

Studies on the Minor Elements in Ore Minerals

By

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1. Introduction

For these several years, the authors^{1,2)} have been studying on the relation between the constitution of minor elements and the genetic circumstance of the minerals that exist in the sulphide deposits in Japan.

Now, as a part of our study, the aspect of concentration of minor constituents incorporated in sphalerites taken from the Tochibora deposit, the so-called contact pyrometasomatic deposit, of the Kamioka Mine was studied and, based upon the result obtained, an attempt was made to estimate the formation temperature of the deposit and thereby deduce the process of the mineralization.

Although many valuable papers concerning this deposit have already been published by several authors such as Watanabe³⁾, Iwafune⁴⁾, and Nishio⁵⁾ and his co-workers, but the report on study of this deposit made from the standpoints of minor elements contained in ore minerals seems to be very few.

Therefore, the present authors have undertaken the study on the mineralization of this deposit from the above mentioned standpoints which have hitherto been scarcely tried by others.

2. Occurrence of Sample

(A) General Statement of the Deposit

According to the early worker⁶⁾, there are two types of deposit, the so-called "Mokuji" and "Shiroji", in this district. Namely, the first type is a contact pyrometasomatic replacement deposit replacing the beds of limestone laid in gneiss series, and it consists mainly of various skarn minerals such as hedenbergite, etc. together with lead-zinc ore minerals. The second type is a mesothermal replacement deposit replacing the remnant layers of crystalline limestone which could not be completely mineralized at the stages of the Mokuji formation, or replacing some parts of the above mentioned skarn zone, and it consists of high grade lead-zinc ore minerals. Moreover, the latter is characterized by a highly developed druse contained in it and also by the association of a great deal of both quartz and calcite, as gangue minerals.

These two types of deposit have various forms of occurrence, however, they can be summarized as follows:

1. Both types of deposit are formed without any mutual relations in the area.
2. The Shiroji deposit is formed in small scale in the outer regions of the Mokuji deposit.
3. The Shiroji deposit is formed intruding frequently into the Mokuji deposit in a ore-pocket-like manner or cutting the Mokuji in veinlets.

(B) Collection of Sample

Twenty-two samples of sphalerite ore have been collected at the -200 M level of the No. 9 ore body of the Tochibora deposit where the operation is at present well advanced and the condition of the deposit is well known. The position from where the specimens were collected is shown in Fig. 1. These specimens were taken from

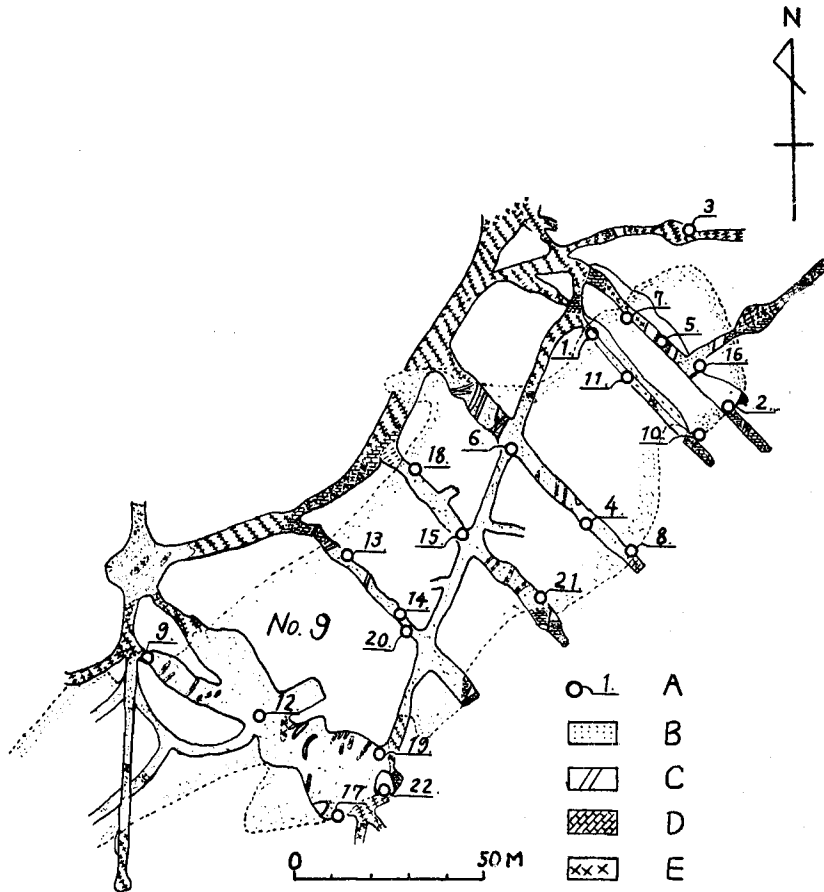


Fig. 1. Geological map of the -200 M level, Tochibora deposit, Kamioka Mine.
 A : Sample number, B : Mokuji deposit, C : Shiroji deposit,
 D : Limestone, E : Gneiss.

horizontal positions with due consideration to their geological environments.

Some part of the study on the vertical variation (change with depth) of minor elements of sphalerites in the No. 9 ore body of the Tochibora has been made public by TAKIMOTO, the co-author, at the Fukuoka Meeting of the Mining Institute of Japan in November 1954.

3. General Property of Sample

(A) Visual Observation

Among the twenty-two samples, six are from the Shiroji ore, and the rest all from the Mokuji ore.

As previously described, the Mokuji ore generally consists of massive aggregates of both sphalerite and galena replacing various skarn minerals. However, their external appearances are not always alike because of the relative quantity and the variety of the skarn minerals contained, the degree of ore grade, and the difference of grain size of both ore minerals and gangue minerals.

