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## SILVER CONTENT AND SILVER MINERALS IN SULPHIDES FROM HYDROTHERMAL DEPOSITS OF SOUTHWESTERN HOKKAIDO

*by*

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(with 2 plates)

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### *Abstract*

In sulphide minerals from hydrothermal deposits the silver content shows generally high value. The distribution of silver was determined by spectroscopic and electron microprobe analysis. Some amount of silver crystallized as silver sulphide mineral in ore deposits. This mineral crystallized generally as pyrargyrite, but it crystallized rarely as miargyrite. The pyrargyrite was not formed by exsolution.

### **Introduction**

In sulphide minerals from "so-called green tuff" area in Hokkaido the silver content shows generally high value. These minerals are predominantly galena and sphalerite. The silver content in these minerals shows less than several hundred ppm in general, but silver in galena reaches rarely several thousand ppm. Yet silver mineral is not always observed under the microscope. It was reported in this paper, that very small grains of silver minerals were observed by electron microprobe analyzer, and determined as pyrargyrite and miargyrite by X-ray powder method.

### **Occurrence of Sulphide Minerals Containing Silver**

The deposits found in Miocene terrain are the main source of copper, lead, zinc and manganese, as well as gold and silver. Most deposits are intimately related to extrusive rocks ranging from andesite to rhyolite. Other deposits are related to acid intrusives.

One of the major mineralization provinces of the inner belt of the Northeast Japan is Southwestern Hokkaido. The deposits occur in various rocks, Miocene shale, sandstone, "so-called green tuff", tuff breccia, andesite,

propylite, and rhyolite.

Important mines of vein type treated in this paper include Jokoku, Ishizaki, Imai-Ishizaki, Tozawa, Yakumo, Inakuraishi, Oye, and Toyoha mines.

Chief ore minerals are predominantly sphalerite, galena, chalcopyrite and rhodochrosite. In some deposits, pyrargyrite, stephanite, polybasite and other silver minerals increase locally. Gangue minerals are invariably quartz with varying amount of carbonates, chlorite, barite and fluorite. Ratio of gangues to ore minerals is highly variable.

In sulphide minerals from hydrothermal deposits the silver content shows generally high value. The veins are divided into two groups according to their structural and mineralogical features. The first group is represented by Pb-Zn veins, and the second group by rhodochrosite veins.

Veins of the first group are formed through earlier mineralization which is characterized by replacement in shear zones along faults and by predominance of quartz among gangue minerals. Main constituent ore minerals are galena, sphalerite, and pyrite with subordinate amounts of silver minerals, chalcopyrite, and hematite.

Veins of the second group are typical fissure-filling veins. They usually show crustified banded structure composed of several nearly monomineralic layers. Besides the above mentioned sulphide minerals, there occur some pyrrhotites in the veins. Rhodochrosite and manganese calcite are the most important gangue minerals.

The silver mineral observed in hand specimens is only pyrargyrite. The pyrargyrite of first group can not be found in earlier stage ores, but occurs in small amount in later stage. That of second group occurs in abundance locally.

### Spectroscopic Analysis

The silver content was analyzed quantitatively by a spectroscope. The number of analyzed minerals is: galena 137; sphalerite 189; and rhodochrosite 74.

According to the results of spectroscopic analysis, the range of the silver content for the galena which crystallized in earlier stage of the first group is around 230 to 65 ppm. Those in the later stage of first and second groups are around 650 to 220 ppm, and 80 to 20 ppm respectively. The range for the sphalerite in the first and second groups are around 220 to 150 ppm, and 75 to 10 ppm respectively. In rhodochrosite silver was scarcely detected. It is concluded that silver content in the first group minerals is more abundant than that in the second group, and that pyrargyrite occurs only in small amount in silver-rich stage, whereas pyrargyrite and other silver minerals occur in

abundance in silver-poor stage.

### Temperature of Formation

An estimation on the temperature of mineral formation was made by measuring homogenization temperatures of fluid inclusions, using a microscope equipped with a heating stage.

