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# Distribution of Some Minor Elements in Sulfide Ores from the Hitachi Mine, Ibaraki Prefecture, Japan

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The contents of some minor elements in copper-bearing ores from the Fujimi ore deposit No 5, the Hitachi mine, were determined. The selenium content in 46 samples was found to vary from 0.5 to 117 ppm. Though selenium seems to be concentrated in the ores rich in chalcopyrite, that is not always the case, as there are pyrite-rich ores with higher selenium contents than those rich in chalcopyrite. The average value of the atomic ratio of Se/S in the pyrite ores was calculated to be $3.48\times10^{-5}$; this value was larger than those found for the ores from the Minenosawa and the Chichibu mines, and about the same as those found for the ores from the Nakase, the Ashio, and the Hanaoka mines. The variations with depth in the atomic ratios of Se/S and Co/Ni are closely related to each other. The atomic ratio of Se/S increased with an increase in that of Co/Ni. It has been concluded that selenium is concentrated in the pyrite ores of the high-temperature-type rather than in those of the low-temperature-type. The mercury content was small in general, but a large content of mercury was observed at the depth where the values of the atomic ratios of Se/S and Co/Ni were at their maxima.

Several papers about the selenium content in sulfide ores have been published.[1-6] For example, Takimoto and Minato compared the selenium content in sulfide ores from several mines in Japan, and discussed the correlation between the selenium contents and the formation temperatures of the ores.

In the present paper, the distribution of such minor elements as selenium, nickel, cobalt, and mercury in the sulfide ores from the Hitachi mine will be reported.

**Geology of the Hitachi Mine[7] and Sampling of Ores.** Rocks of the paleozoic strata occupy the major part of this region, although igneous rocks lie in the northwestern part, as is shown in Fig. 1. The major part of the paleozoic strata consists of dynamo-metamorphosed greenschist and siliceous schist. Granodiorite intruded upon the paleozoic strata at the northwestern part of this region.

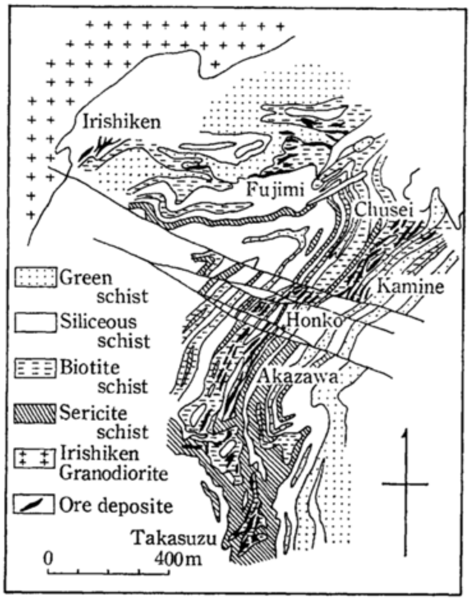

Fig. 1. Geology of Hitachi mine.

The vicinity in contact with this igneous rock suffered thermal metamorphism. The area of the ore deposits is the polymetamorphosed area which suffered both dynamic and thermal metamorphisms.

The ores were obtained from the Fujimi ore deposit No. 5, which suffered a strong thermal metamorphism by the northwestern granodiorite. The samples were obtained at vertical intervals of

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[1] K. Takimoto and T. Minato, *Nippon Kogyo Kaishi (J. Min. Inst. Japan)*, **68**, 405 (1952).

[2] K. Takimoto, T. Minato, T. Okuda and T. Tokita, *Suiyo Kaishi (Trans. Min. Met. Alumni Assoc.)*, **12**, 287 (1954).

[3] K. Takimoto, T. Minato and S. Hirono, *Ganseki Kobutsu Koshogakkaishi (J. Japanese Assoc. Min. Petr. Econ. Geol.)*, **42**, 161 (1958).

[4] T. Minato, *Suiyo Kaishi (Trans. Min. Met. Alumni Assoc.)*, **14**, 301 (1961).