For example, there is, on one hand, a very low grade ore which contains a very small quantity of fine-grained sphalerites (less than 1 mm dia.) and a very high grade ore, such as containing a massive aggregate of coarse-grained sphalerites (from about 2 to 5 mm dia.), which scarcely comprises of any other gangue minerals.

Ore specimens are also varying in color according to their mineral associations; that is, their colors vary from light green to dark green and occasionally blackish. Hedenbergite is usually formed in fibrous or radial aggregates and is the most common among the skarn minerals, and the length of the crystal in direction of c-axis is also ranging from 1 to 10 mm.

Also, among these ores, some of them are extremely hardened by silicification and some are extremely softened by carbonization.

The Shiroji ore consists of sphalerite-galena-aggregates together with a large quantity of quartz and calcite gangue minerals, and this ore is generally higher in grade compared with the Mokuji ores, and the content of galena, especially, seems to be greater. Grain size of the ore mineral ranges from less than 1 mm up to about 5 mm dia. as in the case of the Mokuji ores.

As the Shiroji ores contain invariably much quartz and calcite, the color of it generally varies from gray to dark gray and is lighter than that of the Mokuji ores.

The above mineralogical observations of these specimens — mineral composition, textural feature of ore, and also degree of ore grade, etc.— are summarized in Table 1.

(B) Microscopic Examination

In order to determine both the mineralogical properties and the order of the forma-

Table 1. Ore grade and mineral composition of sphalerite ore.

Sample	Grain size of sphalerite	Ore grade		Main component mineral	Accessory mineral	Inclusions in sphalerite	
		Zn (%)	Pb (%)			Chalcopyrite	Galena
k 1 (M)	s	10.56		Zn	Ga, Po		
k 2 (S)	m	37.09	14.25	Zn, Ga	Py		
k 3 (M)	f	7.96	6.25	Zn, Ga			
k 4 (")	m	14.53		Zn	Ga, M		
k 5 (")	m	18.43		Zn	Ga, M, Po		few
k 6 (")	f	13.34		Zn	Ga		
k 7 (")	f	16.27		Zn	Po		
k 8 (S)	m	16.00	36.51	Zn, Ga			
k 9 (M)	s	12.82		Zn	Ga, Po		
k10 (S)	m	26.75	4.83	Zn, Ga	Cpy	few	
k11 (M)	c	18.98		Zn	Ga, M		
k12 (")	s	14.76		Zn	Ga, M, Po		
k13 (")	f	32.47	4.84	Zn, Ga	Ga, Cpy	numerous	
k14 (S)	m	31.35		Zn	Ga, Po		
k15 (M)	m	19.05		Zn	Ga, M, Cpy	few	few
k16 (S)	m	27.13	19.02	Zn, Ga	Cpy	few	few
k17 (M)	c	23.09		Zn	Ga, M, Cpy, Py	numerous	numerous
k18 (")	s	13.34		Zn	Ga, Po	few	
k19 (")	s	7.33		Zn	Ga, Po		
k20 (")	m	10.08		Zn	Ga, Po		
k21 (")	c	50.19		Zn	Ga, Po		numerous
k22 (S)	s	52.81		Zn	Ga		

Zn: sphalerite, Ga: galena, M: magnetite, Cpy: chalcopryrite, Py: pyrite, Po: pyrrotite.
 f: fine grain, s: small grain, m: medium grain, c: coarse grain. (M): Mokuji ore,
 (S): Shiroji ore.

tion of these minerals, a microscopic examination was carried out on the polished section of every specimen.

Among all the minerals contained, both sphalerite and galena are usually predominant and they seem to be formed in the earliest stage. These minerals are usually replaced in irregular forms or intruded in veinlets by small amounts of the accessory

minerals such as magnetite, hematite, pyrite, pyrrhotite, and chalcopyrite, etc.

Regarding the relation of sphalerite to galena, although it can be recognized in some specimens that the former is formed somewhat earlier than the latter, they are in many cases assumed to have been deposited during the same period.

Furthermore, on examining these polished sections under a high-powered microscope, we can find minute inclusions of grain or string shape occasionally contained

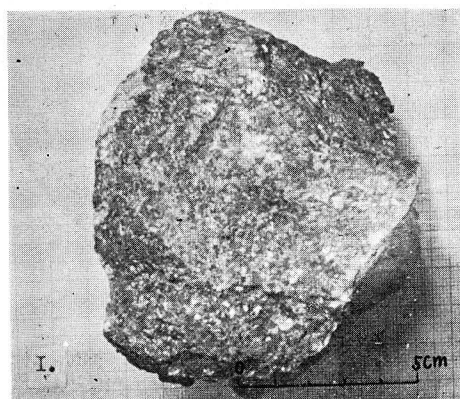


Photo 1. Hand specimen of sphalerite ore from the Mokuji deposit, Tochibora. White—light gray, sphalerite; dark gray, skarn minerals (aggregates of hedenbergite and epidote etc.).

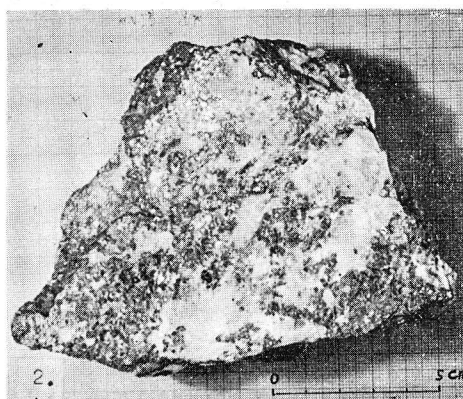


Photo 2. Hand specimen of sphalerite ore from the Shiroji deposit, Tochibora. Grayish white, gangue minerals (quartz and calcite).

