

Siegenite in a caryopilite ore from the Okutama mine, Tokyo

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東京都奥多摩鉱山産カリオピライト質鉱石中のシーゲン鉱

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東京都奥多摩鉱山のマンガン鉱床中に産するカリオピライトを主とする鉱石中からシーゲン鉱を記載した。S=4として計算された実験式は $(\text{Co}_{1.72}\text{Ni}_{1.19}\text{Mn}_{0.09})_{\Sigma 3.00}\text{S}_{4.00}$ を与え、副成分としてのマンガンの存在は硫スピネル系鉱物としては隕石中のものを除いて異常な例と言える。なおカリオピライト質鉱石中にマンガン層状珪酸塩があり、実験式 $(\text{Mn}, \text{Mg}, \text{Fe})_4(\text{Si}, \text{Al}, \text{Fe})_6\text{O}_{15}(\text{OH}, \text{H}_2\text{O})_5$ が与えられたが、分類上の位置は不明である。

Abstract Siegenite from a weakly metamorphosed bedded manganese ore deposit of the Okutama mine is found as a very minor constituent of a caryopilite ore including rhodochrosite and a manganese-bearing layered silicates. The average of five analyses is: Co 33.29, Ni 22.96, Mn 1.59, S 42.17, total 100.01%, and yields the empirical formula $(\text{Co}_{1.72}\text{Ni}_{1.19}\text{Mn}_{0.09})_{\Sigma 3.00}\text{S}_{4.00}$, a rare manganiferous variety. One of the chemical analyses of caryopilite gives: SiO_2 38.65, Al_2O_3 0.72, FeO 2.14, MgO 2.53, CaO 0.05, MnO 46.07, total 90.16%. That of rhodochrosite is: MnO 55.95, CaO 4.78, FeO 0.47, MgO 0.33, total 61.53%. The chemical analyses of the manganese-bearing layered silicate gives: SiO_2 45.78, Al_2O_3 3.02, FeO 1.90, MgO 3.77, MnO 32.60, CaO 0.33, K_2O 2.13, total 89.53%. It yields an empirical formula $\text{K}_{0.32}\text{Ca}_{0.04}(\text{Mn}_{3.28}\text{Mg}_{0.67}\text{Fe}^{2+}_{0.05})_{\Sigma 4.00}(\text{Si}_{5.44}\text{Al}_{0.42}\text{Fe}^{3+}_{0.14})_{\Sigma 6.00}\text{O}_{15.00}(\text{OH})_{1.84} \cdot 3.16\text{H}_2\text{O}$ if the difference to 100% is regarded as H_2O . The mineralogical status is unspecified.

INTRODUCTION

There are many bedded manganese ore deposits in Mesozoic accretional bodies in Japan. All of them accompany chert as their most principal wallrocks, in which subordinate amounts of mudstone, greenstone and limestone exist. Ores therefrom undergo various grades of

regional or contact metamorphism by which many manganese oxides, silicates, carbonates and rarely borates are formed.

The original state of manganese beds is considered to be manganese nodules precipitated on the deep sea floor even currently. The nodules are also a carrier of heavy elements, which are absorbed or involved in manganese dioxide minerals forming nodules. After the diagenesis and subsequent metamorphism, these elements take different geochemical behaviours. Chalcophile elements such as nickel and cobalt form sulphides. Siderophile ones such as iron behave in a partially similar manner to manganese. In the cases of nickel and cobalt, their behaviours are essentially same and produced minerals of these elements involve them in the form of mutual substitution as seen in the present case.

The present siegenite includes a minor fraction of manganese, which is unusual to the members of thiospinels, except for manganoan daubreelite(FeCr_2S_4) and its unnamed Mn^{2+} analogue (KEIL and BRETT, 1974), both being exclusively found in meteorites. The implication of the occurrence is briefly considered.

