Nambulite, (Li,Na)Mn₄Si₅O₁₄(OH), in the Sausar Group of rocks in Central India

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Manganese carbonate-silicate rocks in the Sausar Group, India are often traversed by pegmatite veins. Nambulite, a lithium- and sodium-bearing hydrous manganosilicate, is formed by the reaction of a hydrothermal solution with the host mineral, rhodonite. Despite the similarity of natronambulite and nambulite, the chemical composition shows a variation in the concentration of Na⁺ in the empirical formula: (Li_{0.94-0.60}Na_{0.06-0.40})_{Σ1.00}(Mn_{3.57-3.82}Ca_{0.13-0.07}Mg_{0.36-0.07}Fe_{0.03-0.01})_{Σ3.96-3.86}Si_{5.01-4.98}O₁₄(OH)_{1.00}. This is the first report of the sodium-rich variety from India. Powder X-ray diffraction studies reveal the unit cell parameters of nambulite in the triclinic system as $a = 7.55 \pm 0.06$ Å, $b = 11.77 \pm 0.07$ Å, $c = 6.68 \pm 0.04$ Å, $\alpha = 91.3^\circ \pm 0.8^\circ$, $\beta = 95.4^\circ \pm 0.5^\circ$, $\gamma = 107.2^\circ \pm 0.7^\circ$ and $V = 563 \pm 6$ Å³.

Keywords: Nambulite, Sodian nambulite, Late pegmatite veins, Sausar Group of India

INTRODUCTION

The hydrated rhodonite-like pyroxenoid phase containing lithium was first reported from the Långban Deposit, Sweden, by Engström (1875). Similar Li-bearing hydrous manganese silicate, having essentially the rhodonite composition and structure, was also found in high-grade manganese silicate-oxide rocks (gondite) from India (Ito, 1972). However, no detailed study of this typical hydrosilicate was carried out until the mineral was discovered from the Funakozawa mine, northern Japan by Yoshii et al. (1972). These authors also introduced the name, "nambulite," after Professor Matsuo Nambu of Tohoku University, Japan. Ito (1972) carried out synthesis and crystal chemical studies of Li-hydro-pyroxenoid, an end member of nambulite coexisting with Li-bearing serandite. This study also provided information on the phase relation and pressure-temperature stability limits of nambulite. Subsequently, a similar mineral has been described from Namibia (von Knorring et al., 1978) and Japan (Matsubara et al., 1985). However, the nambulite in these occurrences contains a larger Na (Na > Li) content, and the name "natronambulite" was proposed by Matsubara et al. (1985). In this communication we report

the occurrence of both nambulite and sodium-rich nambulite, from the Tirodi area, Sausar Group of rocks in Central India, and present the crystallochemical characteristics of the mineral. This is the first such report from this area.

GEOLOGICAL BACKGROUND AND MODE OF OCCURRENCE

Manganese carbonate-silicate rocks from the Sausar Group exposed in Tirodi area, were subjected to amphibolite-grade regional metamorphism culminating at $680 \pm 20^\circ\text{C}$ and a pressure of 6 kbar (Roy et al., 1986). Subsequently, several pegmatite veins traverse the rocks. As a result, manganese-silicate rocks from this area developed numerous Li-, Na- and K-bearing hydrosilicates at the interface of these pegmatite veins (Dasgupta et al., 1991). These veins develop close to the pegmatite bodies within the manganiferous rocks in Tirodi area of the Sausar group, India. The samples examined in this work were collected from an outcrop of Mn ores containing rhodonite at the interface of pegmatite dikes.

Nambulite occurs as irregular veins in the host rhodonite. In many places, manganoan phlogopite ($X_{\text{Mg}} = 0.79$) also forms, together with nambulite (Fig. 1). Other phases present in different proportions in the mineral assemblages of this vein include albite, rhodochro-

Figure 1. Backscattered electron image of the veins containing mainly nambulite (NAM) and Mn-bearing phlogopite (MICA), and sometimes hematite hosted by rhodonite (RDN). The scale is shown in the photograph, where the white bar represents 50 μm .

site, hematite $\pm$ quartz.

