Malayaite from the Sampo Mine, Okayama Prefecture, Japan*

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Abstract

Iron-copper deposits of the Sampo mine, Okayama Prefecture are of contact-metasomatic type, and the iron-oxide (magnetite) ores have been known to contain tin with up to 0.5 percent by weight. In these ores, tin appears to occur as minute grains of cassiterite, varying in size up to 100µ across, and they are embedded in calcite immediately adjacent to magnetite.

In this paper, malayaite from clinopyroxene skarn lying between crystalline limestone and leucocratic biotite-granite through magnetite ore on the Yoshiki 9th adit-level of the mine is examined by use of electron-probe X-ray microanalyzer and micro-beam X-ray diffractometer.

The present malayaite occurs as a micro-volume mineral up to 300µ across, euhedral to subhedral in form, and is developed sparsely in the mosaic aggregates of clinopyroxene, actinolitic hornblende and fluor spar. The chemical analyses of Grain (A) by electron microprobe method gave the following chemical composition on the average; SiO₂ 22.22, TiO₂ 0.60, SnO₂ 56.72, Fe₂O₃ 0.05, CaO 20.61, Total 100.20 (all in weight percent). From this, the chemical formula on the basis of five oxygen atoms may be calculated as, Ca₀.₉₈(Sn₁.₀₀Feᵻ₀.₀₀Ti₀.₀₂)₁.₀₂O₁.₀₂Si₀.₉₉O₄, which corresponds closely to CaSnOSiO₄, the stoichiometric composition of malayaite. The principal reflections appearing on the X-ray diffraction patterns are, 5.03Å (35) (011), 3.29Å (20) (200), 3.06Å (35) (002), 2.668Å (>100) (T22, 031) and 2.415Å (25) (211).

As far as the present malayaite is concerned, it might be formed by the reaction of calcium, tin and silica at the frontal zone of skarnization, where tin and other volatile constituents might have been concentrated (TAKENOUCHI and SHOJI, 1969; TAKENOUCHI, 1971).

1. Introduction

Calcium-tin silicate (CaSnOSiO₄), an isostructural compound with sphene (CaTiO SiO₄), had been discovered from Perak, Malaya Peninsula by INGHAM and BRADFOOD (1960), and was named malayaite as a new mineral by ALEXANDER and FLINTER (1965). Immediately after its nomenclature, the occurrence of malayaite from a thin wollastonite-diopside bed in Devonshire, England, was reported by EL SHARKAWI and DEARMAN (1966). Also, JOHN (1967) reported an occurrence of this mineral from the Pinyok mine, Thailand, where the mineral was found in skarns, closely associated with diopside, andradite, cassiterite, calcite and quartz.

In Japan, an occurrence of malayaite-like mineral from skarns of the Sampo mine, Okayama Prefecture, was first reported by IMAI et al. (1967) and that of tin-bearing sphene in the wollastonite-diopside-green garnet zone, which lies between limestone and massive skarn at the Tsumo mine, Shimane Prefecture, was reported by SHIMAZAKI (1968). Subsequently, TAKENOUCHI and SHOJI (1969) advanced their field investigation on some contact-metasomatic tin and tungsten deposits

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in Southwestern Japan, and reported new occurrences of malayaite from the Höei, Mitate and Kuga mines. Moreover, they confirmed the occurrence of malayaite from the Sampo mine.

In connection with their field investigation, for purposes of verifying the physico-chemical environments under which malayaite was formed, the solid solubility relations in the binary system CaSnOSiO₄-CaTiOSiO₄ were investigated under hydrothermal conditions by Takenouchi (1971).

Quite recently, an occurrence of malayaite megascopically recognizable from the Toroku mine, Miyazaki Prefecture, was reported by Miyahisa et al. (1975), and its mineralogical properties in detail were given. Despite the recent accumulation of knowledge on malayaites from Japan, the “Sampo malayaite” which became an important clue to find the Japanese malayaites from other localities, has not been subjected to a close examination, and therefore the study in detail has not appeared so far in any papers, except for the description by Takenouchi and Shoji (1969).

The main purpose of this paper is to provide some mineralogical data on the present Sampo malayaite, together with its mode of occurrence and outline of the ore deposits, and to give some comments on the mineral genesis in relation to ore genesis. This paper is a part of Master Thesis of the present author under the supervisions of Prof. N. Imai, submitted to the Post-graduate School of Science and Engineering, Waseda University (Ogawa, 1975).

