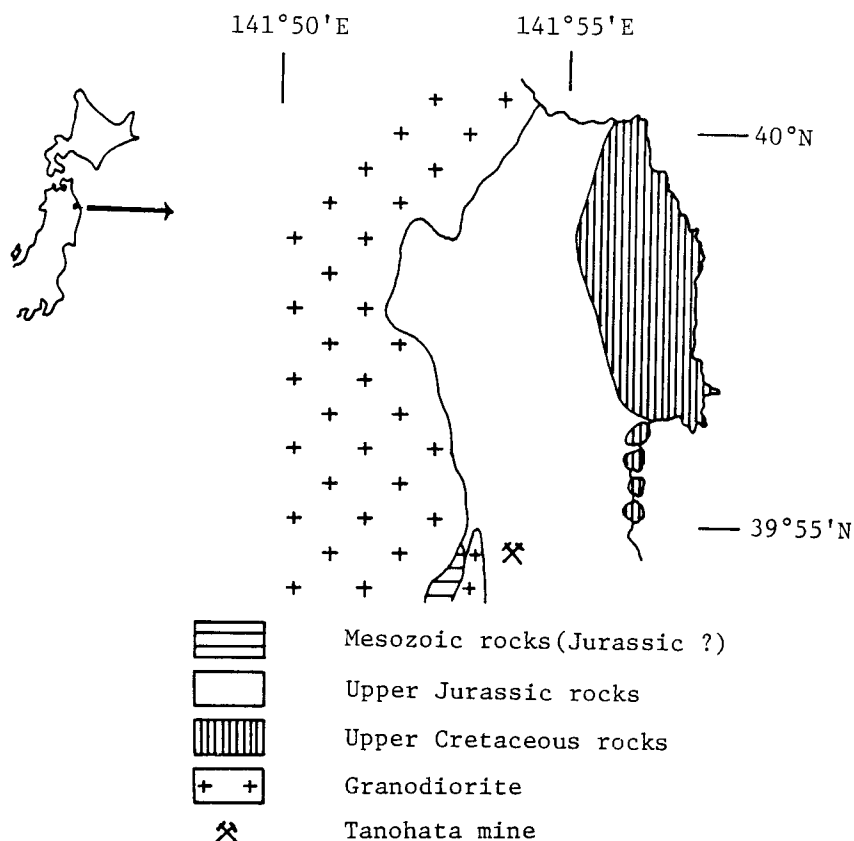

FIG. 1. Index map of the Tanohata mine, Iwate Prefecture.

is located about 1 km west of the locality (Fig. 1).

Natronambulite was found in the dump of No. 3 (Matsumaezawa) Orebody and the studied material consists of coarser-grained mosaic aggregate of natronambulite grains forming a visible banding texture due to the difference in grain size of constitutents and distribution of some manganese minerals. The natronambulite band is in direct contact with thin rhodonite band, which then contacts braunite band. The maximum grain size of natronambulite reaches 7 mm across. Under the microscope, shieve-structured natronambulite grains including subround quartz grains form a mosaic texture and in direct contact with manganoan aegirine and manganoan arfvedsonite (Fig. 2). The other association of natronambulite consists of quartz and rhodonite with manganoan arfvedsonite, which is found as minute inclusions in natronambulite. The natronambulite of this occurrence is more sodic than the previous material as stated later. Also, it is found as a subordinate constituents in albite-microcline-quartz pegmatite including serandite.
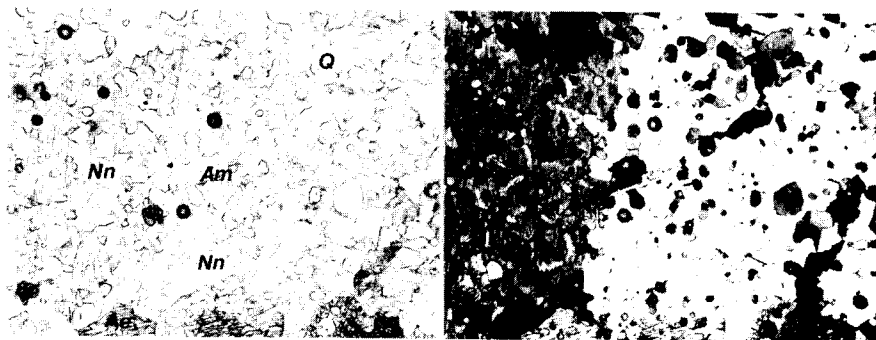

