ON MINOR ELEMENTS IN ORE MINERALS OF THE YAKUMO MINE, HOKKAIDO, JAPAN

By

Tadao SAITO

(With 3 Tables and 2 Figures)

Contribution from the Department of Geology and Mineralogy, Faculty of Science, Hokkaido University, Sapporo. No. 486

Introduction

The Yakumo mine is working lead-zinc-manganese deposits which are developed in the Neogene Tertiary formation. Their mineralization in the deposits is recognized to represent three stages from the mineral association of the ores.

Quartz, rhodochrosite, gelena, zincblende, pyrite and chalcopyrite etc. occur in each stage.

The author studied minor elements contained in each of the ore minerals of the different stages, and inquired into a few relations among these elements.

Acknowledgments

The author wishes to express sincere thanks to Prof. Z. HARADA for his kind guidance throughout this work, and also to thank the staff of the Yakumo mine and Mr. S. HIDAKA, who facilitated the collection of necessary material.

Mineralization in the Yakumo mine

This region is geologically composed of green tuff, shale and intrusived porphyrite. The Yakumo mine has lead-zinc-manganese deposits (hydrothermal deposits) which are developed in the Neogene Tertiary formation. The deposits are formed of two mineral veins. (the one strikes N70–80°W, dip SW70–85°; and the other is almost EW, dip unfixed.). The mineralization of the deposits is recognized to represent three stages from the mineral association of the ores. Quartz, rhodochrosite, galena, zinblende, pyrite and chalcopyrite etc. occur in

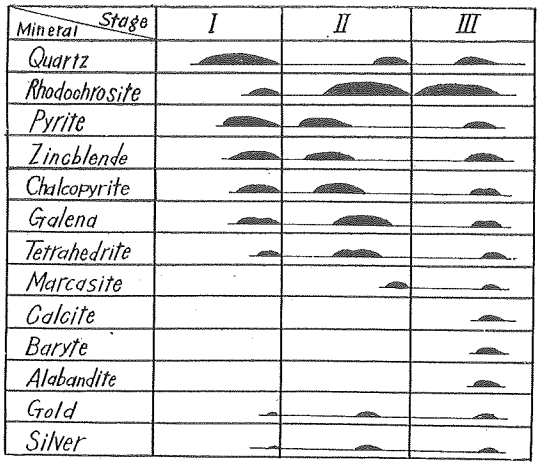

Figure 1. Crystallization in the Yakumo mine.

each stage. Relations among them are obtained as shown in Fig. 1.

Method of Analysis

Many minerals from each stage of the mineralization were chosen. The material for analysis was selected under a binocular microscope and was powdered to 200 mesh fineness. A crater in the lower (positive) electrode of highest purity graphite was filled with sample. Arc spectra of the minerals were recorded on Fuji process by the quartz spectrograph E 2 (made by Adam Hilger, LTD). They are photographed under condition of voltage 110 V., ampere 5 Am. and exposure 30 sec. Comparision with known spectra determined the qualitative presence of minor elements. These results are listed in Table I. In Table I, the numbers I, II and III represent each mineralization stage, (II is a later stage than I, and III is later than II.) and in the numbers I′, I″ etc., I″ indicates the later stage than I′.

Discussion of the Data

Reference to Table I shows that 24 elements (Si, Fe, Mn, Pb, Mg, Zn, Al, Cu, Ba, Sb, As, Ca, Ti, Au, Ag, Ru, Rh, Cd, Be, Ce, V, Ge, Sr and Se) are detected in the minerals from the deposits. Among those elements, Si, Fe, Mn, Al, Mg, Cu, Pb and Zn are commonly discovered in specimens, while Ru, Rh, Cd, Be, Ce, V, Ge, Sr and Ce etc. were less often detected. But no Ni, Co, Pt, Mo, W and Sn were found.

The above cited elements distribute differently in different stages of the mineralization, and the contents are varied in each ore mineral of the different stages.

TABLE I. Minor elements in minerals from the Yakumo mine.