Though sphalerite is one of the main constituent minerals of these deposits, fluid inclusions in ore are rather hard to observe. In this study, inclusions in rhodochrosite, quartz and fluorite were used for the measurements, because these minerals are most abundant gangue minerals in the lead-zinc veins and also crystallized almost contemporaneously with main sulphide minerals according to the mode of occurrence.

The result are shown in Figure 1. The number of measured rhodochrosite (hand specimens) is 35 for Ishizaki mine, 11 for Imai-Ishizaki mine, 6 for Tozawa mine, and 113 for Jokoku mine. The number of fluid inclusions measured in each sample is 15 in average. The filling temperature of inclusions in sample is represented by their arithmetical mean.

In the case of the ore deposits of epithermal vein type, the pressure correction on filling temperatures is not so necessary (Yermakov, 1967). Therefore the filling temperature of inclusion itself was assumed as formation

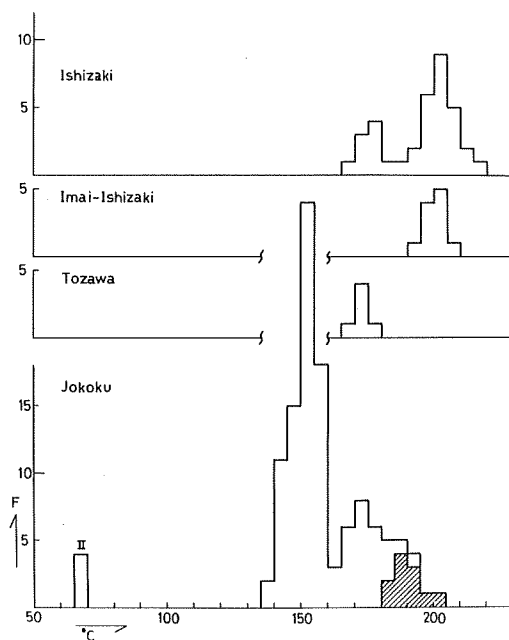


Fig. 1 Temperature frequency diagram on filling temperature of fluid inclusions. Numbers of liquid inclusions observed in each sample are 15 on average. The temperature of each sample is represented by arithmetic mean.

temperature of the minerals in this case.

In a few samples from Jokoku mine, the measurements were carried out on both of co-existing sphalerite and rhodochrosite. Shaded part in Figure 1, shows sphalerite. The maximum filling temperatures were almost same value. Then it can be assumed that the filling temperature of inclusion in rhodochrosite is generally almost the same as that of associated sphalerite, and generally speaking, this temperature represents the temperature of ore deposition of the Jokoku mine.

According to the results of filling temperature measurements, the range of the formation temperature for the main mineralization of the Ishizaki mine is presumed to be around 220°C to 165°C. Those of the Imai-Ishizaki, the Tozawa and the Jokoku mines are around 210°C to 190°C, 180°C to 165°C, and 205°C to 135°C, respectively. Center of frequency of filling temperatures measured for individual mine are about 200°C for the Imai-Ishizaki mine and about 160°C for the Tozawa mine. A bimodal frequency curve with two peaks of 200°C and 170°C was obtained for the Ishizaki mine. Similarly, that with two peaks of 175°C and 150°C was obtained for the Jokoku mine.

Some data reported on the formation temperature of related ore deposits in this area are also shown in Table 1. Formation temperatures of these deposits range from 220°C to 140°C, which is almost the same as that of above-mentioned mines (Nagashima, 1963; Okamura, 1968; Tokunaga, 1970).

### Thermal Experiment

The silver mineral in galena was determined as pyrargyrite under the microscope. Polished samples of this mineral was prepared and heated in nichrome-wound muffle furnace at 200°, 300°, 400°, 450°, 500°, and 550°C for 24 hours. Temperatures were measured by alumel-chromel thermocouples, and errors do not exceed 10°C.

After cooling the sample was observed on polished surface under the microscope. All of the pyrargyrite in galena heated at 200°, 300°, and 400°C remained completely unchanged, while the sample at 450°C was changed slightly and its very small grains was not observed. Finally all pyrargyrite in galena disappeared at 500°C.