FIG. 2.   Photomicrograph of natronambulite (Nn) in association with aegirine (Ae), arfvedsonite (Am) and quartz (Q).
Field view: approximately 1.9 x 1.5 mm; Left: one polar; Right: corssed polars.

Physical and optical properties

The mineral is apparently indistinguishable from nambulite unless analyzed. It has a pinkish orange colour and a vitreous luster. Streak is nearly white but very faintly coloured in orange tint. Harness (Mohs) is 5½ − 6. Cleavage is perfect along [100] and [001]. Density (g/cm^3) measured by the Berman microbalance is 3.51, which is well coincident with the calculated value, 3.50, using the empirical formula. It is optically biaxial and positive, with 2V about 45°, r > v, discernible. The refractive indices measured by the immersion method are: α = 1.706(2), β = 1.710(2), γ = 1.730(5). It has very faintly yellowish colour in thin section, serving to the distinction from rhodonite, pyroxmangite and johannsenite, all of which are virtually

TABLE 1.   X-ray powder diffraction pattern of natronambulite.

1.				2.			1.				2.		
I	d_{obs}	d_{calc}	hkl	I	d_{obs}	hkl	I	d_{obs}	d_{calc}	hkl	I	d_{obs}	hkl
47	7.13	7.13	$\bar{1}10$	25	7.11	$\bar{1}10$	23	2.198	2.201	301	45	2.198	$3\bar{3}1$
44	6.70	6.69	001	25	6.70	001			2.198	$\bar{1}03$			301
				10	5.62	020							$\bar{1}03$
1	5.21	5.25	$\bar{1}20$	15	5.21	$\bar{1}01$					10	2.177	$0\bar{5}1$
		5.20	$\bar{1}01$										$\bar{3}40$
7	4.77	4.75	$1\bar{1}1$	15	4.75	$1\bar{1}1$	3	2.169	2.162	$\bar{1}13$			
1	4.15	4.14	021	10	4.13	021					10	2.116	132
		4.14	$\bar{1}21$			$\bar{1}21$	2	2.081	2.081	$\bar{3}22$			
		4.13	$1\bar{2}1$			$1\bar{2}1$					10	2.071	042
2	3.94	3.91	120	10	3.92	120							$\bar{2}42$
2	3.80	3.79	$\bar{2}10$								10	2.041	$14\bar{2}$
100	3.559	3.564	$\bar{2}20$	20	3.56	$\bar{2}20$							$12\bar{3}$
		3.553	$12\bar{1}$	35	3.54	$12\bar{1}$	4	1.995	1.997	$\bar{2}13$	15	1.996	$\bar{2}13$
40	3.348	3.350	$13\bar{1}$	40	3.34	$13\bar{1}$			1.995	$\bar{2}03$			$23\bar{2}$
		3.346	002			002							$\bar{2}03$
		3.338	$\bar{2}01$			$\bar{2}01$	3	1.931					
1	3.280	3.277	$0\bar{1}2$	10	3.27	$0\bar{1}2$	2	1.889					
20	3.164	3.167	$\bar{1}02$	65	3.17	$\bar{1}02$	2	1.879					
		3.162	031			031	6	1.859			35	1.847	
				55	3.09	$\bar{1}12$	4	1.823					
45	3.078	3.078	$2\bar{2}1$	60	3.07	$2\bar{2}1$					5	1.814	
				10	3.05	201	2	1.777					
2	3.007	3.004	$11\bar{2}$	30	3.01	$11\bar{2}$	5	1.763					
34	2.972	2.977	$0\bar{2}2$	80	2.97	$0\bar{2}2$	1	1.740					
		1.968	$1\bar{1}2$	100	2.96	$1\bar{1}2$	2	1.697			25	1.697	
5	2.917	2.924	$\bar{1}40$	70	2.92	$\bar{1}40$					25	1.695	
		2.924	102			102	2	1.686					
1	2.829	2.826	$\bar{1}22$	10	2.81	$1\bar{2}2$	20	1.673			20	1.675	
		2.828	$1\bar{2}2$								35	1.670	
1	2.778	2.780	022				4	1.637			10	1.637	
15	2.709	2.708	112	35	2.71	112	1	1.594			15	1.592	
		2.703	220			220	10	1.585			15	1.577	
15	2.618	2.620	$\bar{2}12$	40	2.62	$22\bar{1}$	3	1.545			5	1.547	
		2.613	$22\bar{1}$				2	1.532					
38	2.506	2.507	$\bar{2}22$	15	2.51	$\bar{2}22$	4	1.515					
		2.506	$\bar{3}20$			$\bar{3}20$	1	1.483					
				30	2.49	$\bar{1}32$	3	1.478			10	1.460	
1	2.435	2.435	$\bar{3}11$				15	1.423			5	1.417	
				10	2.41	122					25	1.414	
1	2.402	2.406	$\bar{3}21$								15	1.409	
15	2.373	2.377	$2\bar{2}2$	5	2.38	$\bar{3}30$					15	1.406	
		2.376	$\bar{3}30$										
1	2.245	2.245	$1\bar{4}2$	15	2.246	$1\bar{3}1$							
		2.244	$23\bar{1}$			$23\bar{1}$							
		2.244	050			050							
		2.240	$0\bar{4}2$	20	2.241	$2\bar{3}2$							
						$1\bar{4}2$							
1	2.230	2.231	310										
6	2.221	2.221	$0\bar{1}1$	30	2.221	$0\bar{1}1$							