Mineral \ Minor element	Fe	Pb	Al	Sb	Mg	Mn	Ti	Au	Cu	As	Ca	Ag	Se	Zn	Sr	Si	Be	Rh	Ru	V	Ge	Ba	Cd	Ce
Quartz (I)	1	t	2	t	1	1	1	1	1	—	—	1	—	—	—	0	—	—	—	—	—	—	—	—
Quartz (II)	2	t	1	t	1	2	3	t	t	—	—	t	—	—	—	0	—	—	—	—	—	—	—	—
Quartz (III)	1	2	3	2	2	1	t	2	2	—	—	1	—	—	—	0	—	—	—	—	—	—	—	—
Rhodochrosite (I′)	1	2	t	1	3	0	1	1	t	t	1	2	t	2	t	1	1	t	—	—	—	t	t	?
” (II)	1	2	2	1	2	0	1	2	t	2	2	1	t	1	t	1	1	t	—	—	—	t	?	?
” (II′)	2	t	1	t	t	0	2	t	1	t	2	t	t	2	t	3	t	t	—	—	—	?	t	t
” (III)	1	—	t	t	t	0	2	t	1	—	1	t	t	1	1	1	t	t	—	—	—	?	?	1
” (III′)	1	—	t	t	t	0	1	1	t	—	t	t	1	1	2	1	2	1	—	—	—	1	1	1
” (III″)	t	t	t	t	t	0	t	2	t	—	t	1	2	1	2	1	2	2	—	—	—	1	1	1
Galena (I′)	2	0	t	2	1	1	1	t	t	t	—	1	2	2	1	2	—	1	1	1	—	—	1	—
” (II)	1	0	1	t	t	t	1	1	1	t	—	2	—	t	t	1	—	t	t	t	—	—	t	—
” (III)	1	0	2	—	t	t	t	2	2	1	—	2	t	t	1	t	—	1	1	1	—	—	1	—
Zincblende (I′)	2	t	2	t	—	2	—	—	2	2	—	2	2	0	—	2	—	1	t	1	t	—	—	—
” (II)	t	2	1	2	—	1	—	—	1	1	—	t	t	0	—	t	—	t	?	t	?	—	—	—
” (III′)	t	t	t	1	—	t	—	—	t	t	—	t	t	0	—	t	—	—	?	t	?	—	—	—
Pyrite (I)	0	2	t	1	2	2	1	—	t	—	—	—	—	t	—	3	—	t	—	—	—	—	—	—
” (II)	0	1	—	1	1	2	2	—	t	1	—	—	t	2	t	2	—	t	1	—	—	—	—	—
” (II′)	0	t	—	t	t	t	t	—	—	t	—	—	t	—	t	1	—	1	1	—	—	—	—	—
” (III)	0	t	—	—	t	t	t	—	—	—	—	—	—	t	—	t	—	—	t	—	—	—	—	—
” (III′)	0	—	1	—	t	t	—	—	1	—	—	—	—	—	—	t	—	—	—	—	—	—	—	—
” (III″)	0	—	1	—	t	t	—	—	2	—	—	—	—	—	—	t	—	—	—	—	—	—	—	—
Chalcopyrite (II)	0	t	1	—	t	2	1	—	0	—	—	1	—	t	—	3	—	—	—	—	—	—	—	—
” (II′)	0	t	t	—	t	t	t	—	0	—	—	t	—	t	—	t	—	—	—	—	—	—	—	—
” (III)	0	2	—	—	2	2	1	—	0	—	—	t	—	2	—	2	—	—	—	—	—	—	—	—
Calcite (III)	2	—	t	—	2	3	—	—	—	—	0	t	—	1	—	1	—	—	—	—	—	—	—	—
Barite (III)	t	—	t	—	—	1	—	—	—	—	—	—	—	—	—	t	—	—	—	—	—	0	—	—
Tetrahedrite (III)	3	1	t	0	—	1	—	—	0	0	—	2	—	1	—	1	—	1	—	—	—	—	—	—
Alabandite (III)	2	t	—	t	—	0	1	2	t	1	—	1	?	t	?	1	1	—	—	—	—	1	1	t	—

I, II and III indicate the stages of mineralization.

0: main component. 3: strong. 2: medium. 1: weak. t: trace. —: not detected.

The author inquired into the relation among these minor components in each stage as described below.

a) In case of minor components in the same minerals which crystallized in different stages.

As the same minerals crystallize in the different stages of the three, minor components contained in the same minerals (rhodochrosite, galena, zincblende, pyrite and chalcopyrite etc.) which crystallized in earlier stage, middle stage and later stage were investigated.

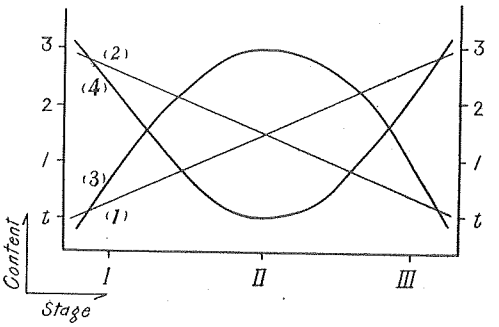

Figure 2. Type of variation of the minor element content in the same minerals in the different stage of mineralization. (idealized figure.)