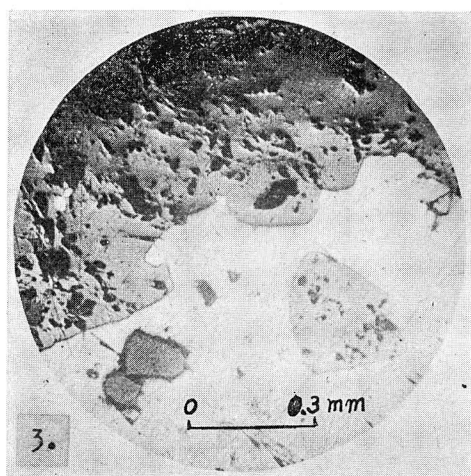


Photo 3. Photomicrograph of polished section showing the relations between sphalerite and galena. Small grains of sphalerite (light gray) are included in galena (white) "island" in the large field of sphalerite. Shiroji ore, Tochibora.

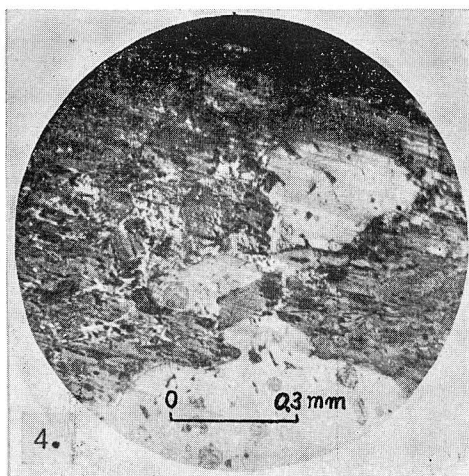


Photo 4. Photomicrograph of polished section. Arachnid magnetite (white, centre) that has replaced skarn minerals (hedenbergite, gray) and also sphalerites (light gray). Mokuji ore, Tochibora.

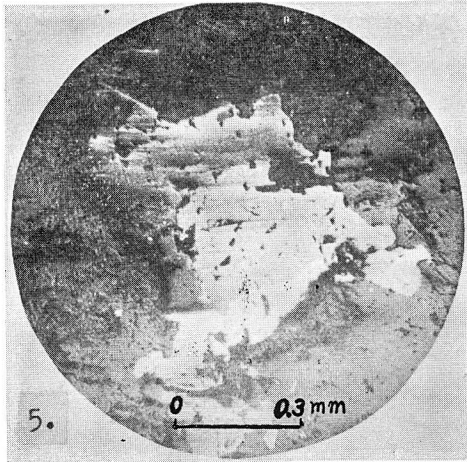


Photo 5. Photomicrograph of polished section. Chalcopyrite (white) replacing sphaerite grains (light gray). Surrounding dark area, skarn mineral. Mokuji ore, Tochibora.

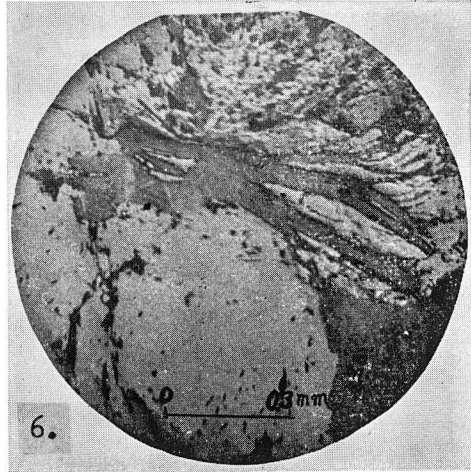


Photo 6. Photomicrograph of polished section showing the usual relations between sphaerite and pyrrhotite. Sphaerite is penetrated by pyrrhotite veins. Upper unsmooth surface area is showing the replacement of sphaerite by magnetite. Right below dark part, gangue mineral. Mokuji ore, Tochibora.

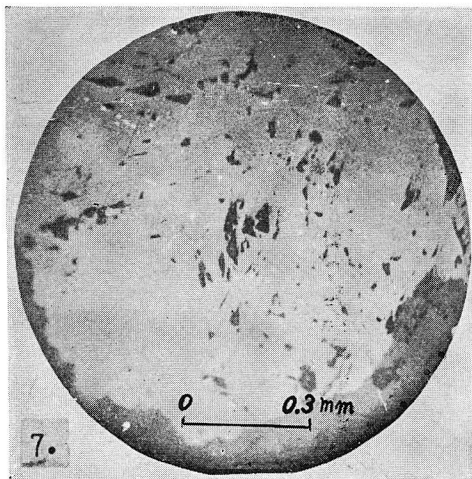


Photo 7. Photomicrograph of polished section. Chalcopyrite within sphaerite occurs as unmixings. Clear dark part below, gangue mineral; black patches are holes in the section. Mokuji ore, Tochibora.

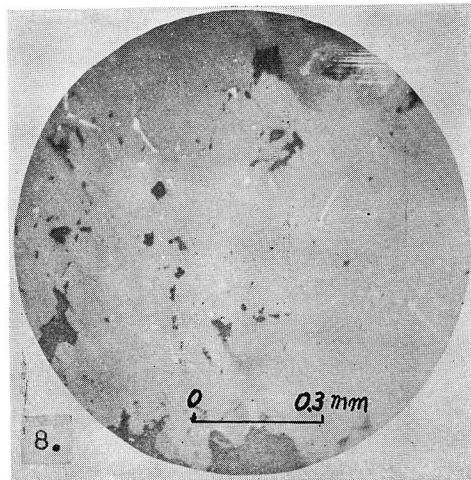


Photo 8. Photomicrograph of polished section. Galena within sphaerite occurs as unmixing units. Clear dark part, gangue mineral. Mokuji ore, Tochibora.

in sphalerite crystals. According to the early workers, these minute inclusions, consisting mainly of chalcopyrite, are interpreted as the results of unmixing.