From the above-mentioned experiments it is concluded that pyrargyrite is homogenized in galena above ca. 450°C, and that the crystals were formed by exsolution from silver-bearing galena formed at temperatures above 450°C with cooling. But it is possible that pyrargyrite crystallizes by exsolution from galena, because galena-pyrargyrite solid solution is not reported up to the present.

Table 1. Filling temperatures of fluid inclusion in minerals from southwestern Hokkaido.

| Mine                  | Mineral       | Number of samples | Filling temperature (°C) |      |      |
|-----------------------|---------------|-------------------|--------------------------|------|------|
|                       |               |                   | max.                     | min. | mean |
| Inakuraishi *         |               |                   |                          |      |      |
| Earlier-stage ore     | Quartz        | 18                | 238                      | 177  | 199  |
|                       | Sphalerite    | 5                 | 201                      | 154  | 175  |
| Later-stage ore       |               |                   |                          |      |      |
| marginal part of vein | Quartz        | 25                | 180                      | 144  | 164  |
|                       | Barite        | 5                 | 175                      | 152  | 164  |
| central part of vein  | Quartz        | 8                 | 163                      | 126  | 145  |
|                       | Barite        | 5                 | 149                      | 126  | 142  |
| Oye *                 | Rhodochrosite | 5                 | 205                      | 180  |      |
|                       | Quartz        | 30                | 280                      | 143  | 220  |
|                       | Sphalerite    | 50                | 275                      | 160  | 210  |
| Jokoku **             | Sphalerite    | 70                | 250                      | 100  | 150  |
| Toyoha ***            |               |                   |                          |      |      |
| Tajima vein           | Quartz        | 111               | 200                      | 140  | 180  |
| Harima vein           | Quartz        | 28                | 190                      | 135  | 165  |
| Soya vein             | Quartz        | 14                | 180                      | 110  |      |
| Ishizaki              | Rhodochrosite | 35                | 220                      | 165  | 192  |
| Imai-Ishizaki         | Rhodochrosite | 11                | 210                      | 190  | 198  |
| Tozawa                | Rhodochrosite | 6                 | 180                      | 165  | 170  |
| Jokoku                | Rhodochrosite | 113               | 205                      | 135  | 158  |
|                       | Sphalerite    | 11                | 205                      | 180  | 190  |

\* Nagashima, K., (1963)

\*\* Okamura, S., (1969)

\*\*\* Tokunaga, M., (1970)

### Electron Microprobe Analysis

Polished samples of the ore minerals were studied with an electron microprobe to determine the distribution of selected elements, particularly silver, in the minerals. Operating conditions were: 20KV, integrated beam current,  $12 \times 10^{-8}$  amperes referenced to all minerals except for galena to which  $5 \times 10^{-8}$  amperes is referenced. The data show some variations that are inherent in the procedures and materials to be analyzed.

The silver minerals could be identified from 23 samples out of 52 samples examined. The results of electron microprobe analysis are shown in Plates 1 and 2. Large subhedral and long prismatic crystals surrounded by sphalerite are pyrrargyrite (Fig. 1 of Plate 1). It is shown in Fig. 2–6, that silver and antimony

are concentrated in pyrargyrite, but lead and arsenic are absent. Pyrargyrite from Toyoha mine crystallized in contact zone between sphalerite and galena. Both of the above-mentioned two specimens give analogous images in electron microprobe analysis.

Pyrargyrite and miargyrite shown in Plate 2 coexist with galena, and it is shown clearly in Fig. 2 of Plate 2, that distribution of silver in miargyrite is less than that in pyrargyrite. The specimen of this kind was observed only in the galena from the second group veins.

### Determination by X-ray Powder Method

Pyrargyrite and the other silver minerals were observed in polished surfaces of galena and sphalerite by microscopic examination. Moreover, silver content was found variable by the electron microprobe analysis. A silver-rich mineral was determined as pyrargyrite, but other silver-poor mineral was unknown. These silver minerals were determined by X-ray powder method under the following condition: Cu K $\alpha$  35KV, 7mA, scanning speed 1 per minute, and the results are given in Table 2, as compared with the data obtained by Toulmin (1963) and Graham (1951).