1.   Natronambulite. Tanohata mine, Iwate Prefecture, Japan. The present study. Diffracto-
meter method. Cu/Ni radiation.
2.   Nambulite. Funakozawa mine, Iwate Prefecture, Japan. After Yoshii et al. (1972).

colourless in thin section with positive optic sign. The most intense yellowish colour is seen along Z'.

X-ray studies

The precession photographs of single crystal showed it to be triclinic, P1 or P$\tilde{1}$, a = 7.620, b = 11.762, c = 6.737Å, α = 92.81°, β = 94.55°, γ = 106.87°. The unit cell contains two molecules of $(Na, Li)(Mn, Ca)_4Si_5O_{14}OH$. These cell edges are very close to those of the original numbulite with Na:Li = 9:11 (Narita et al., 1975). Therefore, the X-ray powder diffraction pattern of natronambulite is very close to that of the original nambulite (Yoshii et al., 1972) as compared in Table 1. However, the cell edges of Na-poor nambulite are discernibly smaller than those of natronambulite (Table 2).

TABLE 2.   Unit cell parameters of natronambulite and nambulites (Na_2O rich and poor).

		1.	2.	3.
Space group		P1 or P$\overline{1}$	P1	P1 or P$\overline{1}$
Cell parameters:	a(Å)	7.620	7.621	7.571
	b(Å)	11.762	1.761	11.733
	c(Å)	6.737	6.731	6.698
	α(°)	92.81	92.77	93.20
	β(°)	94.55	95.08	94.91
	γ(°)	106.87	106.87	105.77

1. Natronambulite. Tanohata mine, Iwate Prefecture. The present study. Chemical analysis No. 1.
2. Nambulite. Funakozawa mine, Iwate Prefecture. After Yoshii et al. (1972). Chemical analysis No. 4. Na_2O-rich material.
3. Nambulite. Gozaisho mine, Fukushima Prefecture. After Matsubara (1977). Chemical analysis No. 7. Na_2O-poor material.

