

Cymrite from the Niro Mine, Shikoku, Japan

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Abstract Microprobe analysis of cymrite from the Niro mine, Shikoku, Japan, gives SiO_2 30.76, Al_2O_3 26.20, BaO 37.97, K_2O 0.47, H_2O 4.61 (calc.), corresponding to $(\text{Ba}_{0.87}\text{K}_{0.04})_{\Sigma 1.01}\text{Al}_{2.01}\text{Si}_{2.00}\text{O}_8 \cdot \text{H}_2\text{O}$. The X-ray powder data are indexed on a hexagonal cell with $a=5.333$, $c=7.711$ Å. It occurs as submillimeter order colourless tablets in massive caryopilite ore. The ore deposit is hosted by bedded chert suffering a regional metamorphism of lower grade. The chemical analyses of the associated tephroite, rhodonite, caryopilite, rhodochrosite, strontianite, and phengite are given. Barium is also contained in strontianite and phengite, but strontium is exclusively found in strontianite only.

Introduction

Cymrite occurs in bedded manganese ore deposits suffering low to high grade metamorphism (SMITH *et al.*, 1949; REINECKE, 1982), in stratabound sulphide deposits (FORTEY & BEDDOE-STEPHENS, 1982), in metagraywacke (ESSENE, 1967), and in xenolith in serpentinite (KATO & MATSUBARA, 1986). In Japanese bedded manganese ore deposits, cymrite is reported from the Shiromaru mine, Tokyo and from the Omiya mine, Saitama Prefecture (MATSUBARA, 1985), forming an essential constituent in the wallrocks, which suffered regional metamorphism of lower grade. The present cymrite is found in a caryopilite-rhodochrosite ore as a metamorphic mineral of lower temperature condition. Also, under such a condition, the distinctive geochemical behaviour of strontium from barium is demonstrated, it being preferentially concentrated in carbonate and excluded by silicate.

Occurrence

The ore deposit of the Niro mine is located about 40 km ENE of Kochi Station, JR Shikoku Line (Fig. 1), and was worked for manganese till about 30 years ago. According to YOSHIMURA (1952), the ore deposit consists of some fault-bound orebodies in bedded chert with slaty and carbonaceous materials. At present some pieces of ores are found in dumps around the excavated orebodies. The examined material was collected by Mr. Yorikuni SHIMOYAMA, who found the presence of minute cleavable tablets in a massive manganese ore, and the chemical and X-ray powder studies informed the tablets to be cymrite.

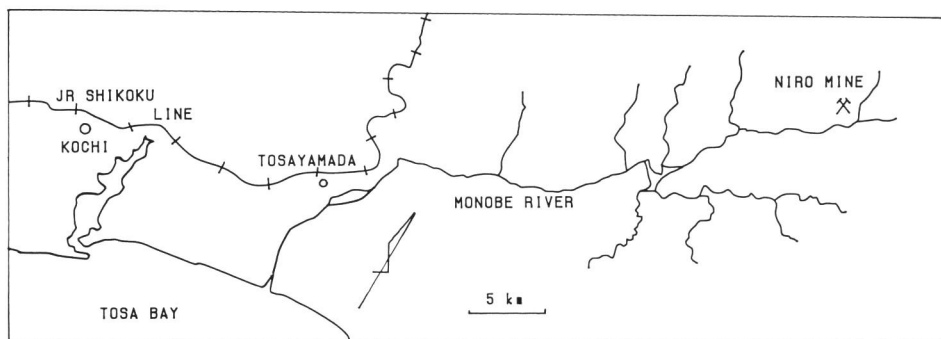


Fig. 1. The index map of the Niro mine (crossed hammer mark).

The massive ore is apparently very heterogeneous and consists of millimeter order chocolate brown, yellow brown and light grey blocks with light to deep brown bedded parts, which are continuous to intersticing materials of above blocks. All of them are intersected by thin veinlets of light pinkish brown rhodochrosite and of colourless barite. Cymrite occurs as randomly oriented submillimeter tablets sparsely distributed in the yellow brown blocks, and as the unique mineral grains of visible dimension therein, except for the vein-forming materials.