Further, it is said that the higher the temperature of formation of sphalerite, the greater is the chance of solution components.

Actually, the authors in the present examinations on their polished sections have found that the minute inclusions observed in each section are not uniform. Citing Graton's⁷⁾ words; Some are "large and numerous", and some are "small and few."

The authors, therefore, attempted to utilize these facts for our purposes — to deduce the formation temperature of sphalerites which is described in the following chapters. The results obtained from microscopic study are given in Table 1 and Photos 1-8.

4. Spectrographic Analysis

In order to determine qualitatively the range of concentration of minor components in sphalerites, a spectrographic study was conducted on these specimens.

Firstly, pure sphalerites were separated carefully from other visual minerals with the aid of a magnifier and then they were ground in an agate-mortar until all grains passed 200 mesh. About 5 milligram of the samples were placed in the lower, or positive, graphite electrode. Next, arc spectra of each sample were recorded on the Fuji Process spectrographic plate, which had the useful range of from 2000 to 4000 Å., using the Shimazu QM-60 Type Quartz Medium Spectrograph. Throughout the experiments, analysis was carried out under the same conditions as follows:

Time: 20 sec. + 10 sec.

Current: DC arc 4-4.5 A—110 V

Gap and Slit: 3 mm—3/100 mm

Results obtained from the analysis are listed in Table 2. Number of tested specimens in this experiment was fourteen in all; that is, twelve sphalerites and two galenas. Of the other specimens, the spectrograph was not applied this time because separation of impurities was rather difficult and we could not obtain pure ones which were appropriate for the spectrographic analysis.

Judging from the results obtained, the following points were deduced; namely, 1-8:

1. Si, Al, Ca, and Mg are always detected in almost all the samples.
2. Ge, Ga, and In are known to exist in hydrothermal sphalerites in various districts but none of them was detected in the present examinations.
3. Sb, Sn, and As were not found either in any samples except in one or two of them.
4. Ag, and Bi were mainly contained in galena. According to the informations by Shiobara⁸⁾ that the several Ag and/or Bi bearing independent minerals, such as native silver, native bismuth, argentite, and matildite, etc., have been found microscopically on some polished sections of galenas taken from this deposit and these two specimens might have been of the same category.

Table 2. Spectrographs of sphalerite and galena.

Sample	Element	Pb	Bi	Ag	Ca	Cd	Cu	In	Mn	Sb	Fe	Zn	Mg	Sn	As	Ga	Al	Ge	Si
Sphalerite	k 1	tr.	min. tr.	±	min. tr.	min. tr.	tr.	-	tr.	-	+	≡	tr.	±	±	-	±	-	≡
	k 4	tr.	-	±	min. tr.	min. tr.	min. tr.	-	tr.	-	+	≡	tr.	±	±	-	±	-	+
	k 7	tr.	min. tr.	min. tr.	±	min. tr.	tr.	-	tr.	-	+	≡	tr.	±	±	-	-	-	≡
	k 9	tr.	min. tr.	min. tr.	min. tr.	min. tr.	+	-	tr.	-	+	≡	tr.	±	±	-	±	-	+
	k11	min. tr.	-	-	min. tr.	min. tr.	tr.	-	tr.	-	+	≡	tr.	±	±	-	±	-	+
	k13	+	tr.	tr.	min. tr.	min. tr.	+	-	tr.	-	+	≡	tr.	±	±	-	±	-	+
	k14	tr.	min. tr.	min. tr.	-	min. tr.	+	-	tr.	-	+	≡	tr.	±	min. tr.	-	-	-	≡
	k17	tr.	tr.	min. tr.	min. tr.	min. tr.	+	-	tr.	-	+	≡	tr.	±	±	-	tr.	-	+
	k18	tr.	tr.	tr.	min. tr.	min. tr.	tr.	-	tr.	-	+	≡	tr.	±	±	-	tr.	-	+
	k20	+	+	tr.	min. tr.	min. tr.	tr.	-	tr.	-	+	≡	tr.	±	±	-	+	-	+
	k21	tr.	min. tr.	min. tr.	±	min. tr.	min. tr.	-	tr.	-	+	≡	tr.	±	±	-	min. tr.	-	+
	k22	+	tr.	tr.	±	min. tr.	min. tr.	-	tr.	-	+	≡	tr.	±	±	-	tr.	-	≡
Galena	k 8	≡	-	+	±	±	tr.	-	tr.	±	+	≡	tr.	±	±	-	tr.	-	tr.
	k16	≡	+	+	±	±	-	-	±	±	tr.	±	tr.	±	±	-	+	-	tr.

The intensities of spectra lines are estimated visually, and they are classified as follows: (-): absent, (±): existence is doubtful, (min. tr.): minute trace, (tr.): trace, (+, ≡, ≡≡): content increases with increase of number of notation.

- Cu was present in every specimen. This element may have been included in the minute chalcopyrite-inclusions observed in sphalerites, which may represent the exsolution units derived from host minerals.
- Fe, Cd, and Mn were also detected in all specimens. Generally, both Fe and Cd are the important components of sphalerite, and owing to their similarities in each lattice dimension with that of sphalerite, they are considered to exist in solid solution of FeS and CdS.

With respect to Mn, Oftedal⁹⁾ proposed that Mn is commonly contained in sphalerite substituting Zn diadochically and is abundant in sphalerite formed at high temperature.

On the other hand, Warren and Thompson¹⁰⁾ wrote in their report:—“The atomic structure of manganese is complex, and as yet no suggestion has been made as to its mode of occurrence in sphalerite. Manganese and Iron are frequently associated in minerals and, consequently, it is possible that manganese replaces isomorphously the Iron which is found in sphalerite.”