Now, when the type of content of minor elements in the same minerals of the different stage is considered, four types will be found. (reference to Fig. 2.). They are as follows, (1) increase in later stage, (2) decrease in later stage, (3) increase in middle stage, (4) decrease in middle stage. As minor elements in the same minerals are applied to this type variation, following results are obtained.

For example, in rhodochrosite, elements which are increased in later stages, are Cd, Ba, Be, Se, Ce, Sr and Rh; elements which are decreased in later stages, are Pb, Sb, Mg and Zn; elements increased in middle stage are Si, Fe, Al, Cu, Ti, As and Ca; and elements decreased in middle stage are Au and Ag. Moreover, in galena, zincblende, pyrite, chalcopyrite and quartz, they are obtained as shown in Table II in similar manner.

Reference to Table II will show the variation of some groups of minor elements. For example, Pb, Sb, Mg and Zn tend to decrease in later stage in rhodochrosite, galena and pyrite; they tend to increase in later stage in quartz and chalcopyrite; and they increase in middle stage in zincblende. As minor components contained in same minerals are investigated in such way, there are four groups of minor elements as shown in Table III. The contents of these minor elements vary in the same minerals in the different stages, with few exceptions. But

TABLE II. Variation of the minor element content in each minerals.

Mineral	Type	Contained minor elements
Rhodochrosite	(1) increase	Cd, Ba, Be, Se, Ce, Sr, Rh.
	(2) decrease	Pb, Sb, Mg, Zn.
	(3) incre. in middle	Si, Fe, Al, Cu, Ti, As, Ca.
	(4) decre. in middle	Au, Ag.
Galena	(1) increase	Al, Cu, Au, Ag.
	(2) decrease	Zn, Sb, Mg, Mn, Si. Ti, Fe.
	(3) incre. in middle	
	(4) decre. in middle	Cd, Se, Sr, Ru, Rh, V, As.
Zincblende	(1) increase	
	(2) decrease	Si, Fe, Mn, Al, Cu, Ag, Se, V, Ge, Ru, Rh, As.
	(3) incre. in middle	Pb, Sb, Mg.
	(4) decre. in middle	
Pyrite	(1) increase	
	(2) decrease	Pb, Sb, Mg, Zn, Si, Mn, Ti.
	(3) incre. in middle	Se, Sr, Ru, Rh.
	(4) decre. in middle	Al, Cu.
Chalcopyrite	(1) increase	Pb, Mg, Zn.
	(2) decrease	Al, Ag.
	(3) incre. in middle	
	(4) decre. in middle	Si, Mn, Ti.
Quartz	(1) increase	Pb, Sb, Mg.
	(2) decrease	
	(3) incre. in middle	Fe, Mn, Ti.
	(4) decre. in middle	Al, Cu, Au, Ag.

TABLE III. Minor elements falling into 4 groups.

Group	Minor elements
1	Pb, Sb, Mg, Zn.
2	Al, Cu, Au, Ag.
3	Si, Fe, Mn, Ti, Ca.
4	Cd, Be, Se, V, Sr, Ce, Ge, Ru, Rh, As.

while some group tends to increase in the later stage, nevertheless in another mineral it may not show increase. According to circumstances it varies in the middle stage.

b) In case of minor elements in different minerals in the same stage.

Typical minor components in different minerals in the same stage were investigated. But, they were a few exceptions, the general ten-

dency only was found.

1) In case of minor elements in each mineral crystallized in earlier stage of mineralization.

Minerals crystallized in earlier stage are quartz, galena, zincblende, pyrite and rhodochrosite etc. Minor components contained in these minerals are Si, Al, Fe, Mg, Mn, Cu and Pb; Sb, Ti, Au, Ag, As, Zn, Se, Rh and Ge etc. which occur or not according to the kind of mineral.

2) In case of minor elements in each mineral crystallized in middle stage of mineralization.

In the middle stage of mineralization, rhodochrosite, zincblende, galena, pyrite and chalcopyrite etc. are crystallized. Mn, Pb, Cu, Zn, Sb, Fe and Si are contained almost certainly, and Al, Ti, Au, Ag, Mg, Ca, Se, Sr, Be, Rh, Cd, Ru and Rh are contained or not according to the kind of mineral, with a few exceptions. As rhodochrosite, galena and zincblende are crystallized predominantly in this stage, the certain existence of Mn, Pb and Zn in all specimens must be related to those mineral occurrence.