Under the microscope the chocolate brown blocks consist principally of hematite with or without rhodochrosite. The yellow blocks are composed of phengite-rhodochrosite aggregates surrounded by caryopillite-phengite aggregates in which cymrite tablets are embedded. The light grey blocks are composed of very fine grains of apatite with minor caryopillite and phengite. Cymrite tablets consist of minute bundles composed of crystals with very slender outline in thin section, or very thin tablets in subparallel arrangement (Fig. 2). They are embedded in the aggregates of caryopillite which demonstrate bird-eye texture and accompany phengite very often. The textural relations suggest the earlier formation of rhodochrosite-phengite aggregates than phengite-caryopillite aggregates at least in part. In these aggregates, rhodochrosite grains are liable to form aggregates involving tephroite grains or rhodonite aggregates accompanying minor strontianite (Fig. 3).

Chemical Analyses

Chemical analysis of cymrite was made after the employment of a Link Systems energy-dispersive X-ray spectrometer (Table 1). Potassium is vicarious to barium as pointed out by REINECKE (1982), who reported the substitution of potassium up to 6 mole % for barium, or 0.75% wt. % of K_2O . Despite the co-existence with strontianite, no strontium was found in cymrite. Therefore, the substitution relations of cymrite to calcium and strontium are similar to the case of celsian to which potassium is uniquely vicarious.



Fig. 2. The back-scattered electron image of cymrite. A bar indicates 10 μm .

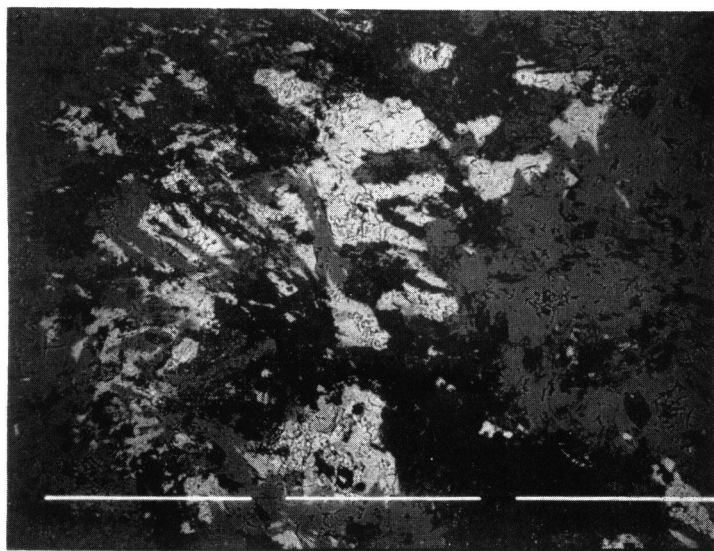


Fig. 3. The back-scattered electron image of strontianite (white), rhodonite (dark gray) and rhodochrosite (black). A bar indicates 100 μm .

The chemical analyses of the associated tephroite, rhodonite, caryopilite, rhodochrosite, strontianite, and phengite are given in Table 2. Tephroite is very close to the theoretical formula and iron is essentially lacking. Likewise, rhodonite is also without

Table 1. Chemical analysis of cymrite

	wt. %	molecular number
SiO ₂	30.76	2.00
Al ₂ O ₃	26.20	2.01
BaO	37.97	0.97
K ₂ O	0.47	0.04
H ₂ O*	4.61	2
total	100.01	

(* calculated)

Empirical formula (basis: O=8 in the anhydrous part):



Table 2. Chemical analyses of tephroite (1), rhodonite (2), caryopilite (3), rhodochrosite (4), strontianite (5) and phengite (6). The totals of (4) and (5) are normalized to 100%.

