

Two Marsturites from Japan

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Abstract Chemical analyses of two marsturites from the Tsurumaki mine, Gifu Prefecture and the Shiromaru mine, Tokyo Metropolis give: SiO₂ 48.05, 40.41; FeO 0.68, 0.52; MgO 0.35, 0.46; MnO 39.85, 29.78; CaO 4.86, 13.25; Na₂O 4.98, 4.76; H₂O(calc.) 1.46, 1.51; total 100.23, 100.69%, respectively. The empirical formulae are: Na_{1.09}Ca_{1.07}(Mn_{6.04}Fe_{0.12}Mg_{0.11})_{Σ7.17}H₂Si_{0.88}O₃₀ and Na_{1.83}Ca_{2.82}(Mn_{5.01}Mg_{0.14}Fe_{0.09})_{Σ5.24}H₂Si_{10.01}O₃₀ (basis: O=29 in the anhydrous part), respectively. These extend the compositional field of marsturite due to the substitution of Ca for Mn from Na₂CaMn₇Si₁₀O₂₈(OH)₂ to Na₂Ca₃Mn₅Si₁₀O₂₈(OH)₂ approximately. The former formula corresponds to the boundary to natronambulite to which the compositional field of marsturite would be continuous. All the analyses are low in FeO and MgO contents alike to those of the materials from the original locality, suggesting this tendency to be one of the compositional characteristics of this mineral.

In both localities here reported, marsturite occurs as a later mineral in weakly metamorphosed bedded manganese ore deposits, where an Na-enriched and Mg- and Fe²⁺-depleted condition might have favoured the formation of marsturite.

Introduction

Marsturite, NaCaMn₃Si₅O₁₄OH, is a pyroxenoid firstly described by PEACOR *et al.* (1978) from Franklin, New Jersey, U.S. as a coating on rhodonite and manganaxinite. The present work is for the first find of this mineral in Japan from two separate localities with discussions on the chemical compositions.

Two compositional characteristics were found. One is an extensive substitution of Ca for Mn ranging approximately from Na₂CaMn₇Si₁₀O₂₈(OH)₂ to Na₂Ca₃Mn₅Si₁₀O₂₈(OH)₂, necessitating a setting of the compositional boundary to natronambulite (MATSUBARA *et al.*, 1985), which is ideally NaMn₄Si₅O₁₄(OH) but actually (Na, Li) (Mn, Ca)Si₅O₁₄OH with Na>Li and Mn>Ca. The boundary of two minerals is drawn at the midpoint of two ideal formulae. The other characteristics is the lower MgO and FeO contents. The associated manganese silicates from the former locality have this characteristics, too. The possibility that the depletion of these ingredients favoured the formation of marsturite is discussed.

Also, the interpretation on the mode of occurrences in two localities informs the necessity of transfer of materials constituting marsturite, especially Na. The discussion reaches a conclusion that the combination of Mg- and Fe²⁺-depletion and incorporation of Na favours the formation of marsturite.

Occurrence

The ore deposit of the Tsurumaki mine is located about 25 km northwest of Ogaki station, Tokaido Line, JR Tokai Co. Ltd. (35°35.0'N, 135°35.0'E), and belongs to bedded manganese ore deposit involved in sedimentary and pyroclastic rocks. The orebody is a lense-formed mass swollen due to folding. It overlies limestone and chert beds, whereas it is covered by another chert bed (Office of Teikoku Mining Co., 1964). The age of sedimentary rocks is very probably Jurassic. The mining works had already ceased about 25 years ago and all the studied materials were collected from the dump composed of abandoned ores and waste rocks located about 4 km east of the deposit. In the dump are found various kinds of manganese ores and the above-mentioned wallrocks and a greenstone. The principal ore minerals recognized are bementite, rhodochrosite, rhodonite, tephroite, hausmannite and alleghanyite in the order of decreasing abundance. Marsturite is found as a constituent of polyminerallic aggregates replacing a low grade ore composed of bementite and a pyroxene tentatively named as aegirine-johannsenite. The ore is a fine-grained massive brick red to light reddish brown one and replaced by slightly yellowish aggregates composed of microscopic grains of marsturite, calcite and ganophyllite. In the most typically developed case, light brown aggregates of bementite of a millimeter across are lined by deeper brown rims rich in aegirine, and this neighbours to light grey yellow zones of ganophyllite scales, and then less yellowish aggregates composed of marsturite and calcite is observed. The maximum width of pyroxene-rich rim and ganophyllite zone is about a millimeter. All the units are minutely intersected by white calcite veinlets along which ores are readily broken as well as the other fractures stained by thin filmy manganese dioxide. White calcite veinlets do not accompany marsturite and are monominerallic.