[5] K. Takimoto and T. Minato, *Kozan Chishitsu (Min. Geol.)*, **11**, 331 (1961).

[6] T. Shirai, S. Hamada, H. Takahashi and I. Saruyama, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 196 (1965).

[7] Section of Exploration of the Hitachi Mine, *Kozan Chishitsu (Min. Geol.)*, **12**, 1 (1962).

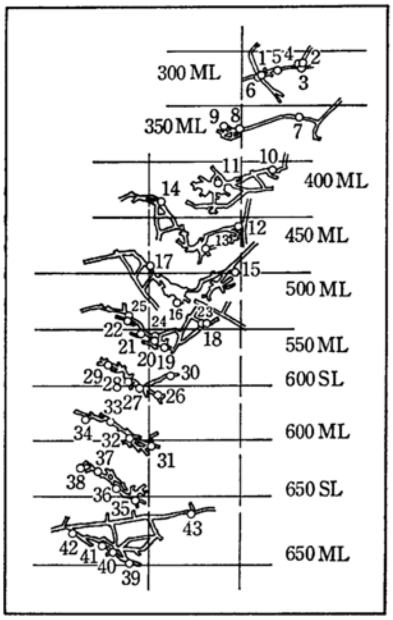

Fig. 2. Locality of ores at Fujimi ore deposit No. 5.

fifty or twenty-five meters over the range from 300 ML to 650 ML.*1 The sampling points are shown in Fig. 2. The ores mainly consisted of intimate aggregates of fine crystals of pyrite. Some of these contained chalcopyrite, pyrrhotite, and other materials. The pyrite ore was separated visually from the crushed sample, and the chalcopyrite ore, from the chalcopyrite-rich sample.

## Experimental

**Determination of Selenium.** The selenium content was estimated by the colorimetric method using 3,3′-diaminobenzidine, as has been described in a previous paper.6)

**Determination of Sulfur.** The sulfur content was estimated by the combustion method of JIS K 1331.

**Determination of Metals.** The iron content was estimated as ferric oxide by the usual gravimetric method. The copper content was estimated as cuprous thiocyanate by the gravimetric method for the high-copper-content ore, and by the polarographic method for the low-copper-content ore. The nickel, cobalt, and mercury contents were estimated by the colorimetric method as nickel dimethylglyoximate,8) as the cobalt complex of Nitroso R salt,9) and as mercury dithizonate10-12) respectively.

## Results

The amounts and the atomic ratios of the several elements in the ores are listed in Table 1.

The selenium content in 46 samples was found to range from 0.5 to 117 ppm. The atomic ratio of Se/S in the chalcopyrite-rich ores was larger than that in the chalcopyrite-poor ores when the respective ores were separated from samples obtained at the same point. However, selenium can not be said to be always concentrated in the chalcopyrite-rich ores, because a higher content of selenium was observed in the pyrite-rich ores than in the chalcopyrite-rich ores.

**The Contents of Nickel and Cobalt.** The nickel content in the pyrite ores was usually about 10—50 ppm. The nickel content was lower than those in the pyrite ores from the Daikoku ore deposit, the Chichibu mine (20—110 ppm, 26 samples), and the Okutomi, the Taisho and the Himi ore deposits, the Tsushu mine (20—100 ppm, 7 samples), and was similar to that from the Kajika ore deposit, the Ashio mine (20—50 ppm, 6 samples).13)

The cobalt content in the pyrite ores was estimated to range from 0.0 to 654 ppm. Unlike the nickel content in the ores, a wide fluctuation of the cobalt content was observed. The cobalt content in the pyrite ores was larger than in those from the Chichibu and the Tsushu mines (10—200 ppm and 20—150 ppm, respectively), and was quite large compared with that from the Ashio mine (10—30 ppm).

**The Mercury Content.** The mercury content in the ores was estimated to range from 0.0 to 176 ppm. No correlation could be found between the contents of copper and mercury.