7. In spite of the considerable difference of mode of occurrence between the two deposits, we could hardly recognize the variations in the minor elements of sphalerite in connection with two types of deposits at the Mokuji and the Shiroji.
8. In general, galena is higher in Ag and Bi, and lower in Cd, Cu, Mn and Fe than sphalerite.

These results are well in accord with the findings of early workers.

5. Indicator of the Formation Temperature

A number of studies dealing with the minor elements in sphalerites from numerous localities have already been published and it is indicated that sphalerite usually contains various elements as its minor components. They are, in general, Au, Ag, Bi, Sb, As, Fe, Mn, Ti, Cu, Pb, Cd, Ge, Ga, In, Sn, and Tl, etc. These minor elements seem to be used as indicators of the formation temperature of sphalerite. For instance, Rankama and Sahama¹¹⁾ wrote:— “The hydrothermal sphalerites formed at high temperatures contain Cobalt and much Iron and Manganese, whereas the content of Ga and Ge is low, and Tl is absent. The content of Cd seems to be relatively independent of the temperature and geological surroundings. Ga and In favor sphalerite formed at intermediate temperature.

Low Iron and Mn content affords proof of an intermediate or low temperature of formation, and Tl is found only in sphalerite formed under such conditions.”

In the present experiments, unfortunately, such rare elements could not be detected in any specimen. Therefore, we have been compelled to take up only the two common elements, Fe and Mn, for our purposes.

Besides, on the basis of the work done by Goldschmidt and Strock¹²⁾, it is generally recognized that the ionic radii of Se^{2-} and S^{2-} are like, as shown in the accompanying Table and, therefore, selenium substitutes sulphur diadochically in sulphide minerals, and replacement occurs more readily at elevated temperature than at low ones. And, also, they indicated that the average S/Se ratio in pneumatolytic and high temperature hydrothermal sulphides is 400:1—20,000:1, and the ratio in intermediate-low temperature sulphides is 70,000:1—250,000:1.

Recently, the present authors¹³⁾ have also examined the manner of occurrence of the same element in various sulphides from several sulphide deposits in Japan.

The results obtained up to date well coincide as a whole with the earlier results obtained by Goldschmidt and others although several anomalies may be found in the above generalization.

After all, judging from the earlier findings just mentioned together with the results of spectrographs of present specimens, both Fe and Mn, and also Se have been selected as indicators. That is, Fe, Mn and Zn are determined by customary chemical

analysis, and then the ratios of Zn/Fe as well as Zn/Mn of each specimen are calculated respectively.

Of selenium content, likewise, the ratios of S/Se are calculated on each specimen.

Table 3 gives the list of Ionic radii of five elements just discussed.

Table 3. Ionic radii of elements.

Element	Ionic radii (K \times)
Zn ⁺	0.83
Fe ⁺	0.83
Mn ⁺	0.91
S ⁻	1.74
Se ⁻	1.91

6. Chemical Analysis

(A) Preparation of sample for the analysis

As all of samples, as they are collected, invariably contain various gangue minerals and others in large quantities, the flotation was performed for the purposes of separating pure sphalerites from other visual impurities. Flotation was performed in the following manner :

First of all, about 150 gr of the sample was crushed to pass 60-mesh. Then, the pulverized ore was mixed with water in the proportion of 200 cc to 50 gr of the sample. The pulp produced was then placed in the tank of 150 gr plant of the Kyodai-Shiki Flotation Machine. Added thereto a 10% CuSO₄ solution at the rate of 0.55 cc : 50 gr of the sample as much as 2/3 of the total volume. Agitated for five minutes. Then added pine oil at the rate of 0.01724 gr : 50 gr of the sample and aroflote at the rate of 0.025 gr : 50 gr of the sample as much as 2/3 of the total volume, respectively. Then a diluted NaOH solution was added to keep the oiled pulp at PH. 7.5-8. The floated concentrate was now removed. Then again a 10% CuSO₄ solution, pine oil, and aroflote were added in order as previously done, this time, as much as 1/3 of the total volume, respectively. The floated concentrate was now removed.

Some samples obtained from the Shiroji ore contained considerable quantities of galena, so that the quantity of Pb was also determined along with the above mentioned five elements.

(B) Methods of Chemical Analysis

Analytical methods used are outlined as follows :

Iron : permanganate volumetric method was employed.

Manganese : oxidized to permanganic acid with ammonium persulphate, and then titrated with the arsenious acid solution.

Zinc : titrated with the ferrocyanide solution.

Lead : chromate method was employed.

Sulphur : precipitated with barium chloride and then weighed.

Selenium^{14,15}) : a current of sulphur dioxide gas was passed until the saturation point into the test solution in the beaker (prepared about 28% concentrated hydro-

chloric acid) and precipitated metallic selenium. It was then filtered off with glass filter. The residue was treated with small amounts of mixings of nitric acid (1:1) and brom water, and then carefully evaporated to dryness on the water bath. Several drops of concentrated hydrochloric acid were added, and again the specimen was carefully evaporated to dryness on the water bath for the second time. The salts then was dissolved with proper quantities of hot water in proportion to the amount of precipitation originally obtained. Now, the solution was colored with a drop of pyrrol

Table 4. Analysis of sphalerite ore.