Under the microscope, aggregates of marsturite consist of mosaic grains without any regularity and accompany minor amount of calcite. The aggregates are adjacent to the massive aggregates of bementite with or without intervening ganophyllite scales and calcite grains. The association of marsturite and calcite is also found as veinlets, which is further veined by monominerallic calcite veinlets stated above. Marsturite grains are indistinguishable from the other pyroxenoid such as rhodonite and pyroxmangite in appearance, and in the grains no cleavage trace is observed probably due to the denser aggregated state, which is more or less resistant to the slicing process. The grain size is the order of 0.1 millimeter or less. Despite the optical homogeneity, all the aggregates of grains are extremely inhomogeneous in the back-scattered electron images, in which screen-like patterns composed of bundles of

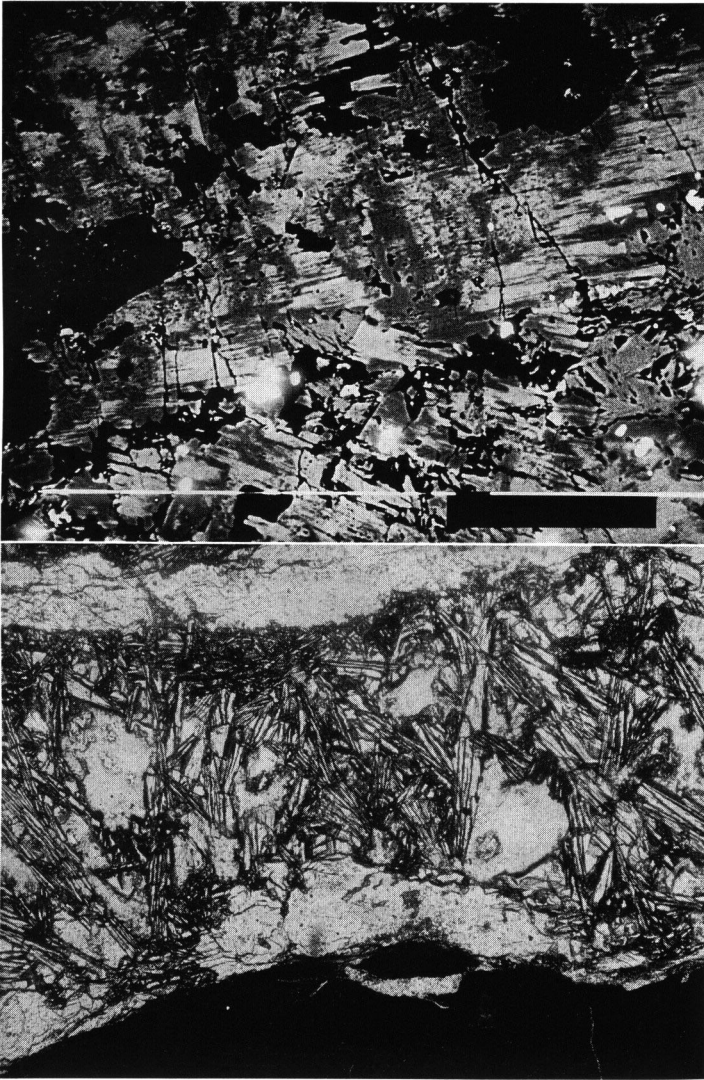


Fig. 1. Back scattered electron image of marsturite from the Tsurumaki mine. A notable heterogeneity of Mn-rich part (light) and Ca-rich part (dark) is observed. Field view: approx. $125 \times 100 \mu\text{m}$.