In the examined caryopilite were analysed four phases, siegenite, caryopilite, rhodochrosite, and a probably hydrous manganese silicate with the probable chemical formula $(\text{Mn, Mg, Fe})_4(\text{Si, Al, Fe})_6\text{O}_{15}(\text{OH, H}_2\text{O})_5$, but the status has not been mineralogically specified.

ORE DEPOSIT, ORES AND THE OCCURRENCE OF SIEGENITE

The ore deposit of the Okutama mine is located about 500 m east of Okutama station, the endpoint of Ome line, Eastern Japan National Railway Co. Ltd. (Fig. 1), or about 70 km westward of the center of Tokyo. Although the history of the mine has not been known in detail, it is said that it had been worked during the World War II. Still the portal and dumps are left, where the examined materials were collected. The heavily ruined condition of the gallery impedes the entrance but the profile of ore bearing bed could be recovered after the observation of materials forming the dumps and of outcrops exposed along a valley leading to the portal in which the dumps are developed.

The wallrocks of manganese bed are dominantly occupied by very weakly recrystallized grey to white massive chert accompanying minor hematite-bearing red one. Both of them are minutely veined by quartz without any apparent regularity. Since the lower grade ores found in the dumps consist of the mixture of caryopilite and quartz of various ratios, the ores in direct contact with the wallrock must have included caryopilite as the most important member in quantity. Besides chert, minor blocks of mudstone and greenstone are found in the dump. From the geological situation that the deposit is located in the southern part of Kanto Mountainland, where regional metamorphic rocks belonging to Sanbagawa belt are extensively exposed, the wallrocks and ores suffered from a very low grade of regional metamorphism, though apparently unmetamorphosed. The mudstone is also found in the outcrop along the valley in a small quantity. Although the existence in chert beds could not be realized, it is very likely that the greenstone exists within chert beds. Also, blocks of sandstone are found in dumps, too, but the origin could not be specified.

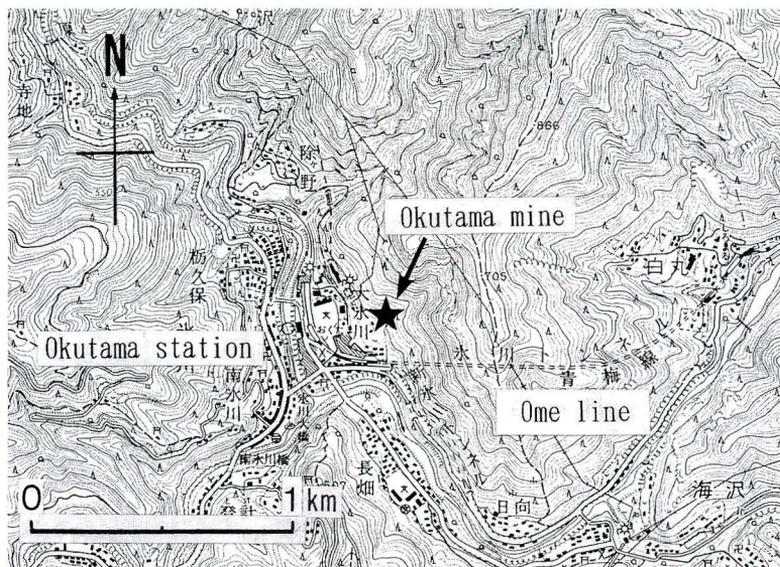


Fig. 1. Index map of the Okutama mine. Map: 1/25,000 Okutamako.
The location is: N 35°48' 23", E 139°06' 16".

The recognized ore minerals include caryopilite, rhodochrosite, rhodonite, ganophyllite, hausmannite, tephroite, neotocite and manganosite in the order of apparent decreasing quantity, and the first one occupies the principal member of the ores. The gangue mineral is quartz with very minor halloysite.