2. Location and Geologic Setting of the Ore Deposits

The Sampo mine is located near Nariwa Township, at Kawakami-mura, Kawakamigun, Okayama Prefecture (lat. 34°45′N; long. 133°30′E). The mine lies about 15 km west of Bichū-Takahashi on the Hakubi line of the Japanese National Railways (Fig. 1). The ore deposits of the mine had been worked for iron and copper, yielding annually about 30,000 tons of iron-copper crude ore, but the mining operation ceased in 1971.
Fig. 2 Idealized profile of the Yoshiki No. 1 orebody along the axis of main syncline.

On the other hand, the Yoshiki No. 2 orebody occupies the minor trough on the northwestern limb of the main syncline. The orebody is made up of oxide-sulphide ores consisting predominantly of pyrrhotites with some pyrite, chalcopyrite and magnetite.

Besides the principal ore minerals mentioned above, such minerals as sphalerite, arsenopyrite, löllingite, bismuthinite and cassiterite are found as either minor or trace minerals (Imai et al., 1967).

The skarns of the mine were principally formed by the replacement of limestone (calcite-marble) and slate (pelitic hornfels).

Dominant skarn-forming minerals involve clinopyroxene, garnet (andradite-grossularite), lieverite, wollastonite, fluorspar, quartz and calcite. The characteristic feature of the ore deposits is an occurrence of the minerals rich in volatile constituents in skarns, such as fluorspar, idocrase, topaz, cuspidine (Kato et al., 1970), and the unidentified silicate containing tin and chlorine (Imai and Mariko, unpublished data).

In the Yoshiki No. 1 orebody, beginning with leucocratic biotite-granite itself which serves as a footwall and proceeding towards calcite-marble, one can find successively several zones: leucocratic biotite-granite, “banded skarns”.

Fig. 3 Geologic plan of the Yoshiki 9th adit-level, showing the occurrence site of the malayaite-bearing skarn under investigation.
Asterisk shows the occurrence site of the specimen (S-6904).
skarn" (±) which is of pelitic hornfels origin and preserves original bedding, garnet skarn, clinopyroxene skarn ("green skarn"), massive magnetite ore, low-grade calcite-magnetite ore, and finally calcite-marble.

A considerable number of narrow post-ore dykes with andesitic and rhyolitic compositions transects the orebodies with clean-cut boundary. They might have intruded into the former high-angle fractures which served as the passages of ore-forming fluids (Imai et al., 1967).

3. Field Occurrence

Fig. 3 is a geologic plan of the Yoshiki 9th adit-level, showing the occurrence site of the clinopyroxene skarn (Specimen S-6904) containing the malayaite now under investigation. On this adit-level, folded structure of the Palaeozoic sediments is represented by a gentle warping, striking syncline on the upper level is no longer recognizable, and the No. 1 orebody separates into two small ore-masses.

As shown in Fig. 3, the specimen was taken from clinopyroxene skarn near the igneous contact of leucocratic biotite-granite. This clinopyroxene skarn grades into garnet skarn with increasing the amount of garnet towards limestone side, and there is a small lenticular ore-mass between outer limestone (calcite-marble) and the garnet skarn.

4. Petrography

In thin section, the clinopyroxene skarn (Specimen S-6904) consists of mosaic aggregates of clinopyroxene and fluorspar with little actinolitic hornblende. The composition of the clinopyroxene has not been determined chemically, but is presumed to be ferrosalite from the following optical properties; X = pale green, Y = brownish green, Z = pale green and c ∩ Z = −43°.

Malayaite, although very minor in abundance, typically occurs as wedge-, spindle- and irregularly-shaped grains in the mosaic aggregates of clinopyroxene and fluorspar with some actinolitic hornblende, indicating simultaneous grain growth with these minerals. This mineral is distinguished from the surrounding clinopyroxene for its higher birefringence. Its grain size varies over a wide range from 20 to 300µ in longer dimension, but the grains less than 100µ across are most common. As shown in the upper and central area of Fig. 4,

Fig. 4 Photomicrographs of the polished thin-section, showing the mode of occurrence of malayaite.
Fig. 5 Photomicrograph and the corresponding electron and X-ray scanning images around Grain # (A) of malayaite.
1. Photomicrograph (one polar), 2. Back-scattered electron image. Symbol A indicates Grain # (A). The $200 \times 180 \mu^2$ rectangle marked in this photograph indicates the area and location of the X-ray scanning images reproduced in 3 ~ 6. 3 ~ 6. X-ray scanning images.
wedge-shaped crystals of the malayaite give cruciform penetration-twin, which is commonly recognized in sphene.