Fig. 2. Photomicrograph of marsturite from the Shiromaru mine. The prismatic crystals (high relief) grow in the veinlet rimmed by Ba-bearing orthoclase (low relief). Field view: approx. $1.9 \times 1.5 \text{ mm}$.

laths with less reflective nature are observed without any relation to the form of constituting grains (Fig. 1). Throughout the materials including marsturite, no trace of parallel texture is observed despite the presence of stratified ores principally composed

of bementite. This suggests the formation of marsturite-bearing aggregates to have invited the obliteration of the original texture. Seeing from the grade of metamorphism of wallrocks, the obliteration is not due to metamorphic recrystallization but to any phenomena such as a hydrothermal recrystallization.

The ore deposit of the Shiromaru mine is located about 1 km west of Hatonosu station, Ome Line, JR Higashi-Nihon Co. Ltd. (35°48.4'N, 139°07.6'E), where the occurrences of some barium silicates are reported (MATSUBARA, 1985) (KATO *et al.*, 1987). The materials from the Shiromaru mine are so few as compared with the case just stated. The fragment comprising marsturite is a small piece of banded ore. It consists of the repeated alternation of two bands of a few millimeter wide, with a reddish brown colour and a light yellowish brown one. The former consists of aggregate of submicroscopic grains of celsian, cymrite, hematite and minor ganophyllite according to the X-ray powder diffraction study, whereas that of the latter is essentially occupied by caryopillite only. Marsturite is found as veinlets with about 5 millimeters thick cutting the bands. They consist of thin wall-coating material composed of white orthoclase and orange lemon long prisms of marsturite in the centre, the maximum length being 3 millimeters. The prisms are grown perpendicular to the walls in subparallel relation to each. The parts occupied by marsturite prisms are nearly monomineralic except for minor orthoclase.

Under the microscope, orthoclase aggregates consist of clear equant grains of a mosaic texture, covering the walls. Marsturite prisms are grown on orthoclase aggregates (Fig. 2) with near perpendicular relation to the walls and the margins of the veinlet are very sharp. They have some prism faces and well-developed cleavage trace parallel to the elongation, possibly *c*-axis. Despite the compositional variance, no optical zoning is observed. The microscopical feature is also very similar to those of pyroxmangite and rhodonite, except for very faint pleochroism from very light orange yellow to nearly colourless observed in thicker grains. It is optically biaxial positive with 2V about 55°. Dispersion: $r > v$, weak. Refractive indices measured by the immersion method are: $\alpha = 1.688$ (2), $\beta = 1.692$ (2), $\gamma = 1.710$ (5). The maximum extinction angle: $c \wedge Z' = 26^\circ$.

Chemical Composition

The chemical compositions of marsturite were determined by using Link Systems energy-dispersive X-ray spectrometer. The material from the Tsurumaki mine is associated with calcite, bementite, ganophyllite and a clinopyroxene tentatively called aegirine-johannsenite, and that from the Shiromaru mine is accompanied by Ba-bearing orthoclase. They are given in Table 1. They are plotted in the (Mn+Mg+Fe+Zn)-Ca-(Na+Li) triangular diagram (Fig. 3), together with two analyses of the materials from Franklin, New Jersey, U.S.A. (Peacor *et al.*, 1978) (DUNN & LEAVENS, 1986). The tendency of the compositional variation of marsturite and the compositional relation to natronambulite (MATSUBARA *et al.*, 1985) are demonstrated. One