Element Sample	Zn (%)	Pb (%)	Fe (%)	Mn (10 ⁻³ %)	S (%)	Se (10 ⁻³ %)	Zn/Fe	Zn/Mn	S/Se
k 1	52.23	0.58	3.75	36	27.74	0.16	13.9	1,450	173,375
k 2	45.30	16.91	2.82	n. d.	25.05	0.56	16.1	—	44,732
k 3	53.27	5.55	3.89	138	29.07	1.12	13.6	386	25,955
k 4	40.38	0.28	5.08	3.5	22.04	0.14	7.9	11,537	157,428
k 5	56.88	0.50	4.09	12	29.54	0.23	13.8	4,740	128,434
k 6	52.20	1.91	4.10	n. d.	28.15	0.67	12.7	—	42,014
k 7	58.14	0.47	2.61	53	29.34	0.14	22.2	1,097	209,571
k 8	14.35	57.43	1.84	n. d.	15.81	0.15	7.7	—	105,400
k 9	58.78	0.48	4.03	11	29.73	0.15	14.5	5,343	198,200
k10	37.36	17.37	4.65	1.0	23.67	0.27	8.0	37,360	87,666
k11	57.86	1.31	5.42	19	29.06	0.92	10.6	3,045	31,586
k12	51.76	1.96	2.42	58	26.35	0.59	21.3	892	44,661
k13	54.71	4.31	2.44	73	28.46	0.80	22.4	749	35,575
k14	50.61	2.32	5.22	20	28.01	0.58	9.6	2,530	48,293
k15	57.97	1.20	5.19	56	30.53	0.28	11.1	1,035	109,035
k16	51.20	8.06	3.74	59	28.18	0.17	13.6	8,677	165,764
k17	51.04	0.78	6.43	71	27.44	1.50	7.8	718	18,293
k18	52.43	0.95	6.02	1.9	28.57	0.33	8.7	27,594	86,575
k19	41.19	2.63	5.46	n. d.	22.14	0.23	7.5	—	96,260
k20	43.36	1.23	5.45	8.1	23.94	0.22	7.9	5,353	108,818
k21	54.07	1.46	5.38	15	28.64	0.83	10.1	3,604	34,506
k22	59.18	2.44	4.23	50	31.01	0.29	10.4	1,183	106,931

reagent*. Then, selenium was determined by measuring the transmittancy of the solution using the Hitachi Electric Photometers.

The results obtained from the present analysis together with the ratios of Zn/Fe, Zn/Mn, and S/Se of each specimen, calculated on the basis of above results, are listed in Table 4.

(C) Consideration of Analytical Results

1. Content of Selenium

The ratio of S/Se in sphalerites showed considerable variations: it ranged from about 20,000 to about 200,000 in the Mokuji ores, and from about 40,000 to 160,000 in the Shiroji ores.

Judging from the hypothesis that selenium in sulphide minerals is chiefly influenced by the formation-temperature of minerals and favor high temperature minerals, the above results obtained in this experiment may be generalized as follows:

Comparison of Se content in sphalerite taken from the Mokuji deposit with the Shiroji deposit, the former is usually more abundant in Se than the latter. Therefore, as a general rule, the Mokuji deposit appears to have been formed at an earlier stage of mineralization and also at high temperature conditions than the Shiroji deposit.

However, it seems most likely that some parts of the Shiroji deposit might have been formed at a considerably high temperature which is comparable to the formation temperatures of some parts of the Mokuji deposit. In other words, it is generally concluded that all of the sphalerites belonged to the Mokuji deposit might not have been formed only in

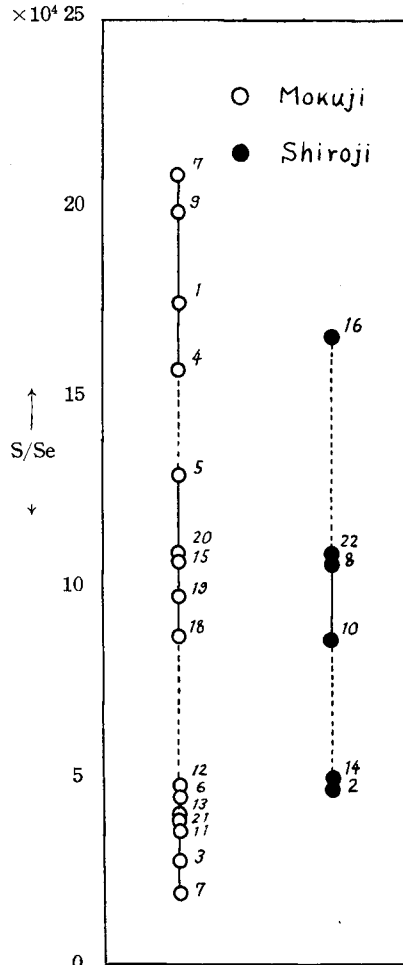


Fig. 2. Variation of the S/Se ratio in sphalerite.

* Pyrrol, $\left(\begin{array}{c} \text{CH:CH} \\ | \\ \text{CH:CH} \end{array} \right) \text{NH}$, gives a blue color with selenious salts in phosphoric acid in the presence of ferric chloride, and the intensity of the color is proportional to the concentration of the element.

the high temperature ranges of the history, but some of them might have been at relatively lower temperatures rather than the formation temperatures of some sphalerites of the Shiroji deposit. In addition, as the sphalerites taken from the Mokuji deposit are always closely associated with the so-called skarn minerals, such as hedenbergite, etc., all of them have generally been overrated to be of high temperature formation on account of their mineral assemblages.

However, this consideration on the formation temperature of the minerals, which is based simply on the mineral association, will be modified in the future, if any useful criteria on the matters are obtained.

2. Content of Iron

The ratio of Zn/Fe in sphalerites from the Mokuji deposit ranged from about 7 to about 22, and those in sphalerites from the Shiroji deposit varied from about 7 to about 16, as shown in Table 4.

In general, it seems that the content of Iron in sphalerites in this area does not vary materially with regard to the difference of type of deposit. But, variations of Fe content in sphalerites within the same type of deposit seem to be somewhat remarkable as shown in Fig. 3. They may be classified, for the sake of convenience, into three groups: less than Zn/Fe=10, from more than Zn/Fe=10 to less than Zn/Fe=20, and more than Zn/Fe=20.