Under a short-wave ultraviolet-light, the particles of the malayaite, showing a distinct yellowish-green fluorescence, are recognized here and there. However, as was pointed out by Takenouchi and Shoji (1969), the impression from the fluorescence tends to overestimate the amount of malayaite.

5. Chemistry

Chemical analyses of the present malayaite have been undertaken by X-ray spectroscopic method with electron microprobe. In this study, a JEOL EPMA (Model JXA-50A) with two-channel detecting system and 35° X-ray take-off angle was used. Analyzing conditions of the EPMA were; accelerating voltage: 15 kV, electron-probe impact diameter: 1~2 μ, electron-probe current: 0.03 μA as measured by Faraday cage, and analyzing crystals used: LiF and PET. As microprobe standards, the following materials were utilized: synthetic wollastonite for silicon and calcium, chemically analyzed hematite from the Waga Sen-nin mine, Iwate Prefecture for iron, chemical reagent of titanium dioxide for titanium, and pure metal for tin.

The intensity ratios (k-values) thus obtained were processed with a computer programme involving ZAF correction (Sweatman and Long's method (1969)) designed by T. Shoji and somewhat modified by the present author, and adopted to HITAC 8700/8800 settled in the Computer Center of University of Tokyo. Quantitative spot analyses were made at ten points on the polished surface of Grain ➥ A

A photomicrographs and the corresponding electron and X-ray images around Grain ➥ A are shown in Fig. 5. Also, the position of ten analytical points is shown in Fig. 6. The results of the analyses are listed in Table 1. Calculation of the chemical formula on the basis of five oxygen atoms from the mean value in Table 1 gave; Ca₀.₉₈(Sn₁₀₀Fe₃+₀₀ Ti₀.₀₂)₁.₀₂O₁.₀₁Si₀.₉₉O₄, which corresponds closely to CaSnO₄SiO₄, the stoichiometric composition of malayaite. In Table 2, the mean value in Table 1 is compared with those for malayaites from other sources. As shown in Table 1, the present malayaite is characterized by the compositional heterogeneity with respect to titanium and tin contents.

6. X-ray Microdiffraction

In the present X-ray diffraction study, taking the small particle-size and small
Table 2 Chemical analyses of malayaites.

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<td>Total</td>
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1. Sampõ mine, Okayama Prefecture, Japan (the present work). *: not determined.

The sample preparations were made under a short-wave ultraviolet-light in the following two ways; 1) the minute another particle of malayaite were extracted from hand specimens, and 2) thin film of malayaite (Grain 1(A)) was separated from the polished thin section.

The X-ray diffraction patterns from the two samples thus prepared are shown in Fig. 7, and the diffraction data (1) are compared with those for malayaites both natural and synthetic from other sources in Table 3. Although the reflections appearing on the X-ray diffraction patterns are so small in number on account of the preferred orientation of the crystals, excluding the reflections from impurities, there occur the reflections characteristic to malayaite, i.e., 5.03Å (35 011), 3.29Å (20 200), 3.06Å (35 002), 2.66Å (>100) (122, 031), 2.415Å (25 211), 2.097Å (10 140).

Table 3 X-ray diffraction data for malayaites.

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<td>37</td>
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1. Sampõ mine (the present work).
2. Toroku mine (MIYAHISA et al., 1975).
5. plus 0.9% insoluble residue.
6. d-Spacing is expressed in Å unit.
7. Discussion

Summarizing the data given so far, it may be said that the present Sampō malayaite is low in titanium and iron contents, and its chemical composition is very close to the stoichiometric composition of malayaite. In the clinopyroxene skarn in the mine, there is found tin-bearing sphene in the vicinity of malayaite, although tin content of the sphene has not been determined quantitatively by electron microprobe. According to the synthetic data by Takenouchi (1971), the formation temperature of the Sampō malayaite would have been relatively low, if these two minerals were formed in equilibrium.

Based upon the mode of occurrence of malayaites from several mines in Southwestern Japan, Takenouchi and Shoji (1969) and Takenouchi (1971) suggested that this mineral would have been formed by the following three processes. 1) Tin has been concentrated at the frontal zone of skarnization or at the zone of silicification, and malayaite would have been formed by the reaction of tin with calcium and silica. 2) Calcium- and silica-bearing hydrothermal solutions have reacted with the pre-existing tin-bearing minerals such as cassiterite, tin-bearing andradite in skarn, and malayaite would have been formed. 3) Tin-, calcium- and silica-bearing solution have been introduced into minor fractures to form veinlet in which malayaite has been formed with quartz and calcite.