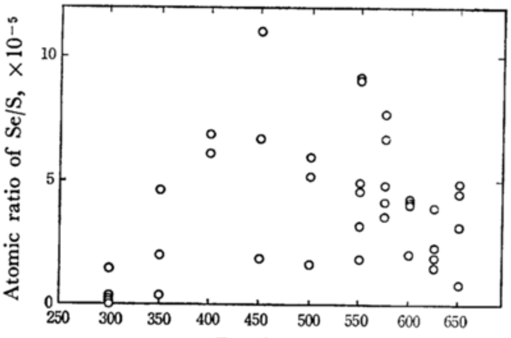

Fig. 3. Plot of atomic ratio of Se/S in pyrite ores against depth.

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*1 The symbol "ML (meter level)" is the depth measured from the base level of the Hitachi mine, 350 m above sea level. The symbol "SL (sublevel)" is 25 m above each ML.

8) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Interscience Publishers, New York (1959), p. 665.

9) *Ibid.*, p. 409.

10) H. Irving, G. Andrew and E. J. Risdon, *J. Chem. Soc.*, **1949**, 537.

11) S. Uehara and S. Hamada, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **63**, 1580 (1960).

12) T. Kato, N. Takei and A. Okaue, *Japan Analyst*, **5**, 689 (1956).

13) K. Takimoto, T. Minato and S. Hirono, *Ganseki Kobutsu Koshogakkaishi (J. Japanese Assoc. Min. Petr. Econ. Geol.)*, **50**, 118 (1963).