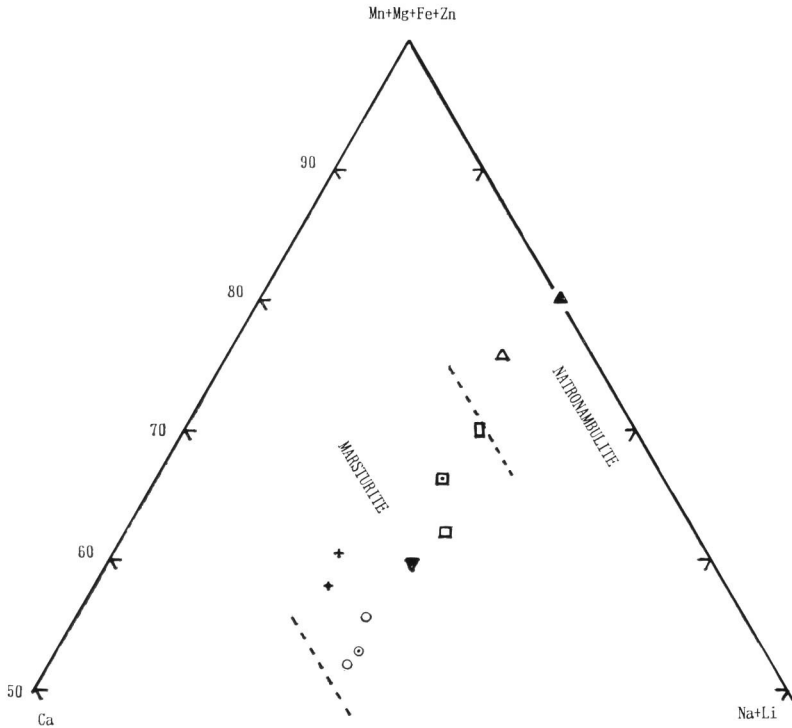


Fig. 3. (Mn+Mg+Fe+Zn)–Ca–(Na+Li) diagram. Solid triangle: ideal natronambulite. Open triangle: natural natronambulite (MATSUBARA *et al.*, 1985). Solid inverted triangle: ideal marsturite. Open square: Mn-richest and poorest (=Ca-poorest and richest) marsturites from the Tsurumaki mine. Center-pointed square: average of 9 analyses of the materials from the Tsurumaki mine. Open circle: Mn-richest and poorest (=Ca-poorest) marsturites from the Shiromaru mine. Center-pointed circle: average of 6 analyses of the materials from the Shiromaru mine. Cross: marsturite from Franklin (average of 3 analyses) (PEACOR *et al.*, 1978). Center-pointed cross: marsturite from Franklin (DUNN & LEAVENS, 1986).

of the apex is taken as (Na+Li) not Na, since Li is obviously essential in natronambulite.

All the determined compositions are concentrated on a line connecting Na_2Mn_3 and $\text{Na}_2\text{Ca}_2\text{Mn}_6$ or its extension, demonstrating that the compositional variation of marsturite newly determined is represented by the substitution of Ca for Mn. The first formula given above corresponds to the ideal formula of natronambulite (MATSUBARA *et al.*, 1985), whereas the latter is for marsturite. It is very natural that the boundary between two is drawn at the midpoint, $\text{Na}_2\text{CaMn}_7\text{Si}_{10}\text{O}_{28}(\text{OH})_2$, which is very close to the most Mn-rich analysis of the material from the Tsurumaki mine. While, the chemical compositions of the Shiromaru materials are plotted in the Ca-richer side of the line extended beyond the ideal formula of marsturite approximately

Table 1. Chemical analyses of marsturite

Weight percentage (*calculated)

	1.	2.	3.	4.	5.	6.	7.	8.	9.
SiO ₂	48.05	48.45	48.10	48.71	49.30	49.83	50.43	50.25	49.91
MgO	0.35		0.10			0.52	0.87	0.59	
FeO	0.68		0.38				0.98	0.39	
MnO	39.85	36.96	38.18	40.26	34.93	31.92	28.55	30.02	29.46
CaO	4.86	7.84	7.05	4.55	9.20	11.72	13.35	12.77	13.98
Na ₂ O	4.98	5.41	4.76	5.02	5.09	4.95	5.12	5.16	5.15
H ₂ O*	1.46	1.47	1.46	1.46	1.48	1.44	1.51	1.51	1.50
total	100.23	100.13	100.03	100.00	100.00	99.95	100.81	100.69	100.00
mole %									
Mn + Fe + Mg	70.1	62.4	66.2	70	60	55.7	52.0	52.9	50
Ca	10.5	16.7	15.2	10	20	25.1	28.3	27.2	30
Na	19.4	20.9	18.6	20	20	19.2	19.6	19.9	20

1. Tsurumaki mine. The most Mn-rich analysis.

Empirical formula**: Na_{1.00}Ca_{1.07}(Mn_{6.04}Fe_{0.12}Mg_{0.11})_{Σ7.17}Si_{9.88}O₂₈(OH)₂.