Almost all of garnets in the garnet skarn of the mine have brownish-red colour, but some garnet is dark green in colour. It has often been pointed out that tin-bearing garnet usually
assumes dark green colour (e.g., El Sharkawi and Dearman, 1966). However, the Sampô green garnet has been shown by both electron microprobe and X-ray fluorescence analyses not to contain tin.

Thus, as far as the genesis of the present malayaite is concerned, its formation would have followed the process 1), that is, it might have been formed by the reaction of calcium, tin and silica at the frontal zone of skarnization, where tin and other volatile constituents such as fluorine, chlorine and boron would have been concentrated.

Iron-copper mineralization at the Sampô mine is considered to have intimate connection with leucocratic biotite-granite belonging to “Central Plutonic Group” of late Cretaceous or early Tertiary age in Southwestern Japan (Yoshida, 1961), and would have begun immediately after the solidification of the intrusive bodies. As mentioned before, the Sampô ore deposits are characterized by the abundance of the minerals rich in volatile constituents within both skarns and orebodies. However, it is a matter for much speculations whether this represents the characteristics of the Sampô ore deposits themselves or represents in common those of the contact-metasomatic deposits related to the magmatism of “Central Plutonic Group” in Southwestern Japan.

Acknowledgements

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岡山県山宝鉱山産マラヤ石について

小川勝美

要 旨

山宝鉱山の鉱・鋼鉱床は、二酸系“中村石灰岩”と中央深成岩群の一員である白亜質雲母花崗岩との境界部で、主として前後に胚芽した典型的な接触交代鉱床である。この鉱鉱物（鉱鉱石）鉱石は最大の0.5重亜パーセントの錂を含み、これがどんな实体鉱物に由来するかは以前から問題にしていた。すでに、今井直哉（1967）はこの点に注目して、この鉱鉱物鉱鉱石、鉱硫化物鉱石およびスカルカム鉱鉱石等を鉱鉱石と定義し、EPMAなどにより時識し、鉱鉱物鉱鉱石のなかに錂石の微粒 (<100 μ) の存在を認めたとともに、単斜鉱鉱石錂石のなかに化学組成からみて、マラヤ石と推定し得る微小鉱物の存在を推定した。つづいて、武内寿久弥・正路徳也（1969）は、この“緑色スカルカム”・ホルンフェルスのなかにマラヤ石が存在することを確認した。しかし、この“山宝マラヤ石”については、その後くわしい研究が行なわれていません現在に至っている。

この論文は、山宝鉱床の生成環境やこのマラヤ石の産状を述べるとともに、その後のEPMA、マイクロプローブX線ディフラクトメーターなどによる研究結果を基礎にしてその鉱物学的諸性質を明らかにし、さらにこの鉱物の成因について言及したものである。このたび、研究の対象としたマラヤ石は、吉木坑9番レベルの“緑色スカルカム”中のもので、単斜錂石・アクチノライト異角閃石・黑鉱の弱木状集合体に伴うものである。その粒子 radius(A)（長径：300 μ）の10点について行なったEPMAによる化学分析の平均値は以下の通りである。

\[ SiO_2 22.22, TiO_2 0.60, SnO_2 56.72, Fe_2O_3 0.05, CaO 20.61, \text{和}100.20(\text{重量パーセント}) \]

これから酸素原子数を5として計算された化学式は\[ Ca_{0.98} (Sn_{1.00} Fe^{2+}_{0.00} Ti_{0.00})_1 O_1 Si_{0.98} O_4 \]となり、マラヤ石の化学基礎の組成に一致。また、そのX線回折パターンに出現する主要な回折線は、5.03Å（35）（011）、3.29Å（20）（200）、3.06Å（35）（002）、2.68Å（>100）（122）、0.31より2.415Å（25）（211）である。そのX線回折データはこれまでに発表されたマラヤ石のそれと良好な一致を示す。

これまでにマラヤ石の成因についてはいくつかの見解が述べられているが、このたびの“山宝マラヤ石”は、恐らく錂やほかの揮発性成分（酸素、塩素など）が濃集したスカルカム化作用の前線帯で、カルシウム、錠および硫黄の反応により形成されたものと考えられる（武内寿久弥・正路徳也、1969; Takenouchi, 1971).