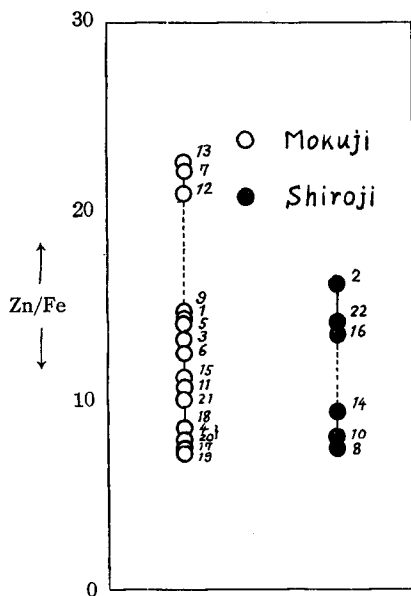


Fig. 3. Variation of the Zn/Fe ratio in sphalerite

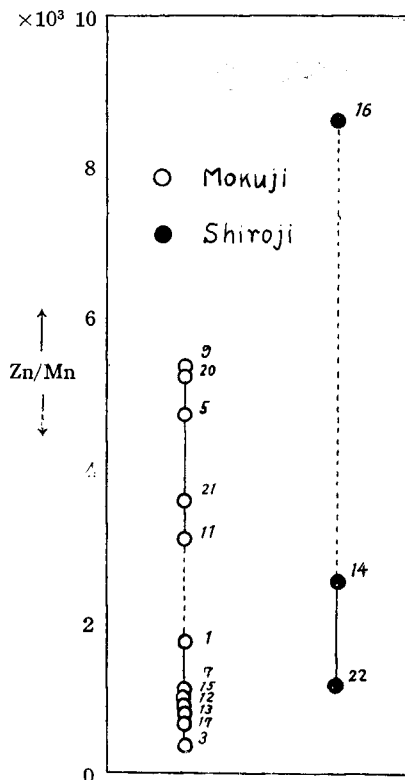


Fig. 4. Variation of the Zn/Mn ratio in sphalerite.

Then, a study of Table 5 shows that the relations of Fe content to Se content in sphalerites are not always in a definite linearity.

3. Content of Manganese

The results obtained are shown in Table 4. The ratio of Zn/Mn in sphalerites from the Mokuji deposit ranged from about 400 to about 30,000, and they may be classified into three groups as shown in Fig. 4. But, with respect to the Shiroji ores, we could not obtain any satisfactory conclusions in the present examinations, because the samples analyzed were very few. A study of Table 5 indicates that Mn and Se contents in sphalerites show regular relationships as a whole, i.e. the content of Mn in sphalerites increases as the Se content increases. This regularity, however, tends to decrease somewhat when the values of both Se and Mn in the minerals are low.

In addition, the relations between Mn and Fe contents do not show any linearity in almost all specimens.

Table 5. Ratios of S/Se, Zn/Fe, and Zn/Mn, and aspects of occurrence of umixings in sphalerite.

Sample	Aspect of occurrence of umixings in sphalerite	Ratios of		
		S/Se	Zn/Fe	Zn/Mn
k 1 (M)			△	○
k 2 (S)		○	△	
k 3 (M)		○	△	○
k 4 (")			○	
k 5 (")	△	△	△	△
k 6 (")		○	△	
k 7 (")				○
k 8 (S)		△	○	
k 9 (M)			△	△
k10 (S)	△	△	○	
k11 (M)		○	△	△
k12 (")		○		○
k13 (")	○	○		○
k14 (S)		○	○	△
k15 (M)	△	△	△	○
k16 (S)	△		△	
k17 (M)	○	○	○	○
k18 (")	△	△	○	
k19 (")		△	○	
k20 (")		△	○	△
k21 (")	○	○	○	△
k22 (S)		△	△	○

Mineral is estimated to be formed at high temperature (○), or intermediate (△), or low (□). (M): Mokuji, (S): Shiroji.

7. Summation of Experimental Results

(A) Formation Temperature of Deposit

In this section, the authors have attempted to deduce geologically the distribution of the formation temperature of the deposits on the same level of individual ore body, on the basis of experimental data obtained from both microscopic and chemical examinations and also spectrographs of given sphalerite specimens. For this purpose, we first attempted to determine the formation temperature of each specimen. That is, the following four factors were taken as its indicators of the formation temperatures. They were:

1. "Large and numerous" unmixings in sphalerite.
2. "High" selenium content in sphalerite.
3. "High" iron content in sphalerite.
4. "High" manganese content in sphalerite.

Although it was questionable whether or not these factors would give any useful evidences in the indication of the formation temperature of minerals, we felt that they were useful for our purpose within the scope of our present knowledge.

Then, as shown in Table 5, each pigeon-hole was marked with such signs as small empty circle or small empty triangle according to the indication of each factor on each sample, respectively.

By summarizing each line with respect to each row in Table 5, these can be classified as a whole in the three groups of high, intermediate, and low temperature.*,**

Fig. 5 was obtained by

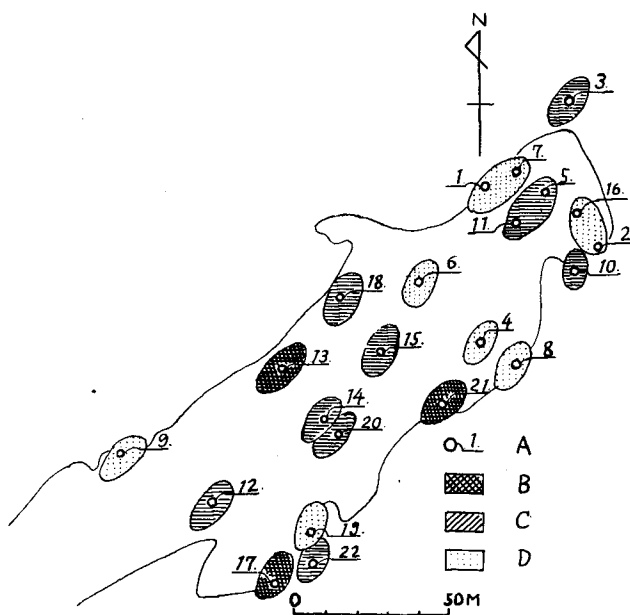


Fig. 5. Diagram showing the distribution of the formation temperature of the deposit. (-200 M level, Tochibora deposit, Kamioka Mine). A: Sample number, B: High temperature zone, C: Intermediate temperature zone, D: Low temperature zone.