Chemical analysis

The chemical composition was determined after the microprobe and wet chemical analyses, the latter being for the qualitative measurements for Li_2O and $H_2O(\pm)$ on hand-picked binocular pure material, as given in Table 3, where it is compared with those of above stated more sodic material and some nambulites including the material described by von Knorring et al. (1978) after renaming it as natronambulite, together with rhodonite accompanied by more sodic natronambulite. After the reference to the available analyses, a triangular diagram of chemical compositions of nambulite-

TABLE 3. Chemical compositions of natronambulite, nambulite and rhodonite.

	1.	2.	3.	4.	5.	6.	7.	8.
SiO_2	50.39	49.20	48.97	49.23	50.33	50.53	50.12	46.96
TiO_2	0.03	–	–	0.01	–	–	0.00	–
Al_2O_3	–	–	–	0.37	–	–	0.06	–
FeO	0.31	0.11	0.15	–	0.25	0.20	0.44	0.00
MnO	38.94	39.46	40.30	40.67	43.22	41.09	41.13	47.98
MgO	1.24	1.11	2.16	1.32	0.51	0.07	2.23	0.82
CaO	3.66	3.42	2.87	0.81	0.93	3.10	0.75	4.44
Na_2O	3.55	4.14	3.12	2.49	1.08	1.84	0.42	0.07
Li_2O	0.43	0.44*	0.98	1.55	1.98*	1.63*	2.02	–
H_2O+	1.46	1.48*	1.50	1.63	1.51*	1.52*	–	–
H_2O-	0.54	–	0.20	0.26	–	–	1.52	–
Total	100.55	99.36	100.25	98.99**	99.81	99.98	98.75***	100.27

Empirical formulae (basis O = 15):

1. $(Na_{0.69}Li_{0.17})_{\Sigma 0.86}(Mn_{3.32}Ca_{0.39}Mg_{0.19}Fe_{0.03})_{\Sigma 3.93}Si_{5.07}O_{14.02}(OH)_{0.98}$.
2. $(Na_{0.82}Li_{0.18})_{\Sigma 1.00}(Mn_{3.41}Ca_{0.37}Mg_{0.17}Fe_{0.01})_{\Sigma 3.96}Si_{5.02}O_{14.00}(OH)_{1.00}$.
3. $(Na_{0.61}Li_{0.40})_{\Sigma 1.01}(Mn_{3.45}Mg_{0.33}Ca_{0.31}Fe_{0.01})_{\Sigma 4.10}Si_{4.95}O_{13.99}(OH)_{1.01}$.
4. $(Li_{0.50}Na_{0.49}K_{0.05})_{\Sigma 1.04}(Mn_{3.475}Mg_{0.20}Li_{0.135}Ca_{0.09}Al_{0.045}Fe_{0.03})_{\Sigma 3.975}Si_{5.00}O_{13.985}$
   $(OH)_{1.105}$.
   The above formula has been later revised by Narita et al. (1975) to $(Li_{0.45}Na_{0.43}K_{0.01})$
   $_{\Sigma 0.98}(Mn_{3.60}Mg_{0.20}Ca_{0.09}Al_{0.05}Fe^{3+}_{0.03})_{\Sigma 3.97}Si_{4.98}O_{13.90}(OH)_{1.10}$.
5. $(Li_{0.80}Na_{0.21})_{\Sigma 1.01}(Mn_{3.68}Ca_{0.10}Mg_{0.08}Fe_{0.02})_{\Sigma 3.88}Si_{5.06}O_{13.99}(OH)_{1.01}$.
6. $(Li_{0.65}Na_{0.36})_{\Sigma 1.01}(Mn_{3.49}Ca_{0.33}Fe_{0.02}Mg_{0.01})_{\Sigma 3.85}Si_{5.07}O_{13.98}(OH)_{1.02}$.
7. $(Li_{0.82}Na_{0.08})_{\Sigma 0.90}(Mn_{3.50}Mg_{0.33}Ca_{0.08}Fe_{0.04}Al_{0.01})_{\Sigma 3.96}Si_{5.04}O_{13.98}(OH)_{1.02}$.
8. $(Mn_{4.34}Ca_{0.51}Mg_{0.13}Na_{0.01})_{\Sigma 4.99}Si_{5.00}O_{15.00}$.