TABLE 1. CHEMICAL COMPOSITION OF SULFIDE ORES

| Sampling point | Level | Cu % | Fe % | S % | Se ppm | Zn % | Ni ppm | Co ppm | Hg ppm | Se/S $\times 10^{-5}$ | Co/Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 300 ML | 12.82 | 34.91 | 35.94 | 2.9 | 2.88 | 20.8 | 49.7 | 0.3 | 0.327 | 2.38 |
| 2 | 300 ML | tr. | 48.59 | 49.25 | 0.5 | 0.83 | 33.6 | 30.8 | 0.0 | 0.04 | 0.91 |
| 3 | 300 ML | 8.44 | 44.79 | 43.14 | 14.6 | 3.86 | 28.6 | 89.7 | 2.2 | 1.38 | 3.12 |
| 4 | 300 ML | 0.046 | 47.83 | 48.02 | 3.1 | 1.75 | 22.6 | 8.1 | 0.0 | 0.262 | 0.36 |
| 5 | 300 ML | 0.040 | 47.53 | 47.72 | 2.1 | 1.21 | 14.0 | 3.0 | 0.0 | 0.178 | 0.21 |
| 6 | 300 ML | 2.14 | 47.13 | 46.61 | 16.2 | 2.41 | 24.4 | 1.2 | 19.7 | 1.41 | 0.05 |
| 7 | 350 ML | 0.79 | 35.90 | 30.26 | 34.6 | 0.05 | 5.5 | 1.8 | 1.4 | 4.64 | 0.33 |
| 8 | 350 ML | 0.077 | 45.59 | 45.26 | 4.5 | 2.94 | 12.2 | 1.8 | 5.3 | 0.404 | 0.15 |
| 9 | 350 ML | 1.82 | 43.93 | 42.59 | 21.2 | 1.53 | 39.8 | 9.6 | 85.1 | 2.02 | 0.24 |
| 10 | 400 ML | 0.10 | 49.16 | 47.76 | 81.1 | tr. | 17.3 | 297.0 | 9.1 | 6.89 | 17.1 |
| 11 | 400 ML | 1.61 | 46.19 | 45.65 | 69.0 | 0.19 | 10.3 | 96.3 | 55.0 | 6.14 | 9.34 |
| 12 | 450 ML | 1.87 | 45.11 | 43.07 | 116.6 | 0.07 | 9.0 | 445.3 | 112.8 | 11.0 | 49.4 |
| 13 | 450 ML | 0.80 | 46.43 | 48.48 | 80.4 | 0.04 | 10.6 | 72.6 | 137.7 | 6.72 | 6.81 |
| 14 | 450 ML | 0.013 | 46.49 | 44.67 | 20.9 | 0.37 | 20.0 | 70.0 | 2.0 | 1.90 | 0.54 |
| 15 | 500 ML | 0.11 | 49.98 | 47.89 | 70.5 | 0.42 | 10.1 | 220.9 | 8.1 | 5.98 | 21.8 |
| 16-1 | 500 ML | 3.28 | 46.35 | 43.52 | 18.0 | 0.21 | 48.3 | 97.7 | 10.6 | 1.68 | 2.02 |
| 16-2 | 500 ML | 28.10 | 34.27 | 30.88 | 38.2 | 0.89 | 16.0 | 0.0 | 9.4 | 5.02 | 0.0 |
| 17 | 500 ML | 2.73 | 46.10 | 40.25 | 51.8 | 0.12 | 43.2 | 73.5 | 176.2 | 5.22 | 1.69 |
| 18 | 500 ML | 25.66 | 33.86 | 33.22 | 13.0 | 1.05 | 23.1 | 4.98 | 9.4 | 1.59 | 0.22 |
| 19 | 550 ML | 27.82 | 34.69 | 33.23 | 44.3 | 0.71 | 14.7 | 6.18 | 12.4 | 5.42 | 0.42 |
| 20 | 550 ML | 2.53 | 46.95 | 47.50 | 22.1 | 0.23 | 28.3 | 48.2 | 2.1 | 1.89 | 1.70 |
| 21 | 550 ML | 1.58 | 47.77 | 49.64 | 39.5 | 0.16 | 31.3 | 103.4 | 0.0 | 3.23 | 3.29 |
| 22 | 550 ML | 1.80 | 47.84 | 49.38 | 60.3 | 0.09 | 53.8 | 130.6 | 40.0 | 4.96 | 2.42 |
| 23 | 550 ML | 0.058 | 45.87 | 47.33 | 107.1 | 0.03 | 1.8 | 422.4 | 7.0 | 9.19 | 231 |
| 24 | 550 ML | 5.00 | 44.62 | 46.91 | 105.7 | 0.04 | 26.0 | 113.3 | 9.0 | 9.15 | 4.34 |
| 25 | 550 ML | 0.90 | 46.84 | 50.45 | 57.3 | 0.02 | 25.0 | 49.4 | 2.0 | 4.61 | 1.97 |
| 26 | 600 SL | 0.78 | 46.25 | 49.73 | 82.6 | tr. | 32.5 | 138.8 | 3.8 | 6.74 | 4.25 |
| 27 | 600 SL | 0.67 | 47.83 | 50.48 | 60.3 | 0.06 | 15.9 | 142.1 | 2.6 | 4.85 | 8.90 |
| 28 | 600 SL | 1.37 | 49.24 | 49.60 | 43.7 | 0.01 | 27.9 | 118.6 | 2.2 | 3.58 | 4.24 |
| 29 | 600 SL | 0.45 | 47.75 | 51.45 | 52.8 | tr. | 12.5 | 98.9 | 11.1 | 4.17 | 7.88 |
| 30 | 600 SL | 0.09 | 46.91 | 49.45 | 94.3 | tr. | 19.4 | 147.7 | 0.0 | 7.74 | 7.58 |
| 31-1 | 600 ML | 0.68 | 48.36 | 50.10 | 51.4 | 0.33 | 35.3 | 58.9 | 3.4 | 4.17 | 1.66 |
| 31-2 | 600 ML | 7.19 | 39.48 | 39.27 | 81.3 | 2.42 | 20.2 | 40.0 | 40.4 | 8.41 | 1.97 |
| 32 | 600 ML | 0.89 | 48.73 | 48.16 | 24.4 | 0.13 | 20.1 | 83.4 | 1.4 | 2.06 | 4.13 |
| 33 | 600 ML | 0.26 | 48.06 | 50.20 | 52.1 | tr. | 16.1 | 64.2 | 4.0 | 4.15 | 3.97 |
| 34 | 600 ML | 0.41 | 47.83 | 48.96 | 50.7 | tr. | 34.7 | 119.3 | 2.1 | 4.20 | 3.42 |
| 35 | 650 SL | 0.38 | 46.69 | 49.11 | 28.4 | 0.02 | 19.8 | 68.4 | 2.5 | 2.35 | 3.44 |
| 36 | 650 SL | 0.53 | 46.77 | 49.78 | 23.4 | 0.04 | 25.2 | 76.7 | 1.5 | 1.91 | 3.03 |
| 37 | 650 SL | 0.40 | 45.18 | 48.67 | 47.0 | tr. | 22.5 | 74.8 | 1.8 | 3.92 | 3.31 |
| 38-1 | 650 SL | 0.98 | 47.97 | 47.87 | 17.8 | 0.03 | 33.7 | 91.5 | 4.0 | 1.51 | 2.70 |
| 38-2 | 650 SL | 29.07 | 36.05 | 33.49 | 36.5 | 1.26 | 16.6 | 76.6 | 8.9 | 4.42 | 4.60 |
| 39 | 650 ML | 1.29 | 47.97 | 47.34 | 36.5 | 0.28 | 26.4 | 75.1 | 7.6 | 3.13 | 2.83 |
| 40 | 650 ML | 0.74 | 49.26 | 48.59 | 53.8 | 0.02 | 24.8 | 95.7 | 2.8 | 4.50 | 3.84 |
| 41 | 650 ML | 0.78 | 49.75 | 49.57 | 59.9 | 0.02 | 38.3 | 141.4 | 5.9 | 4.91 | 3.68 |
| 42 | 650 ML | 27.84 | 34.93 | 33.14 | 49.8 | 0.56 | 26.2 | 12.2 | 14.1 | 3.49 | 0.46 |
| 43 | 650 ML | 0.01 | 48.81 | 48.44 | 10.2 | 1.33 | 20.4 | 8.5 | 2.8 | 0.854 | 0.41 |