The most principal and nearly unique ore mineral is caryopilite with which variable amount of quartz coexists. Most of caryopilite ores have bandings composed of vari-coloured caryopilite. The colours include light brown, greyish salmon pink, and light brownish grey. The thickness of bands is from a few millimeters to a centimeter order. All of ores are very fine-grained and minutely intersected by veinlets of the following assemblages: 1) rhodochrosite, 2) rhodochrosite-rhodonite, 3) rhodonite-ganophyllite, and 4) neotocite. The first one consists of rather coarse-grained white to grey white rhodochrosite. The second one is occupied by a pink material composed of fine-grained rhodochrosite and rhodonite. The third one is exclusively found in higher grade ores. The rhodonite is somewhat coarser in grain size and the colour is rather rosy. The neotocite veinlets are found in caryopilite ores only and devoid of any other associated phases. It is brown in colour and semi-transparent in the fresh state. All the veinlets are of millimeter to submillimeter thick, and found in ores of moderate to high grades.

Rhodochrosite is exclusively found as veinlets cutting caryopilite ores. Rhodonite occurs principally in veinlets as stated above. Besides this, the aggregate of rhodonite and rhodochrosite is found between wider bands in caryopilite ores, where the aggregate embodies light bluish grey mass of tephroite. Hausmannite is found as chocolate brown thin seams of millimeter thick intercalating with brown caryopilite forming the highest grade of ore in this

deposit. Some caryopilite bands are interposed by rhodochrosite spots in which tiny grains of manganosite with or without hausmannite are involved. In the examined caryopilite ore, very small pearly-lustered white spots composed of fragile flaky mineral are found. The chemical analysis gives an empirical formula $(\text{Mn, Mg, Fe})_4(\text{Si, Al, Fe})_6\text{O}_{15}(\text{OH, H}_2\text{O})_5$ if the difference is entirely occupied by H_2O .

Siegenite is generally found as extremely tiny grains in a caryopilite ore without banding, which is rare in the dump. It is barely visible under magnifier and in direct contact with caryopilite and rhodochrosite. No external form is observed (Fig. 2). It is unique opaque mineral in this ore. Under the microscope, caryopilite forms aggregates composed of random oriented felty aggregates of very fine flakes. It is moderately pleochroic with yellowish brown to brown colour, and has rather high birefringence. The extinction is parallel with positive elongation. The aggregate involves variable amounts of rhodochrosite and quartz along with the examined siegenite-bearing material, the former being of visible dimension (Fig. 3). The white spots stated above consists of radially aggregated flakes partially replaced by rhodochrosite (Fig. 4). It is colourless in thin section and the extinction is parallel to the trace of one perfect cleavage with positive elongation and very low birefringence.

Besides these phases, the X-ray powder diffractometer study of some different fractions of the caryopilite ore including siegenite provides diffractions out of those due to caryopilite. In the obtained patterns are also slight differences, which will be due to quantitative difference of constituting minerals. Since the patterns are all rather of inferior quality, the interpretation did not reach any conclusive identification of phases except caryopilite. In Table 1, one of the representative patterns comprising the other diffractions than those of caryopilite is given. All the diffractions in the pattern are all rather broad and weak to suggest the lower crystallinity despite the higher birefringence of caryopilite. Although the stronger diffraction $d=10.8$ corresponds approximately to that of yofortierite (PERRAULT et al., 1975), no phase with the yofortierite composition has been found.

The powder pattern of caryopilite from Hurricane Claim, Washington, compared in Table 2 (Guggenheim et al., 1982) is slightly discrepant from that of the present material, and these two material are also slightly different in chemical composition as discussed later, although the authors describing the compared material refer to another material from Swizerland with the chemical composition very close to the present material as caryopilite.

CHEMICAL ANALYSES

Electron microprobe analyses of siegenite, caryopilite, rhodochrosite, and a manganese-bearing layered silicate using Link Systems energy dispersive X-ray spectrometer are given in Table 2, in which their empirical formula are also demonstrated.