1. Natronambulite. Tanohata mine, Iwate Prefecture. The present study.
2. Natronambulite. Tanohata mine, Iwate Prefecture. The present study.
3. Natronambulite renamed from nambulite. Kombat, Namibia. After von Knorring et al. (1978).
4. Nambulite. Funakozawa mine, Iwate Prefecture. After Yoshii et al. (1972).
5. Nambulite. Tanohata mine, Iwate Prefecture. The present study.
6. Nambulite. Tanohata mine, Iwate Prefecture. The present study.
7. Nambulite. Gozaisho mine, Fukushima Prefecture. After Matsubara (1977).
8. Rhodonite. Tanohata mine, Iwate Prefecture. The present study.

    * calculated on the basis of (Na + Li) = 1 and H = 1.
  ** includes Fe_2O_3 0.40, K_2O 0.04, P_2O_5 0.02, CO_2 0.19 wt.%.
 *** includes NiO 0.44, Cr_2O_3 0.02 wt.%.

natronambulite-marsturite is drawn (Fig. 3), where a near linear relation between Na/(Na + Li) and Ca/(Ca + Mn) ratios in their compositons could be deciphered.

Crystallochemical consideration

The available analyses of nambulites and natronambulites demonstrate that their compositional variations are not given by a simple substitution of Na for Li but
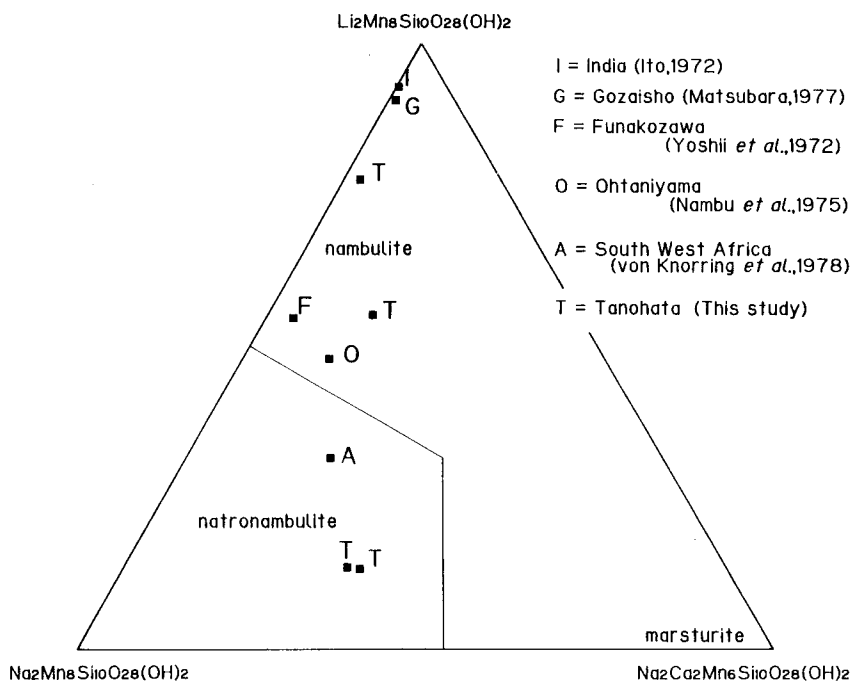
FIG. 3.   Triangular diagram of chemical compositions of nambulite-natronambulite-marsturite.