**The Relationship between the Depth and the Atomic Ratio of Se/S.** The atomic ratio of Se/S in the pyrite ores changed within the range from $4\times 10^{-7}$ to $1.10\times 10^{-4}$. The atomic ratio of Se/S in the pyrite ores was correlative with the depth within the range from 300 ML to 650 ML, as is shown in Fig. 3. The atomic ratios of Se/S at 300 ML were quite small, but the ratio increased with an increase in the depth, the maximum appearing at the depth of 450 ML—550 ML.

**The Relationship between the Depth and the Atomic Ratio of Co/Ni.** Figure 4 shows the relationship between the depth and the atomic ratio of Co/Ni. The values of the atomic ratio of Co/Ni were small at the upper part of the ore deposit, but they increased with an increase in the depth. The maximum appeared at the depths from 450 ML to 550 ML, as with the atomic ratio of Se/S. Increases in the atomic ratio of Co/Ni with an increase in the depth were observed at the Chichibu mine (within the range of 120 m), the Tsushu mine (within the range of 150 m), and the Ashio mine (within the range of 100 m). The atomic ratio of Se/S in the pyrite ores increased with an increase in that of Co/Ni, as is shown in Fig. 5. The coefficient of the correlation of Fig. 5 is 0.70; therefore, the correlation is significant.

**The Relationship between the Depth and the Mercury Content.** The mercury content is generally very small, but quite a large content of mercury was observed at the depth of 450 ML—550 ML, in which range the maxima of the atomic ratios of Se/S and Co/Ni appeared, as is shown in Fig. 6.

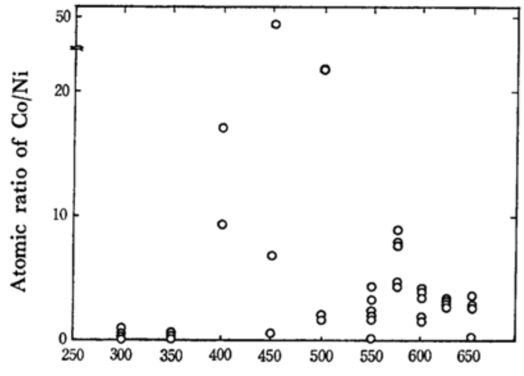

Fig. 4. Plot of atomic ratio of Co/Ni in pyrite ores against depth.