2. Tsurumaki mine. The most Ca-rich analysis.

Empirical formula: Na_{2.14}Ca_{1.72}Mn_{6.40}Si_{9.91}O₂₈(OH)₂.

3. Tsurumaki mine. Average of 9 analyses.

Empirical formula: Na_{1.90}Ca_{1.55}(Mn_{6.64}Fe_{0.07}Mg_{0.03})_{Σ6.74}Si_{9.88}O₂₈(OH)₂.4. Theoretical Na₂CaMn₇Si₁₀O₂₈(OH)₂.5. Theoretical Na₂Ca₂Mn₆Si₁₀O₂₈(OH)₂.

6. Shiromaru mine. The most Mn-rich analysis.

Empirical formula: Na_{1.92}Ca_{2.51}(Mn_{5.41}Mg_{0.16})_{Σ5.57}Si₁₀O₂₈(OH)₂.

7. Shiromaru mine. The most Ca-rich analysis.

Empirical formula: Na_{1.97}Ca_{2.83}(Mn_{4.79}Mg_{0.26}Fe_{0.16})_{Σ5.21}Si₁₀O₂₈(OH)₂.

8. Shiromaru mine. Average of 6 analyses.

Empirical formula: Na_{1.99}Ca_{2.72}(Mn_{5.06}Mg_{0.17}Fe_{0.06})_{Σ5.29}Si₁₀O₂₈(OH)₂.9. Theoretical Na₂Ca₃Mn₅Si₁₀O₂₈(OH)₂.

(**all the empirical formulae are calculated on the basis of O = 29 in the anhydrous parts, respectively.)

to Na₂Ca₃Mn₅Si₁₀O₂₈(OH)₂, which is derived from the most Ca-rich analysis.

As stated later, the X-ray powder patterns of materials with different chemical compositions are very similar, suggesting the crystallographic continuity among them. This proves that the variation of chemical compositions of marsturite has been extended to the range stated above. Provided that the result of synthetic works by ITO (1972) reporting the failure of synthesizing the Li-free natronambulite, Na₂Mn₅Si₁₀O₂₈(OH)₂, is applicable to the present case, the line denoting the compositional variation of marsturite does not reach the side of (Mn + Fe + Mg + Zn)–(Na + Li), if Li is not considered. The unique analysis of natronambulite contains minor but essential CaO up to 3.66% in weight. As already discussed by MATSUBARA *et al.* (1985), the substitution of Na for Li in nambulite and natronambulite invites sympathetic substitution of Ca for Mn. This may necessitate the check of Li in marsturite especially the mate-

Table 2. The chemical analyses of the associated minerals with marsturite

	10.	11.	12.	13.	14.	15.	16.	17.	18.
SiO ₂	45.37	46.65	29.15	24.58	21.98	50.85	50.64	36.52	62.13
Al ₂ O ₃					0.50			1.00	18.33
Fe ₂ O ₃ *						23.65	23.09		
MgO						1.44	1.90	2.33	
FeO*		0.82						0.97	
MnO	50.31	45.79	70.59	73.26	70.01	9.08	7.69	49.56	
CaO	4.70	10.68				5.24	6.50	0.34	
Na ₂ O						9.99	9.55		
K ₂ O									15.85
BaO									2.44
H ₂ O**				3.71	8.44			8.40	
total	100.38	99.89	99.74	101.55	100.93	100.25	99.37	99.12	98.75

(*total Fe; **calculated)