ANALYTICAL METHODS

The chemical composition of the phases in this study was determined using a JEOL-JXA 733 electron microprobe analyzer (EMPA) at Hiroshima University, Japan. The instrument was operated at an accelerating voltage of 15 kV, a beam diameter of $2 \cdot 10 \mu\text{m}$, and a specimen current of 10 nA. Natural mineral standards were used, and the raw analytical data were corrected by the ZAF method. Representative chemical compositions of the phases are given in Table 1. The vein material was powdered to study the X-ray diffraction (XRD) pattern, and the results are given in Figure 2 and Table 2. The XRD studies were performed using the following parameters: tube voltage 40 kV, tube current 100 mA, target 1.54056 Å (Cu), sampling width 0.02 deg, and scan speed 2.0 deg/min. The peak-profile data were corrected using the

Table 1. Representative chemical composition of nambulite and associated rhodonite

n	Nambulite				Rhodonite 6
wt. %					
SiO ₂	50.57	50.38	49.57	48.80	47.24
TiO ₂	0.00	0.03	0.00	0.04	0.00
Al ₂ O ₃	0.00	0.00	0.02	0.02	0.01
FeO	0.41	0.34	0.23	0.11	0.07
MnO	42.68	42.83	42.93	44.16	49.27
Cr ₂ O ₃	0.00	0.01	0.02	0.00	0.00
MgO	2.44	2.17	1.15	0.45	1.60
CaO	0.65	0.62	1.10	1.15	3.39
Na ₂ O	0.31	0.31	0.79	2.02	0.02
K ₂ O	0.00	0.01	0.01	0.00	0.00
Li ₂ O	2.37	2.36	2.08	1.46	----
H ₂ O*	1.41	1.41	1.40	1.39	
Total	100.84	100.14	99.29	99.60	101.60
	Cation (O = 14.5)				Cation (O = 24)
Si	4.99	5.00	5.01	4.98	7.97
Ti	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.00	0.00	0.00	0.00
Fe	0.03	0.03	0.02	0.01	0.01
Mn	3.57	3.60	3.67	3.82	7.04
Cr	0.00	0.00	0.00	0.00	0.00
Mg	0.36	0.32	0.17	0.07	0.40
Ca	0.07	0.07	0.12	0.13	0.61
Na	0.06	0.06	0.15	0.40	0.01
K	0.00	0.00	0.00	0.00	0.00
Li*	0.94	0.94	0.85	0.60	-----

n = number of analyses averaged.

Empirical formulae of nambulite (basis O = 14.5) : $(\text{Li}_{0.94-0.60}\text{Na}_{0.06-0.40})_{\Sigma 1.00}$
 $(\text{Mn}_{3.82-3.57}\text{Ca}_{0.13-0.07}\text{Mg}_{0.36-0.07}\text{Fe}_{0.03-0.01})_{\Sigma 3.96-3.86}\text{Si}_{4.98-5.01}\text{O}_{14}(\text{OH})_{1.00}$.

*Calculated on the basis of (Na + Li) = 1 and H = 1

Figure 2. Powder X-ray diffraction peak profile. The indexed peaks (using CuK α) belong to a nambulite-natronambulite group. The other peaks are mostly of phlogopite (M) and albite (A). Some small peaks resemble those of natronambulite.

peak profiles of Si as an external standard.

RESULTS

The chemical composition was determined by EMPA in which Li was normalized on the basis of Li + Na = 1 and H = 1 (Matsubara et al., 1985).