	1.	2.	3.	4.	5.	6.
SiO ₂	30.23	47.00	36.91			49.09
Al ₂ O ₃			2.26			15.29
MgO	0.17	0.44	1.71	0.55		10.95
FeO*	0.16		2.39	0.23		5.39
MnO	70.01	45.70	47.75	53.12		6.43
CaO	0.14	6.41	0.14	6.96	7.75	0.36
SrO					55.97	
BaO			0.76		4.99	0.82
K ₂ O			0.05			8.99
CO ₂ **				39.15	31.29	
H ₂ O**			7.64			4.30
total	100.71	99.55	99.61	100.01	100.00	101.62

(* total Fe; ** calculated)

Empirical formulae:

1. $(\text{Mn}_{1.97}\text{Mg}_{0.01}\text{Ca}_{0.01})_{\Sigma 1.98}\text{Si}_{1.01}\text{O}_4$ (basis: O=4)
2. $(\text{Ca}_{0.73}\text{Mn}_{0.27})_{\Sigma 1.00}(\text{Mn}_{3.87}\text{Mg}_{0.07})_{\Sigma 3.94}\text{Si}_{5.03}\text{O}_{15}$ (basis: O=15)
3. $(\text{Mn}_{4.28}\text{Mg}_{0.27}\text{Fe}^{2+}_{0.21}\text{Al}_{0.18}\text{Ba}_{0.03}\text{Ca}_{0.02}\text{K}_{0.01})_{\Sigma 5.00}(\text{Si}_{3.81}\text{Al}_{0.10})_{\Sigma 4.00}\text{O}_{10}$
 $((\text{OH})_{5.88}\text{O}_{0.12})_{\Sigma 6.00}$ (basis: total cation=9)
4. $(\text{Mn}_{0.84}\text{Ca}_{0.14}\text{Mg}_{0.02})_{\Sigma 1.00}\text{CO}_3$ (basis: total cation=1)
5. $(\text{Sr}_{0.76}\text{Ca}_{0.19}\text{Ba}_{0.05})_{\Sigma 1.00}\text{CO}_3$ (basis: total cation=1)
6. $(\text{K}_{0.80}\text{Ca}_{0.03}\text{Ba}_{0.02})_{\Sigma 0.85}(\text{Mg}_{1.14}\text{Al}_{0.85}\text{Mn}_{0.38}\text{Fe}^{2+}_{0.31})_{\Sigma 2.51}$
 $(\text{Si}_{3.42}\text{Al}_{0.58})_{\Sigma 4.00}\text{O}_{10}(\text{OH})_2$ (basis: total of positive charge=22 provided that rion is divalent)

any FeO. The same relation is also seen in rhodochrosite. The valency states of iron in caryopilite and phengite are uncertain, since both of them are capable of containing of both of di- and trivalent iron. As to the derivation of the empirical formula of caryopilite, a tentative basis that the total number of cations is 9 is taken after the

Table 3. X-ray powder data for cymrites

1.		2.			hkil
I	d	I	d _{obs.}	d _{calc.}	
50	7.71	100	7.715	7.711	0001
10	4.62	10	4.619	4.619	10 $\bar{1}$ 0
90	3.96	15	3.973	3.962	10 $\bar{1}$ 1
10	3.85	5	3.844	3.855	0002
100	2.96	30	2.963	2.959	10 $\bar{1}$ 2
70	2.67	5	2.665	2.666	22 $\bar{4}$ 0
10	2.57	5	2.569	2.570	0003
10	2.53	5	2.521	2.520	11 $\bar{2}$ 1
20	2.31				20 $\bar{2}$ 0
40	2.24	5	2.245	2.245	10 $\bar{1}$ 3
40	2.21	20	2.212	2.212	20 $\bar{2}$ 1
10	2.195				11 $\bar{2}$ 2
10	1.982				20 $\bar{2}$ 2
30	1.925	35	1.924	1.928	0004
40	1.850	5	1.850	1.851	11 $\bar{2}$ 3
5	1.778				10 $\bar{1}$ 4
30	1.591				21 $\bar{3}$ 2
20	1.560	5	1.563	1.562	11 $\bar{2}$ 4
20	1.541				0005, 30 $\bar{3}$ 0
$a=5.334 \text{ \AA}$		$a=5.333 \text{ \AA}$			
$c=7.705 \text{ \AA}$		$c=7.711 \text{ \AA}$			