10. Rhodonite. Tsurumaki mine. Ca-poorer analysis. Empirical formula: $(\text{Mn}_{0.92}\text{Ca}_{0.11})_{\Sigma 1.03}\text{Si}_{0.98}\text{O}_3$. (basis: O=3)
11. Rhodonite. Tsurumaki mine. Ca-richer analysis. Empirical formula: $(\text{Mn}_{0.74}\text{Ca}_{0.24}\text{Mg}_{0.02}\text{Fe}_{0.01})_{\Sigma 1.01}\text{Si}_{0.98}\text{O}_3$. (basis: O=3)
12. Tephroite. Tsurumaki mine. Empirical formula: $\text{Mn}_{2.08}\text{Si}_{0.99}\text{O}_4$. (basis: O=4)
13. Alleghanyite. Tsurumaki mine. Empirical formula: $\text{Mn}_{5.02}\text{Si}_{1.96}\text{O}_5(\text{OH})_2$. (basis: O=9 in the anhydrous part)
14. Gageite. Tsurumaki mine. Empirical formula: $\text{Mn}_{21.07}(\text{Si}_{7.81}\text{Al}_{0.20})_{\Sigma 8.01}\text{O}_{27}(\text{OH})_{20}$. (basis: O=21 in the anhydrous part)
15. "Aegirine-johannsenite". Tsurumaki mine. Mn-richer analysis. Empirical formula: $(\text{Na}_{0.76}\text{Ca}_{0.22})_{\Sigma 0.98}(\text{Fe}^{3+}_{0.70}\text{Mn}^{2+}_{0.30}\text{Mg}_{0.05})_{\Sigma 1.05}\text{Si}_{1.99}\text{O}_6$. (basis: O=6)
16. "Aegirine-johannsenite". Tsurumaki mine. Mn-poorer analysis. Empirical formula: $(\text{Na}_{0.73}\text{Ca}_{0.27})_{\Sigma 1.00}(\text{Fe}^{3+}_{0.68}\text{Mn}^{2+}_{0.26}\text{Mg}_{0.11})_{\Sigma 1.05}\text{Si}_{1.99}\text{O}_6$. (basis: O=6)
17. Bementite. Tsurumaki mine. Empirical formula: $(\text{Mn}_{4.49}\text{Mg}_{0.37}\text{Fe}_{0.09}\text{Ca}_{0.04})_{\Sigma 4.99}(\text{Si}_{3.91}\text{Al}_{0.13})_{\Sigma 4.04}\text{O}_{10}(\text{OH})_6$. (basis: O=13 in the anhydrous part)
18. Orthoclase. Shiromaru mine. Empirical formula: $(\text{K}_{0.96}\text{Ba}_{0.05})_{\Sigma 1.01}(\text{Si}_{2.96}\text{Al}_{1.03})_{\Sigma 3.99}\text{O}_8$. (basis: O=8)

rials low in Na₂O content. Since most of chemical analyses of these minerals are due to the microprobe technique, the presence of Li might have been overlooked.

Another chemical characteristics disclosed by the study of this time is the lower MgO and FeO contents. The maximum contents are found in the same analysis, the Mn-poorest one in the material from the Shiromaru mine, and about 1% in weight. It is very likely that the formation of marsturite is favoured under Mg- and Fe²⁺-depleted conditions.

In order to corroborate this tendency, chemical analyses were made on the other manganese silicates found in the ores, i.e., on rhodonite, tephroite, alleghanyite, gageite and bementite, as included in Table 2. All of them are found to be very low in FeO and MgO, the maxima of them being in bementite, 0.77 and 2.33 wt. %, respectively. Besides them, the chemical composition of a clinopyroxene in association with marsturite is found to be an intermediate member between aegirine and johann-

senite, corresponding the Mn^{2+} analogue of aegirine-augite defined by Subcommittee on Pyroxenes, I.M.A. (1988), and this is tentatively labelled as "aegirine-johannsenite". A manganiferous clinopyroxene from the Noda-Tamagawa mine, Iwate Prefecture (NAMBU *et al.*, 1967) has a slightly lower MnO content than them but is the compositional intermediate between aegirine and johannsenite, too.