Siegenite was analysed on one grain. Since five spot analyses provided the ratio of total metal/sulphur to be very close to 3/4 and that the variation ranges of metal constituents are so small, the average of five chemical analyses is representatively given. The chemical analyses of caryopilite indicated the narrower ranges of all the constituents. The tabulated analyses is

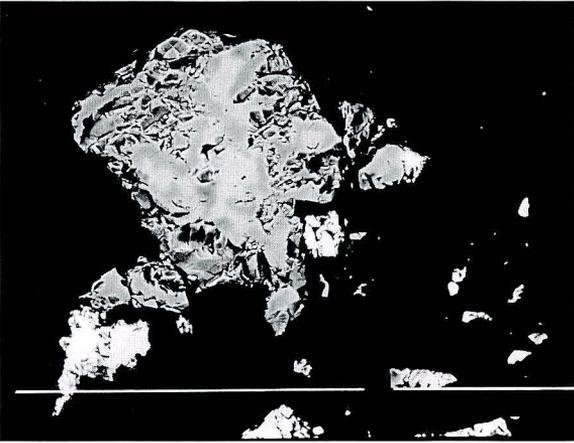


Fig. 2. Back scattered electron image of siegenite grains surrounded by rhodochrosite. A bar indicates 0.07 mm.



Fig. 3. Back scattered electron image of caryopilite (dark grey) with rhodochrosite (grey), which consists of the aggregate of a few larger grains after microscopic observation. A bar indicates 0.07 mm.



Fig. 4. Back scattered electron image of a manganese-bearing silicate (dark grey) with a micaceous cleavage. It is replaced by rhodochrosite (grey white), which also replaces caryopilite (medium grey). A bar indicates 0.1 mm.

Table 1. X-ray powder pattern of the caryopilite ore

1		2		3		4	
d(A)	I	d(A)	I	d(A)	I	d(A)	I
15.1	20			2.104	5	2.101	35
10.8	100			1.965	5	1.968	20
10.0	5					1.850	2
7.31	60	7.30	80			1.820	2
4.60	5			1.737	5	1.731	25
3.66	70*	3.639	50	1.692	15		
2.86	100*	2.825	60	1.654	15	1.643	35
2.768	50			1.621	30	1.626	20
		2.648	5	1.606	10b	1.603	25
2.571	10			1.539	10b	1.535	3
2.524	70	2.521	100			1.494	10
		2.427	7	1.454	5b	1.453	10
		2.382	20			1.445	10
		2.239	4	1.423	20	1.420	10

1. Caryopilite ore. Okutama mine, Tokyo. Cu/Ni radiation. Diffractometer method. *: enhanced intensity due to rhodochrosite. b = broad.
2. Caryopilite. Hurricane Claim, Olympic Peninsula, Wash., U. S. A. FeK α radiation. Camera method. After Guggenheim et al. (1982).

a representative. A tentative calculation on the basis of Si=2 and the assumption that the difference is occupied by H₂O only provides a significant vacancy in the octahedral sites as pointed out by Guggenheim et al. (1982), who presented a few caryopilite analyses ranging from (Mn_{2.50}Al_{0.05}Mg_{0.05}Fe*_{0.03})_{Σ2.63}Si_{2.00}(Fe* = Fe²⁺ + Fe³⁺ calculated as Fe²⁺) (X-ray'd material from Hurricane Claim, Washington) to (Mn_{2.10}Mg_{0.22}Al_{0.05}Fe*_{0.04})_{Σ2.41}Si_{2.00} (material from Switzerland) along with the anhydrous parts after rounding by the present authors. Although the formula of the present material, (Mn_{2.02}Mg_{0.19}Fe*_{0.09}Al_{0.04})_{Σ2.34}Si_{2.00}, is close to the latter, it is out of the range, or the octahedral vacancy is more remarkable. Guggenheim et al. (1982) suggested the presence of two phases, monoclinic and triclinic ones, in their X-ray and chemically studied material from Hurricane Claim, although the authors call the compositionally different materials under the same name caryopilite. It is still uncertain whether the difference between the X-ray powder pattern of the present and Hurricane Claim materials is ascribable to the compositional difference or not. In order to create an unequivocal mineralogical status of caryopilite, it is highly desirable to carry out the X-ray and chemical studies of caryopilite with higher crystallinity and purity. The chemical analyses of the manganese-bearing layered silicate was tentatively calculated on the total of octahedral and tetrahedral cation = 10. The low summation is handled as due to H₂O. Such tentative settings enable to correlate the derived empirical formula to the formula of sepiolite in which Mg is to be dominantly replaced by Mn. But the identification is inconclusive due to the lack of any positive proof in the X-ray powder data.