accompanied by a concomitant substitution of Ca for Mn in conformity with the increase of Na/(Na + Li) ratio (Fig. 3). However, the synthetic works of Ito (1972) presented the compositional variation range of Na-substituted Li-hydrorhodonite (= nambulite) to be from $LiMn_4Si_5O_{14}OH$ to $Li_{0.7}Na_{0.3}Mn_4Si_5O_{14}OH$, and the latter was synthesized at 740°C and 2kb, and reported the failure of synthesis of Na end member under the same condition. From these results, it is plausible that the substitution of Na for Li in nambulite cannot be attained without any lodging of substituting cation in the site of Mn beyond the above stated limit, and, seeing from the larger ionic radius of Na^+ than Li^+, the lodging cation should have larger dimension than Mn, and Ca is the case, though the reverse relation is not true, since Ito (1972) succeeded in synthesizing $LiCaMn_3Si_5O_{14}OH$ or Li analogue of marsturite (Peacor et al., 1978), proving that the substitution of Ca for Mn is not always accompanied by the substitution of Na for Li, as verified by No. 6 in Table 3.

If the substitution of Ca for Mn is concomitantly accompanied by the substitution of Na for Li with one-by-one relation, the product of ultimate substitution should be indentical with the ideal marsturite, $NaCaMn_3Si_5O_{14}OH$, in which the site for Ca is predicted to be discrete from that of Mn (Peacor et al., 1978). In the present

mineral, the corresponding site seems to be occupied by (Mn, Ca) where Mn > Ca, if the site preference is complete. If so, this is the unique and decisive distinction from marsturite. A formulated expression of ideal natronambulite is thus (Na, Li) (Mn, Ca)$Mn_3Si_5O_{14}OH$, where Na > Li and Mn > Ca in the parentheses, and marsturite is with Ca > Mn in the parentheses and without Li.

Also, it should be noted that there is a significant difference between the role of Ca and Mn parenthesized in the formula above. That is, Ca is at any occasions extant, whereas Mn in the parentheses can be entirely substituted by Ca. The formula of Ca-free compound $NaMn_4Si_5O_{14}OH$ can be differentiated into serandite ($NaMn_2Si_3O_8OH$) plus rhodonite or pyroxmangite ($MnSiO_3$):

$$NaMn_4Si_5O_{14}OH = NaMn_2Si_3O_8OH + 2 \, MnSiO_3,$$
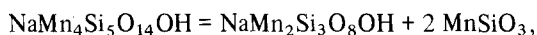
and the right sides must be stable. Although the association of two phases of the right side in their pure states is not known, the co-existence of calcian serandite with calcian rhodonite is observed in an albite-quartz pegmatite cutting an ore from the Tanohata mine. This corresponds approximately to the association of the right side of above equation. The formation of marsturite will need higher concentration of available Ca than the present case.

While, the presence of Li for Na invites the formation of nambulite or natronambulite under the lower Ca/(Ca + Mn) ratio than the case where marsturite is formed. This also suggests the essential nature of Li in natronambulite, validating the assignment of the ideal formula (Na, Li)(Mn, Ca)$Mn_3Si_5O_{14}OH$ where Na > Li and Mn > Ca in the parentheses, rather than $NaMn_4Si_5O_{14}OH$.

The known compositional variations of natronambulite and marsturite are discrete, i.e., that of the former is represented by the substitution of Na for Li, whereas that of the latter is by that of Ca for Mn within the compositional variation range of this mineral, i.e., without exceeding the limit of range given by the ideal formula of marsturite. Therefore, the presence of compositional intermediate between two minerals is expected with difficulty as far as the products formed under the similar condition to those responsible for phases here referred to.

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