Rhodonite, tephroite, alleghanyite, and gageite are very low in MgO and FeO. A slightly higher summation of alleghanyite may be due to the presence of F. These are not direct associates with marsturite. In the analyses of "aegirine-johannsenite", both of the empirical formulae are slightly off the theoretical values, needing a partial conversion of Mn^{2+} to Mn^{3+} , since the mole numbers of Na in the formulae are larger than Fe^{3+} in both. This suggests the condition of formation of this pyroxene to be fairly oxidizing and responsible for the depletion of Fe^{2+} . The ideal formula of bementite has not been satisfactorily fixed yet. The present identification is, therefore, tentative. The calculation indicates the ratio of total octahedral cations to (Si+Al) to be very close to 5:4. Accordingly, a tentative formula $M^{2+}_5Si_4O_{13}$ is given to the anhydrous part. The calculated water content is derived from the general formula of phyllosilicates, Si:O=1:2.5, with additive (OH) for charge balance. Since the water content thus derived gives good summation, validating this estimation. The unique associate of the Shiromaru mine is a Ba-bearing orthoclase. It contains about 5% of celsian molecule.

X-ray Powder Study

The X-ray powder studies on two materials were made for identification after the employment of X-ray diffractometer. The patterns of both materials are essentially same and well comparable with that of the original material. In Table 3, the patterns of the original and Shiromaru materials are compared. They are essentially identical to reflect the similar composition. The difference in intensity may be ascribed to the difference in the method and the crystal habit as well as the well-developed cleavage, probably {110} and {1 $\bar{1}$ 0}.

Geochemical Consideration

In order to consider the chemical condition favouring the formation of marsturite, the mineral associations of ores from the Tsurumaki mine is better for this purpose, since they comprise various kinds of manganese silicates, a part of which were chemically specified. It is certain that all the components forming marsturite are also contained in the associated minerals, namely, Na in "aegirine-johannsenite", Ca in calcite, and Mn in bementite. Among them, "aegirine-johannsenite" and bementite are obviously older than marsturite from the textural relations. This means that no incorporation of extra ingredient is needed as to the formation of marsturite, that is, if such a phenomena as a hydrothermal recrystallization of existing minerals takes place, marsturite

Table 3. X-ray powder patterns of marsturites

1.		2.			1.		2.				
I	d	I	d _{obs.}	d _{cal.}	h k l	I	d	I	d _{obs.}	d _{cal.}	h k l
20	7.21	18	7.190	7.181	1 0 0	10	2.258	1	2.260	2.263	3 $\bar{4}$ 0
20	6.76	35	6.763	6.751	0 0 1					2.261	2 1 2
5	4.81	10	4.807	4.810	1 0 1			1	2.233	2.235	1 4 1
		2	4.164	4.158	1 1 $\bar{1}$					2.233	2 $\bar{3}$ 2
		2	3.840	3.842	2 $\bar{1}$ 0					2.232	0 1 3
		2	3.675	3.679	2 $\bar{2}$ 0	30	2.219				0 4 2
5	3.57	12	3.587	3.590	2 0 0			30	2.209	2.206	3 $\bar{4}$ $\bar{1}$
10	3.36	24	3.376	3.376	0 0 2			4	2.180	2.182	0 1 $\bar{3}$
40	3.18	50	3.184	3.181	0 $\bar{1}$ 2					2.176	1 3 $\bar{2}$
30	3.11	42	3.110	3.112	2 0 1	20	2.118	3	2.120	2.120	1 0 3
				3.110	2 1 0	20	2.086	3	2.091	2.089	3 $\bar{4}$ 1
80	2.999	100	3.000	3.002	1 0 2					2.089	3 $\bar{1}$ $\bar{2}$
				2.997	1 $\bar{2}$ 2			3	2.004	2.003	2 $\bar{1}$ $\bar{3}$
				2.996	1 $\bar{4}$ 0			3	1.880	1.880	0 $\bar{3}$ 3
90	2.916	17	2.915	2.916	1 3 0			2	1.847	1.844	2 1 $\bar{3}$
100	2.725	7	2.730	2.732	2 $\bar{4}$ 0	5	1.714	4	1.715	1.714	2 2 $\bar{3}$
20	2.640				0 4 1	30	1.695	14	1.685	1.684	3 4 4
		16	2.630	2.627	1 $\bar{3}$ 1	10	1.650				
				2.627	2 $\bar{1}$ 2	10	1.603	7	1.604	1.603	3 0 3
		2	2.552	2.556	3 $\bar{2}$ 0			2	1.590	1.592	3 1 $\bar{3}$
20	2.534	10	2.529	2.534	0 $\bar{4}$ 1					1.592	3 $\bar{3}$ 3
				2.533	3 $\bar{1}$ 0			2	1.587	1.586	2 3 3
20	2.453	3	2.452	2.455	2 $\bar{4}$ 1	5	1.555	5	1.554	1.558	3 3 $\bar{2}$
				2.453	2 $\bar{1}$ 2			2	1.490	1.491	3 2 $\bar{3}$
				2.453	3 $\bar{3}$ 0	40	1.441	10	1.442	1.442	2 4 $\bar{3}$
				2.453	3 $\bar{2}$ $\bar{1}$	5	1.416				
				2.452	2 2 $\bar{1}$	5	1.395	2	1.394		
		2	2.399	2.394	3 0 0						
		2	2.326	2.325	3 $\bar{1}$ 1						
		2	2.317	2.315	2 1 2						
						$a=7.70\text{\AA}$	$a=7.71\text{\AA}$				
						$b=12.03$	$b=12.03$				
						$c=6.78$	$c=6.78$				
						$\alpha=85.26^\circ$	$\alpha=85.4^\circ$				
						$\beta=94.10^\circ$	$\beta=94.1^\circ$				
						$\gamma=111.04^\circ$	$\gamma=111.2^\circ$				