3) In case of minor elements in each mineral crystallized in later stage, of mineralization.

All minerals which are present in this deposit have been crystallized in later stage. Si, Fe, Mn, As, Sb and Ag are contained in all specimens, while Cu, Mg, Ti, Pb, Zn, Au, Ba, Se, Sr, Be, Ca, Rh, Ru and Ge are contained or not according to the kind of mineral, with a few exceptions.

As above, speaking generally, minerals crystallized in the earlier stage of mineralization are apt to contain Si, Fe, Mg, Ti, Al, Cu, Pb and Zn, while the later crystallized minerals have Mn, Sb, Au, Ag and As. But there are also exceptions in the case of a few elements. Those tendencies may be considered to be related to the condition of the ore-formation under which those minerals crystallized.

c) Comparison with past studies and consideration.

There are few studies of the relation among minor elements contained in minerals and their mineralization. But there are some data indicating that minor components contained in minerals may be related to the condition of the ore-formation under which those minerals crystallized. For example, in manganese minerals from south-western Hokkaido, Japan,[2] Al, Si, Fe, Mg, Ti, Ca, V, Ce, Na, K and Cu etc. were detected in all specimens of manganese minerals, irrespectively of the

types of deposit or their occurrences. Among those elements, Sn, In, Co and Cr etc. are contained in manganese minerals, which occurred in metasomatic replacement deposits in Palaeozoic. Ag, As and Ba were detected in the Neogene Tertiary. But Ni, Co and Cr etc. were determined a little or none in manganese minerals in Tertiary deposits, while Ag, As and Ba were never contained in minerals formed in the Palaeozoics. It is reported that the ore from the epithermal deposits contains large quantities of low temperature minor elements such as Pb, As, Hg, Ag, Cu, Zn, Au, Sb and Fe, but usually no high temperature elements.[3] Moreover, on minor elements in tin minerals from Japan, it has been stated that Ni, Co and Cr are found in tin minerals of high temperature, while Ag, Cu, Pb and Zn are contained in tin minerals of low temperature.[4] Also, R. E. STOIBER[5] who studied the minor elements in sphalerite says "The variation in minor element content is correlated with the type of mineral deposit in which the sphalerite occurs. Sb, Hg, Ta and As are largely restricted to sphalerite from mineral deposits commonly considered to have formed at low temperatures. Other elements are widely distributed in sphalerite from many types of deposits", and furthermore, "The minor element content of sphalerite can be related not only to the temperature at which the sphalerite is formed, but also, and perhaps in large part, to the chemical character of the ore-bearing solutions of each metallogenetic province". Also, other studies of minor components in minerals have been made by V. F. ROST,[6] P. E. AUGER[7] and G. P. BARSANOR[8]; they have said that minor elements in minerals related to the condition of crystallization.

In the Yakumo deposits, these minor elements differ by the stage of mineralization. That is, in case of minor components in the same minerals which crystallized in different stages of mineralization, variation into 4 groups of minor elements are observed, and in the case of minor elements in different minerals in the same stage, minerals crystallized in earlier stage are apt to contain Si, Fe, Mg, Ti, Al, Cu, Pb and Zn, while the later crystallized minerals have Mn, Sb, Au, Ag and As. These minor components are considered to epithermal in origin; no Ni, Co, Pt, Mo, W and Sn are found.

The present author's results are similar to the above reported results, and explain the character of contained minor elements. They will be considered to indicate that minor components in minerals are related to the condition of crystallization.

Moreover, on the effects of the adsorbed foreign substances upon crystal growth, many studies have been reported already; particularly concerning NaCl, $KClO_3$, $NaClO_3$, K_2SO_4 and $KMnO_4$. etc. in detail. It has been pointed out that contained substances (minor elements) are not adsorbed accidentally nor secondarily, but they will be included rationally at the time of crystal growth. Moreover, they may play some important roles in affecting the formation of crystal, in association with pressure or temperature.[9]

It is recognized that mixed crystals are formed comprising main components and minor elements. So, ion-radius of above 4 group elements are similar or are multiples of an integral number*. For example, in the group of Pb, Sb, Mg and Zn, ion-radius by Pauling, are 1.21, 0.62, 0.65 and 0.74 respectively, so they are at the ratio of about 2 : 1 : 1 : 1. In other groups, the ion-radius represent the multiples of an integral number with a few exceptions. These results suggest that minor components are not contained in minerals irregularlly.