The values of  $d(\text{\AA})$  reported here are in good agreement with these of pyrargyrite and miargyrite, but intensity of the latter is not in agreement with the data of Graham, because the former coexists in abundance.

### Conclusion

The following conclusions are drawn from the present study:

(1) The veins in this area are divided into two groups according to the mineralogical features. Veins of the first group are formed during earlier mineralization which is characterized by main ore minerals consisting of galena and sphalerite, with subordinate amounts of pyrargyrite. Veins of the second group usually show abundant rhodochrosite with subordinate amounts of sulphide minerals.

(2) The silver content in earlier stage ores is more abundant than that in later stage ores. Besides, pyrargyrite occurs in small amount in silver-rich stage, but pyrargyrite and miargyrite occur locally in abundance in silver-poor stage.

(3) The range of formation temperature of these deposits is estimated from 220° to 140°C. Therefore, it is not possible that pyrargyrite was formed by exsolution.

(4) Silver mineral in the hydrothermal deposits crystallized generally as pyrargyrite, but rarely it crystallized as miargyrite with decreasing silver

Table 2. X-ray powder data of silver minerals.

| (1)   |     |     | (2)  |    |                    | (3)   |     |              |      |     |
|-------|-----|-----|------|----|--------------------|-------|-----|--------------|------|-----|
| d(Å)  | I   | hkl | d(Å) | I  | hkl                | d(Å)  | I   |              |      |     |
| 3.95  | 20  | 012 | 3.45 | 90 | 211                | 3.96  | 17  |              |      |     |
| 3.34  | 80  | 211 |      |    |                    | 3.45  | 19  |              |      |     |
| 3.22  | 90  | 202 |      |    |                    | 3.32  | 77  |              |      |     |
| 3.18  | 70  | 300 | 3.19 | 20 | 004                | 3.21  | 92  |              |      |     |
|       |     |     |      |    |                    | 3.10  | 20  | 40 $\bar{2}$ | 3.16 | 68  |
|       |     |     |      |    |                    |       |     |              | 2.89 | 100 |
| 2.779 | 100 | 122 | 2.75 | 80 | 402                | 2.77  | 100 |              |      |     |
| 2.566 | 97  | 113 | 2.21 | 5  | 020                | 2.75  | 17  |              |      |     |
| 2.532 | 90  | 131 |      |    |                    | 2.54  | 93  |              |      |     |
| 2.260 | 30  | 312 |      |    |                    | 2.53  | 91  |              |      |     |
| 2.121 | 20  | 104 | 1.96 | 40 | 6 $\bar{1}\bar{1}$ | 2.25  | 32  |              |      |     |
| 2.085 | 10  | 410 |      |    |                    | 2.11  | 22  |              |      |     |
| 1.957 | 50  | 232 |      |    |                    | 2.01  | 8   |              |      |     |
| 1.864 | 30  | 214 | 1.91 | 30 | 40 $\bar{6}$       | 2.07  | 13  |              |      |     |
| 1.838 | 10  | 330 |      |    |                    | 1.95  | 9   |              |      |     |
| 1.751 | 20  | 502 |      |    |                    | 1.90  | 6   |              |      |     |
|       |     |     | 1.80 | 10 | 024                | 1.85  | 27  |              |      |     |
|       |     |     | 1.79 | 20 | 42 $\bar{2}$       | 1.84  | 12  |              |      |     |
| 1.704 | 10  | 413 | 1.71 | 5  | 422                | 1.75  | 23  |              |      |     |
|       |     |     |      |    |                    | 1.68  | 30  | 613          | 1.70 | 8   |
|       |     |     |      |    |                    | 1.669 | 20  | 422          | 1.68 | 37  |
| 1.609 | 20  | 404 | 1.66 | 10 | 406                | 1.663 | 18  |              |      |     |
|       |     |     |      |    |                    | 1.604 | 19  |              |      |     |

(1) Synthetic pyrargyrite (Toulmin 1963).