Table 2. Chemical analyses of siegenite(1), caryopilite(2), rhodochrosite(3), and a manganese-bearing silicate(4).

Weight percentages: (FeO* : total Fe)

	1		2	3	4
Co	33.29	SiO ₂	38.65		45.78
Ni	22.96	Al ₂ O ₃	0.72		3.02
Mn	1.59	FeO*	2.14	0.47	1.90
S	42.57	MgO	2.53	0.33	3.77
		MnO	46.07	55.95	32.60
		CaO		4.78	0.33
		K ₂ O			2.13
Total	100.01		90.16	61.53	89.53

Empirical formula: (* total Fe calculated as FeO)

1. (Co_{1.72}Ni_{1.19}Mn_{0.09})_{Σ3.00}S_{4.00} (basis: S = 4)
2. (Mn_{2.02}Mg_{0.19}Fe*_{0.09}Al_{0.04})_{Σ2.34}Si_{2.00}O₅(OH)_{2.72} · 0.44H₂O (basis: Si = 2; after addition of H₂O 9.84%)
3. (Mn_{0.89}Ca_{0.10}Mg_{0.01}Fe_{0.01})_{Σ1.01}CO₃ (basis: total cations = 1; after addition of CO₂ 39.11% (total 100.64%))
4. K_{0.22}Ca_{0.04}(Mn_{3.28}Mg_{0.67}Fe²⁺_{0.05})_{Σ4.00}(Si_{5.44}Al_{0.42}Fe³⁺_{0.14})_{Σ6.00}O_{15.00}(OH)_{1.84} · 3.16H₂O (basis: total of tetrahedral and octahedral cations = 10; after FeO and Fe₂O₃ allotment(1.57, 0.50) and addition of H₂O 10.30%)

IMPLICATION OF THE OCCURRENCE OF SIEGENITE

In Japanese bedded manganese ore deposits is known the occurrence of siegenite from two localities. One is from the Kamo Mine, Mie Prefecture, where it is found as a very minor constituent in a caryopilite ore (Matsubara and Kato, 1989). The other is known at Itaga, Kanuma City, Tochigi Prefecture, where it occurs as a rare constituent of aggregates of rhodonite and spessartine (Matsubara and Kato, 1986). The former is similar to the present case in the low grade of regional metamorphism which the wallrocks underwent and favoured the occurrence of caryopilite. The assemblage of manganese silicates at the latter case is the product of contact metamorphism due to nearby granitic intrusion. The occurrence of siegenite in these two localities where different metamorphic conditions were prevalent means that this mineral has an extensive range of formation ranging from lower to higher temperature conditions where the behaviours of nickel and cobalt are geochemically equal.

In metamorphosed bedded manganese ore deposits in Japan, the known nickel and cobalt minerals besides siegenite include gersdorffite, cobaltite, pentlandite, and niccolite. Although they are generally fine in grain size, they can be noticed even during the field observation. As far as examined, none of them contain manganese as their minor constituent. It is likely that siegenite in manganese ores suffering very low grade of metamorphism is capable of containing manganese.

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