1. Marsturite. Franklin, New Jersey, U.S.A. Cu/Ni rad. Gandolfi camera method. After PEACOR *et al.* (1978).

2. Marsturite. Shiromaru mine, Tokyo. Cu/Ni rad. Diffractometer Method. The present study.

is to be formed as far as chemical conditions concern.

In metamorphosed bedded manganese ore deposits of the similar mode of occurrence to the present cases, Na is extant in such silicates as a clinopyroxene rich in aegirine molecule, albite, alkali amphiboles, ganophyllite, bannisterite, and rarely

serandite, nambulite and natronambulite. While, the existence of Ca is more common than Na, since it readily substitutes Mn^{2+} in silicates and carbonates, *vice versa*. In case of deficiency of Na, an alternate of marsturite may appear. If so, it is so likely that it contains Mn^{2+} and Ca as its essential constituents and the formation is independent of Na.

The most probable candidate satisfying above conditions is rhodonite, which occurs in bedded manganese ore deposits suffering the metamorphism of comparable grade with the present cases, and, furthermore, in the similar mode of occurrence to marsturite. In case of the Tsurumaki mine, rhodonite is also found as an essential constituents of a lower grade of ore as given in Table 1, Nos. 10 and 11. Including this rhodonite and marsturite, it is worthy of note that all of pyroxenoids from the Tsurumaki mine are very low in MgO and FeO contents, together with the other ore-forming manganese silicates. Thus, it is very likely that marsturite owes the formation to Mg- and Fe^{2+} -depleted condition besides the presence of available Na.

The chemical analyses of "aegirine-johannsenite" from the Tsurumaki mine allow the reasonable interpretation that they require a partial conversion of Mn^{2+} into Mn^{3+} . This suggests that the condition favouring the formation of such a material is rather oxidizing. In case of the Shiromaru mine, the low grade ore intersected by marsturite-bearing veinlet comprises hematite. It is very likely that the ore deposit itself had been already low in FeO at the time of formation due to its oxidation to Fe^{3+} .

At the Shiromaru mine, the wallrocks of ore deposit comprise albite as one of the essential constituents. Also, the occurrence of calcian serandite (Mn: Ca=3:2) (KATO *et al.*, 1987) is known in banalsite-bearing veinlets cutting a Ba-silicate-bearing rock of similar mineral composition in the same manner as the present case. In this locality a potential source of Na is located closely to the site of formation of marsturite.

The complete substitution of Mn for Ca in this mineral seems impossible according to the synthetic works of ITO (1972). According to WATANABE *et al.* (1976), low Ca serandite (Mn: Ca=93:7) from the Tanohata mine, Iwate Prefecture, is accompanied by rhodonite. Unless this rhodonite is highly calcian, this association is interpreted to favour the application of the conclusion of ITO (1972), provided that the serandite and rhodonite are in equilibrium relation.

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