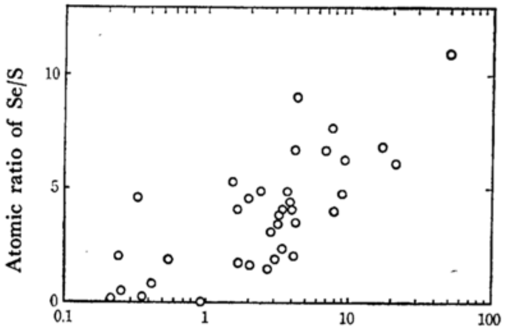

Fig. 5. Plot of atomic ratio of Se/S against atomic ratio of Co/Ni.

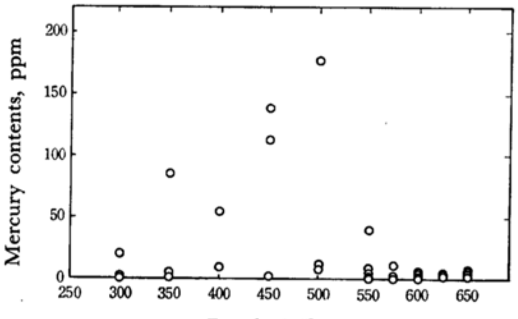

Fig. 6. Plot of mercury content in pyrite ores against depth.

## Discussion

The atomic ratios of Se/S and Co/Ni are found to vary with the depth in the same manner at the Fujimi ore deposit No 5. This suggests that a certain correlation between the atomic ratios of Se/S and Co/Ni should exist. Carstens[14] reported that cobalt was concentrated in the pyrite ores of the high-temperature-type rather than in those of the low-temperature-type, and large values of the atomic ratio of Co/Ni were observed when the ore deposits were formed by the hydrothermal process. Hawley[15] described how large values of the atomic ratio of Co/Ni were observed in the pyrite ores of high formation temperatures when several pyrite ores of known formation temperatures were examined. Hegeman[16] stated that the values of the atomic ratio of Co/Ni became larger as the degree of metamorphism rises. The values of the atomic ratio of Co/Ni in the pyrite ores of the high-temperature-type from the lower part of the Daikoku ore deposit, the Chichibu mine, which is of contact-metasomatic origin (2.7—6.5), were larger than those of the low-temperature-type from the upper part of the ore deposit, which is of hydrothermal origin (0.2—1.6).[13] The formation or metamorphism temperatures of the lower part of the Fujimi ore deposit No. 5 were probably higher than those of the upper part, because the vertical distribution of the atomic ratio of Co/Ni showed a dependence on the depth. This is supported by the fact that sphalerite of the low-temperature-type exists in the upper part of the ore body and chalcopyrite of the high-temperature-type, in the lower part. Therefore, it may be considered that selenium is concentrated in the pyrite ores of the high-temperature-type rather than in those of the low-temperature-type; this conclusion agrees with Takimoto's results.[2,5]

Krauskopf[17] reported that mercury in vein fluid was transported as mercuric chloride or as free mercury and free sulfur in a high-temperature gas phase. In both case, merucry should be concentrated in the low-temperature-type ores. Therefore, the vertical distribution of mercury is

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[14] C. W. Carstens, *Kgl. Norske Videnskabs Selskabs Forh.*, **15**, 165 (1942).

[15] J. E. Hawley, *Econ. Geol.* **47**, 260 (1952).

[16] F. Hegeman, *Z. angew. Mineral*, **4**, 122 (1941).

[17] K. B. Krauskopf, *Econ. Geol.*, **46**, 498 (1951).

contradictory to that of the atomic ratios of Se/S and Co/Ni on the temperature-type of the ores. This discrepancy has not yet been solved, because it is not evident whether the present distributions of selenium, cobalt, and nickel in pyrite ores at the Fujimi ore deposit were formed at the same time with that of mercury or not.

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