(2) Miargyrite from Braundorf, Saxony (Graham 1951).

(3) Miargyrite coexisting with pyargyrite from Inakuraishi mine (this paper).

content in mineral solution.

(5) This is the first occurrence of miargyrite in Hokkaido.

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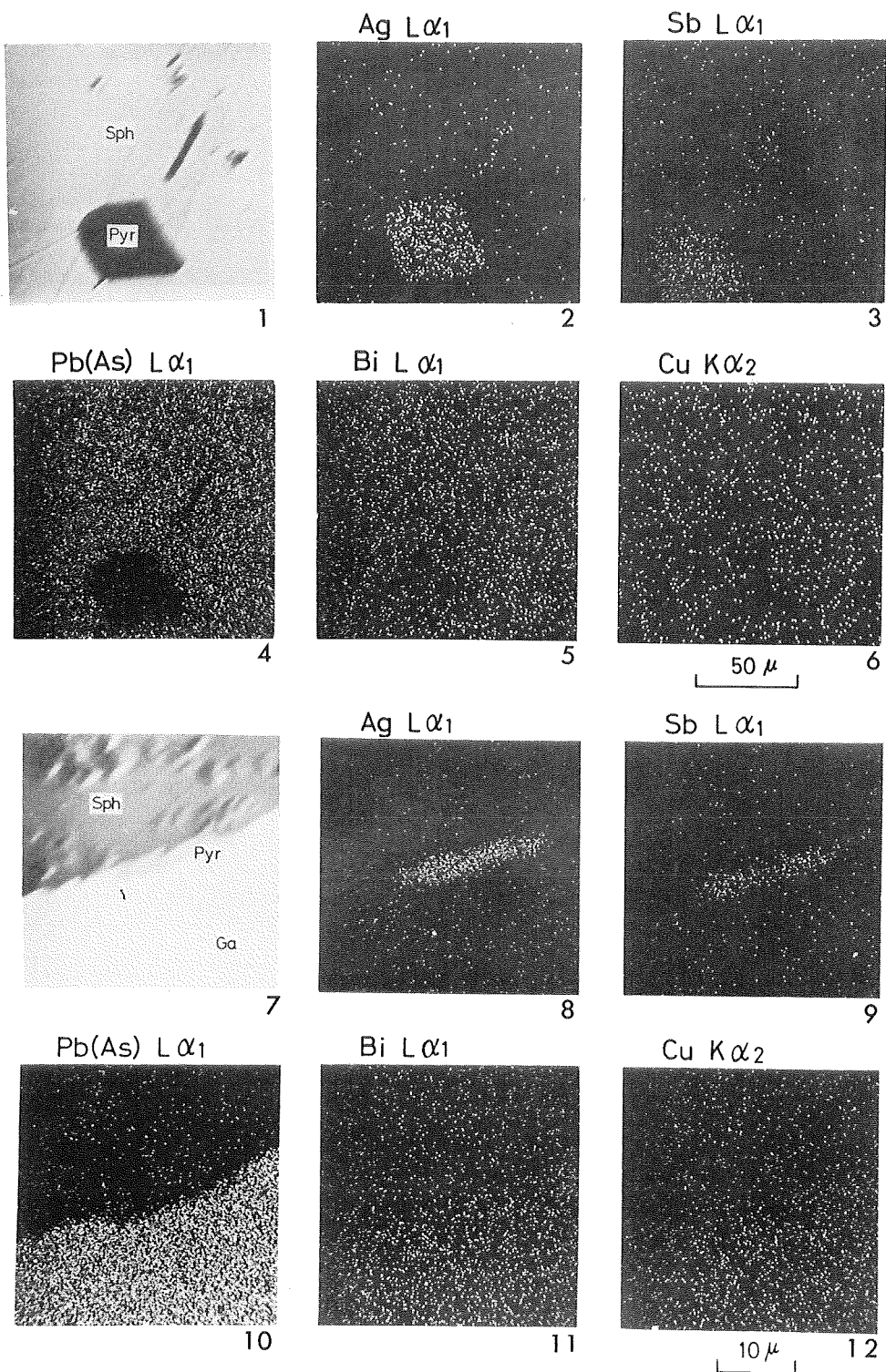
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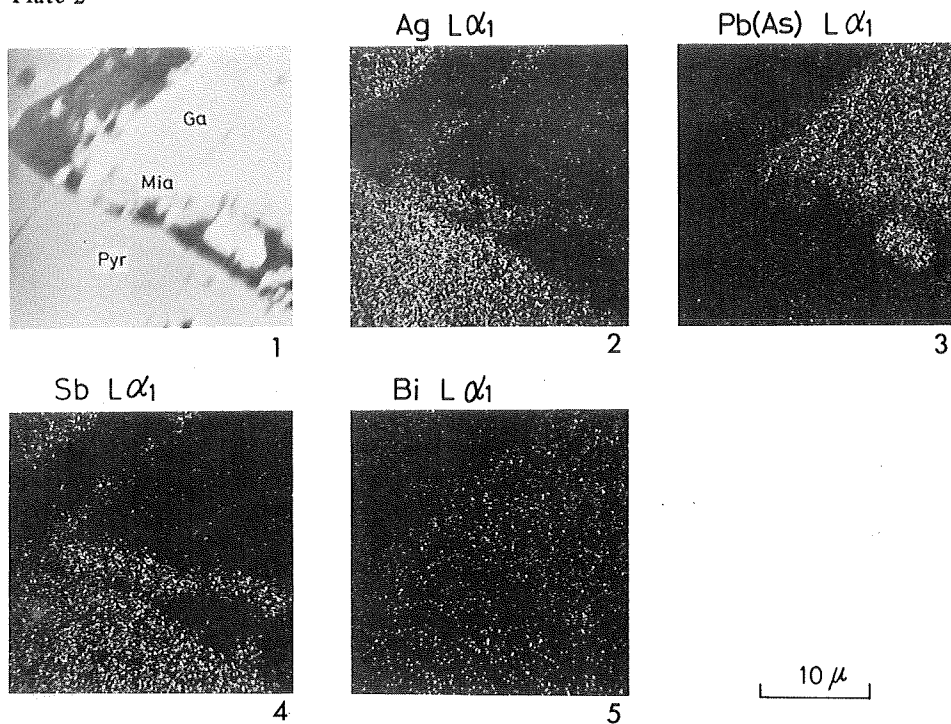
### Explanation of Plate 1