1. Brooks Range, Alaska, U.S.A. Fe/Mn radiation. Camera method. After RUNNELS (1964)

2. Niro mine, Shikoku, Japan. Cu/Ni radiation. Diffractometer method. The present study.

reference to the formula $\text{Mn}_5[(\text{OH})_6|\text{Si}_4\text{O}_{10}]$. Strontianite has higher CaO and BaO contents. Phengite contains appreciable amounts of MnO and FeO* (Fe in unspecified valency state) and minor BaO. The calculation of the empirical formula is tentative, since a basis of total of octahedral and tetrahedral cations=7 delivers the total valency more than 22. Therefore, the total valency of octahedral and tetrahedral cations is taken as 22, where iron is considered as divalent. The identification is tentative, since there is a significant omission in the octahedral site.

Physical Properties

It is nearly colourless with a vitreous luster and a perfect basal cleavage on which the luster is somewhat pearly. Under the microscope, it is colourless and the extinction is parallel to the outline and the sign of elongation is positive.

X-Ray Powder Study

The X-ray powder diffraction data for cymrite were obtained by the diffracto-

meter method and compared in Table 3. The unit cell parameters calculated after the indexing are: $a=5.333$, $c=7.711$ Å, well conformable with the known values.

Consideration on the Genesis

The occurrence of cymrite as a metamorphic mineral has been debated on Californian (ESSENE, 1967) and Greek materials (REINECKE, 1982), which are one of the rock-forming minerals in metagraywacke and a manganese-rich rock, respectively. In the latter case, cymrite is in association with celsian, which is replaced by cymrite (REINECKE, 1982), and the metamorphic grade is greenschist facies. At the present locality, no celsian is found and the texture of cymrite suggests that the primary state of formation is preserved.

The described evidence has another implication as to the geochemical behaviours of alkali earth elements in such a manganese ore suffering lower temperature metamorphism. Barium is included in cymrite, strontianite, phengite and barite in the ore, whereas strontium is exclusively found in strontianite. This is interpreted that cymrite allows no substitution of strontium under such a condition. This tendency is also found by KATO and MATSUBARA (1986) on cymrite accompanied by slawsonite in basic xenoliths involved in serpentinite from Kochi Prefecture. Also, at Andros Island, Greece, the metamorphosed manganese-rich rocks include strontium, which is contained in hollandite (REINECKE, 1982). In the examined material calcium is the essential constituents of apatite, rhodonite and the subordinant one of rhodochrosite.

Although the formation of cymrite seems to have no relation to the degree of oxidation state, the mineral associations of cymrite from bedded manganese ore deposits are characterized by such minerals as hematite in the Benallt mine, Carnarvonshire (HEY, pers. comm.), hematite and braunite in the Shiromaru mine, Japan (MATSUBARA, 1985), hollandite, braunite and piemontite in Andros Island, Greece (REINECKE, 1982) and hematite in the present case. This proves that the presence of ferric iron does not interfere the formation of such a barium silicate as cymrite in such manganese ores including the present one. Although the conditions of formation are far discrepant, the contact metamorphism of higher temperature condition allows the formation of such barium silicates containing ferrous iron as fresnoite (ALFORS *et al.*, 1967).

The source of barium will be ascribed to the absorbed component of manganese nodules precipitated in the deep sea bottom, where manganese was in tetravalent state as far as nodules are not covered by sediments of subsequent deposition. Once nodules are covered by sediments, reduction begins to proceed to form minerals of manganese of lower valency. The examined material has very heterogeneous texture composed of such a hydrous mineral as phengite and caryopilite indicating the lower metamorphic grade, which served to reserve the heterogeneous texture involving significant difference in the contents of neighbouring mineral aggregates.

Acknowledgements

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