As above, it follows that the contained minor elements are related to the condition of the crystallization, and it is recognized that they may play some important roles in affecting the formation of crystal. Moreover, they may be considered to be related to the condition of the ore-formation in which those minerals crystallized. These concrete relations will be explained in future studies.

Summary

The Yakumo mine is working lead-zinc-manganese deposits which are developed in the Neogene Tertiery formation; their mineralization in the deposits is recognized to occur in three stages from the mineral association of the ore. Quartz, rhodochrosite, galena, zincblende, pyrite and chalcopyrite etc. occur in each stage.

The author studied minor elements contained in each of the ore minerals in the different stages, and the following results are obtained:

1) 24 elements (Si, Fe, Mn, Pb, Zn, Al, Cu, Ag, Ba, Sb, As, Ca, Ti, Au, Mg, Ru, Cd, Be, Ce, V, Rh, Ge, Sr and Se) are detected in the minerals from the deposits.

Among those elements, Si, Fe, Mn, Al, Mg, Cu, Pb and Zn are discovered in specimens commonly, whilst Ru, Rh, Cd, Be, Ce, V, Ge, Sr

*) These relations will be stated in other papers in detail.

and Ce etc. are less often detected. But no Ni, Co, Pt, Mo, W and Sn are found.

2) Above cited elements distribute differently in the different stages of the mineralization.

a) In case of minor components in the same minerals which crystallized in different stages, variation (increase or decrease) of the following 4 groups of minor elements is observed. The groups are 1) Pb, Sb, Mg and Zn. 2) Al, Cu, Au and Ag. 3) Si, Fe, Mn, Ti and Ca. 4) Cd, Be, Se, V, Sr, Ce, Ge, Ru, Rh and As. Contents of several minor elements vary in the minerals in the different stages, with a few exceptions. But as some group tends to increase in the later stage, nevertheless in other minerals it may not increase. According to circumstances it varies in the middle stage.

b) In case of minor elements in different minerals in the same stage, minerals crystallized in earlier stage are apt to contain Si, Fe, Mg, Cu, Zn and Pb, while the later crystallized minerals have As, Ag, Sb, Au, Mn and Ca. Bnt there are also exceptions in a few elements.

Those minor elements have been found in minerals of epithermal origin. They may be considered to have some relation not only to the chemical character of the ore solution, but also to the condition of the ore-formation under which those minerals crystallized.

Literatures

1) H. Kayser: Tablle der Hauptlinien der Linienspektra Aller der Elemente. Berlin. 1926.
F. Löwe: Atlas der letzten Linien der wichtigsten Elemente. Dresden & Leissig. 1928. components
2) T. Saito: Minor elements in manganese minerals from the south-western Hokkaido, Japan. Jour. Jap. Assoc. Min. Pet. Eco. Vol. 36, 1 1952.
3) K. Kinoshita & K. Muta: Minor elements in the minerals from the epithermal deposits. Jour. Geol. Soc. Japan. Vol. 56, 423. 1950.
4) K. Takimoto: Studies of tin minerals from Japan. Jour. Geol. Soc. Japan. Vol. 50, 82. 1943.
5) R. E. Stoiber: Minor element in sphalerite. Econ. Geol. Vol. 35, 501. 1940.
6) V. F. Rost: Spektralanalytische Untersuchungen an sulphidischen Erzlagerstäten des Ostbayerischen Grenzgebirges; Ein Beitrag zur Geochemie von Nickel und Kobalt. Zeit. Angew. Miner. Vol. 2, 29. 1939.
7) P. E. Auger: Zoning and district variation of minor elements in pyrite of Canadian gold deposits. Econ. Geol. Vol. 36, 401. 1941.

8) G. P. Barsanor & S. A. Borovick: On the rare elements in little Caucasus ores. (Russian). Abstract. Jour. Geol. Soc. Japan. Vol. 48, 158. 1941.

9) H. E. Buckley: The oriented inclusion of impurities in crystals. Zeit. Krist. Bd. 88, 248. 1934.

C. Frondel: The size of crystals. Am. Min. Vol. 20, 469. 1935.

H. Haberlandt & A. Schiener: Uber Farbverteilungen beim Fluorit in ihrem Zusammenhang mit dem Kristallbau. Zeit. Krist. Bd. 90, 193. 1935.