- Fig. 1 Current image of specimen by back scattering beam (pyr, pyrargyrite; Sph, Sphalerite). Pyrargyrite from the Jokoku Mine.  
 Fig. 2 ditto. Characteristic X-ray image showing the distribution of Ag prepared by electron beam scanning. Background scatter shown by randomly distributed points.  
 Fig. 3 ditto. Sb.  
 Fig. 4 ditto. Pb(As).  
 Fig. 5 ditto. Bi.  
 Fig. 6 ditto. Cu.  
 Fig. 7 Current image of specimen by back scattering beam (Ga, Galena; Pyr, Pyrargyrite; Sph, Sphalerite). Pyrargyrite from the Toyoha mine.  
 Fig. 8 ditto. Ag.  
 Fig. 9 ditto. Sb.  
 Fig. 10 ditto. Pb(As).  
 Fig. 11 ditto. Bi.  
 Fig. 12 ditto. Cu.

Plate 1



## Plate 2



## Explanation of Plate 2

**Fig. 1** Current image of specimen by back scattering electron beam (Ga, Galena; Mia, Miargyrite; Pyr, Pyrargyrite). Miargyrite from the Inakuraishi Mine.

**Fig. 2** ditto. Characteristic X-ray image showing the distribution of Ag prepared by electron beam scanning. Background scatter is shown by irregularly distributed points.

**Fig. 3** ditto. Pb(As).

**Fig. 4** ditto. Sb.

**Fig. 5** ditto. Bi.