* Hydrothermal temperature range was conveniently classified into three categories.

** This grouping differs somewhat from the ones in which each factor is individually used. But, the general tendency in each case is similar to the present classification.

plotting these results on Fig. 1. This schema, we consider, suggests approximately the aspects of distribution of the formation temperatures of deposits in one section of the ore body. A further detailed study on many samples collected horizontally as well as vertically within an individual ore body will give us the more distinct knowledges on such matters.

(B) Relation between the Formation Temperature and Ore Grade

As above mentioned, the authors undertook to deduce the relative temperatures of formation of minerals by means of optical as well as chemical examinations. Now, we intend to examine the relationship between the formation temperature of each specimen thus obtained and its degree of ore grade. These relations are as shown in Fig. 6.

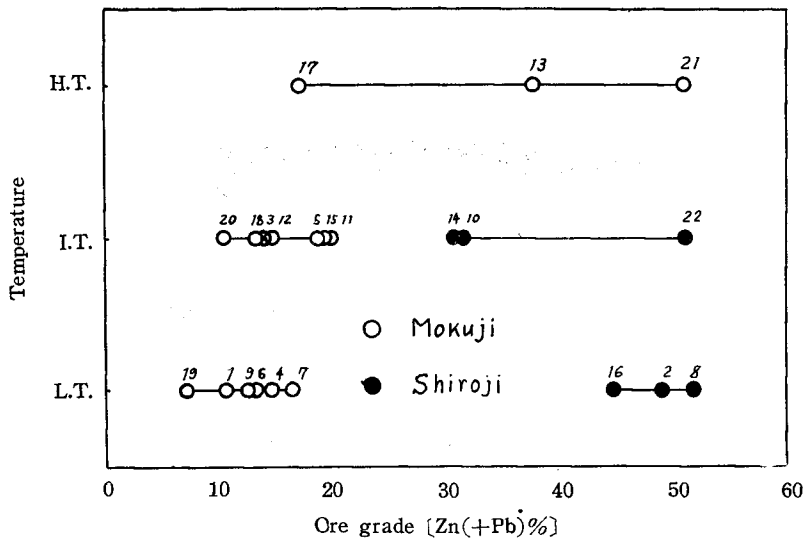


Fig. 6. Diagram showing the relations between the ore grade and the formation temperature of the ore.

The formation temperatures of the ores are classified as follows:

H.T.: High temperature, I.T.: Intermediate temperature,
L.T.: Low temperature.

Judging from this diagram, it can be concluded that in the formation of the Mokuji deposit, most of the high grade mineral ore had precipitated in the early stages of history when a high temperature was still maintained in the ore-forming solutions, whereas almost all low grade mineral ore, such as disseminated ores, had been mainly deposited in low temperature conditions.

On the other hand, the formation of the Shiroji deposit seems to be that, although the temperature of ore-forming solutions at the beginning of the mineralization might not have been so high compared with that in the early stages of the Mokuji formation,

the highly concentrated ore-forming fluids had continually precipitated the high grade ores throughout all stages of its formation even in the relatively later stages in which the temperature had fallen considerably.

Furthermore, as to the periods of the principal mineralizing activities of these two types of deposit, we can presume them partly from their modes of occurrence and partly from their mineral association, and it seems to be as follows: When the main mineralization of the Mokuji deposit was in its termination stage, the degraded mineralizing activities were rejuvenated once again by a new introduction of highly concentrated metallic solutions from probably the same ore source. As a result, the temperature of ore-forming solutions had also risen to some extent. Under such conditions, the mineralization of the Shiroji deposit might have commenced.

However, it is also assumable that these two types of mineralization might have occurred overlapping each other in some areas of the district.

Moreover, judging from the aspects of concentration of minor constituents of sphalerites, especially of selenium, the range of mineralization of both the Mokuji and the Shiroji deposit appears to be comparatively wide, that is, varying from a considerably high temperature to a considerably low one.

8. Conclusion

It is an important subject for economic geologists to deduce the formation temperature of an ore deposit and also to assume the process of the mineralization that had taken place there. On these problems, a number of excellent studies have hitherto been carried out, and consequently, numerous reports have already been published by many workers.

And then, of these thesis, it is common in almost all cases that the several geological features, such as the mineral assemblages and the manner of occurrence of the deposit and also the geological structure of the deposit, etc., have chiefly been discussed as the key points of the subjects, because it is generally recognized that the formation conditions of the deposit are well indicated by currently observable geological characters.

However, as the diagnostic of this sorts of geologic features just mentioned tends, in most cases, to be considerably influenced by an individual subjectivity of each man and, as a result, some of the results obtained are sometimes accompanied with both some obscurity and fastidiousness. Therefore, any data concerning the origin of the deposit, which may be helpful to the present knowledge, are in need by many economic geologists.

Although the foregoing experiment performed by the present authors may comprise many points for consideration, it appears to offer one objective authority which will go far in facilitating the explanation of the genetics of the deposit.

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