EMPA data indicated a variation in elements such as Mn, Mg, Ca, and in particular, Na. Accordingly, the recalculated Li content also varied. The possibility of alkali loss during analysis was eliminated by using a defocused beam. From this analytical study, it is evident that there exists an inverse relation between the Na and Mg content, but a positive relation between Na and Ca. The variation in Mn with increasing Na is not very evident, but it appears to be increasing. This implies that the compositional variation in nambulite is caused by substitution of Na for Li, coupled concomitantly with substitution of elements of larger ionic radii, such as Ca for Mg (and/or Mn). Contrary to the observations of Matsubara et al. (1985), the sodian nambulites have more substitution by Ca of Mg, rather than of Mn. Figure 3 represents the chemical variation of the nambulites from the present study, together with the natural compositions that have been reported so far. There is a wide spread in the present data.

The d -values of the peaks for nambulite, and the corresponding hkl indices, derived from the reported mineral

index card are compared. Regarding the triclinic system $h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^*\cos\alpha^* + 2lhc^*a^*\cos\beta^* + 2hka^*b^*\cos\gamma^* = 1/d^2 = Q$, (where, a^* , b^* , c^* , α^* , β^* , γ^* are the reciprocal lattice parameters): the reciprocal lattice parameters have been calculated for all the peaks by a least-squares method that minimizes the difference between Q_{observed} and $Q_{\text{calculated}}$ (Miura, 2003). After this refinement the actual unit cell parameters were calculated from these reciprocal values, yielding the following cell parameter values: $a = 7.55 \pm 0.06 \text{ \AA}$, $b = 11.77 \pm 0.07 \text{ \AA}$, $c = 6.68 \pm 0.04 \text{ \AA}$, $\alpha = 91.3^\circ \pm 0.8^\circ$, $\beta = 95.4^\circ \pm 0.5^\circ$, $\gamma = 107.2^\circ \pm 0.7^\circ$ and $V = 563 \pm 6 \text{ \AA}^3$.

This XRD study shows that the unit-cell parameters are very similar for both nambulite and natronambulite. However, the Na₂O content as observed from the phase chemical analysis indicates that the mineral is closer to the nambulite end with a variation on the basis of the Na⁺ content i.e. sodian nambulite. However, considering the lattice parameters, in particular the b -cell edge, implies that incorporation of excess Na⁺ may cause expansion of the unit cell.

Based on the textural relation and compositional constraints, the formation of nambulite to sodian nambulite can be expressed by the following model reaction:

Table 2. Peak data as observed from the X-ray powder diffraction pattern of nambulite

2θ	d_{obs}	hkl	2θ	d_{obs}	hkl
12.50	7.076	$\bar{1}10$	38.00	2.366	$\bar{2}\bar{2}2$
13.30	6.652	001	40.56	2.222	$0\bar{1}\bar{3}$
18.68	4.746	$1\bar{1}1$	40.86	2.207	$\bar{2}50$
21.54	4.122	$\bar{1}21$	42.74	2.114	132
23.34	3.808	$\bar{1}30$	43.44	2.081	$\bar{3}22$
25.10	3.545	$\bar{2}20$	44.84	2.020	311
26.72	3.334	$\bar{2}01$	45.82	1.979	150
27.96	3.189	$\bar{1}02$	48.12	1.889	$\bar{1}52$
28.44	3.136	012	49.82	1.829	033
28.92	3.085	$\bar{2}30$	51.42	1.776	232
29.30	3.046	$\bar{2}\bar{2}1$	53.12	1.723	213
30.12	2.965	$1\bar{1}2$	54.04	1.696	160
30.46	2.932	$\bar{1}40$	54.36	1.686	401
31.86	2.807	$\bar{2}31$	55.14	1.664	$\bar{1}53$
33.02	2.711	220	57.32	1.606	070
33.80	2.650	$\bar{1}41$	58.16	1.585	$\bar{2}71$
34.52	2.596	$\bar{2}12$	62.88	1.477	034
35.86	2.502	$\bar{2}22$	65.08	1.432	$\bar{3}24$
37.54	2.394	122	66.04	1.414	$\bar{5}\bar{4}1$

Unit cell parameters of nambulite

$$\begin{aligned}
 a &= 7.55 \pm 0.06 \text{ \AA} & \alpha &= 91.3^\circ \pm 0.8^\circ \\
 b &= 11.77 \pm 0.07 \text{ \AA} & \beta &= 95.4^\circ \pm 0.5^\circ \\
 c &= 6.68 \pm 0.04 \text{ \AA} & \gamma &= 107.2^\circ \pm 0.7^\circ \\
 a : b : c &= 0.641 : 1 : 0.567 & V &= 563 \pm 6 \text{ \AA}^3
 \end{aligned}$$

All the 38 diffraction data were used to calculate the cell parameters using the method by Miura (2003).

Figure 3. Triangular diagram of the chemical composition of nambulite and natronambulites with variations of Ca replacing Mg and/or Mn. The filled circles are the compositions of natural occurrences (e.g. I, India; G, Gozaisho; T, Tanohata; F, Funakozawa; O, Ohtaniyama; A, Africa. Ref. Matsubara et al., 1985), while the stars represent the compositions from the present study.

The Li^+ , Na^+ and the hydrous fluid (probably aqueous silica-bearing) were contributed from the pegmatite vein. A compositional plot of the reacting Li-Na-rich hydrous fluid, on a $(\text{MnO} + \text{MgO} + \text{CaO}) \cdot \text{Li}_2\text{O} \cdot \text{Na}_2\text{O}$ space, projected from quartz and H_2O (Fig. 4), shows a reaction relation that varies smoothly with changing X_{Na} ($\text{Na}/(\text{Na} + \text{Li})$). In Figure 4 rhodonite is plotted at the $(\text{MnO} + \text{MgO} + \text{CaO})$ -end of the compositional triangle.

DISCUSSION

Nambulite from the pegmatitic veins in the manganese ores of the Precambrian Sausar Group in central India, has certain variation in its chemical composition. In particular the Na:Li ratio varies from that of nambulite, to a

Figure 4. Compositional plot on (MnO+MgO+CaO)-Li₂O-Na₂O space, projected from quartz and H₂O showing the compositional variation of nambulite. Note the sweeping tie lines between rhodonite as plotted at the (MnO+MgO+CaO)-end, and the Na-Li rich hydrous fluid to produce the compositional variation in nambulite.

value close to that of natronambulite (Fig. 3). There are other associated variations in the chemical component as shown in Figure 3. Such wide-ranging chemistry in the present occurrence is quite intriguing. Nambulite often occurs in association with hematite. This implies that some of the Mn and Fe might be in a higher valence state, thus leading to an increase in the amount of Na, probably because the oxygen fugacity is high. However, experiments at the hematite-magnetite buffer failed to observe any composition with an increased amount of Mn⁺³ and Na in the nambulite structure (Ito, 1972). This experimental results showed a wide pressure-temperature range (i.e. 400°C to 800°C) at 1.5 kbar ($P_{\text{Total}} = P_{\text{H}_2\text{O}}$) for Li-end-member of nambulite. Near the upper thermal stability limit nambulite dehydrates to form rhodonite + quartz + Na-Li-rich hydrous liquid. Hence nambulite can form along a retrograde cooling path, but the present occurrence of this phase only in veins, leads to the conclusion that this is due to a metasomatic reaction at some later stage of formation from the host rhodonite. Moreover, sodium enrichment of more than Na:Li = 3:7 could not be synthesized in a *P-T* range similar to the stability field of nambulite. Though the conditions for formation for natronambulite is not yet clearly understood, a lower pressure during late stage pegmatitic veining would help to stabilize a larger structure of Na-rich nambulite than Na-poor nambulite. Nevertheless, the chemical variation in nambu-

lites in the present study is more likely controlled by the local bulk chemistry during the metasomatic changes of the host rhodonite by an aqueous silica-bearing fluid that is rich in Na-Li.

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