Distribution of sulfur isotopes in the Ryusei vein of the Akenobe mine, Hyogo Prefecture, Japan

MASAHIRO YAMAMOTO

Department of Earth Science, Faculty of Science,
Okayama University, Okayama 700, Japan

(Received March 6, 1974)

Abstract—Sulfide samples (mostly chalcopyrite with some sphalerite and bornite) from the Ryusei vein of the Akenobe mine exhibit a narrow spread in $\delta^{34}\text{S}$ value ranging from -4.4 to -0.4‰ . The range is lower than those of other Japanese sulfide deposits so far studied. The frequency diagram of $\delta^{34}\text{S}$ values for chalcopyrite indicates that the $\delta^{34}\text{S}$ distribution is bimodal; one peak at -3.0 to -2.5‰ and the other at -1.5 to -0.5‰ . This suggests that chalcopyrite in the Ryusei vein was formed in at least two different stages of mineralization.

Of 9 sphalerite-chalcopyrite pairs studied (including 2 pairs from different veins), 8 pairs are isotopically in disequilibrium; sphalerite is up to 2.7‰ lighter than coexisting chalcopyrite.

From the isotopic and chemical equilibrium relationship between the aqueous and mineral species of the Cu-Fe-S-O system, $\delta^{34}\text{S}$ values of the ore-forming solutions were speculated to be rather similar to those of chalcopyrite ($0 \sim -5\text{‰}$).

INTRODUCTION

We have been studying the distribution of sulfur isotopes in various types of Japanese sulfide deposits in order to understand geochemical behaviors of sulfur isotopes in ore-forming processes. The results on the Yanahara massive pyritic ore deposits of Kieslager-type (YAMAMOTO *et al.*, 1968), the Hitachi cupriferous pyrite deposits of Kieslager-type (YAMAMOTO and KASE, 1973), and the Iwami Kuroko deposits (YAMAMOTO, 1974) have been reported.

In the present paper the sulfur isotope ratios of sulfide minerals from the Ryusei vein of the Akenobe mine, Hyogo Prefecture, Japan, will be reported and discussed. The deposits are well known as the representative of xenothermal deposits. The study was initiated with the purpose of revealing the distribution of sulfur isotopes within a single vein and sulfur isotopic fractionation among different sulfide minerals within single hand specimens.

OUTLINE OF THE DEPOSITS OF THE AKENOBE MINE

The Akenobe mine is situated in Hyogo Prefecture, Japan, and is producing copper, zinc, lead, tin and tungsten. The geology and ore deposits of the mining area have been described in detail by SAIGUSA (1958), ABE (1963), MURAOKA and IKEDA (1968), IKEDA (1970) and KOJIMA and ASADA (1973).

The mining area of 4 ~ 5 km square is composed mainly of Paleozoic green rocks (basic lava and its tuff) and slate (KOJIMA and ASADA, 1973). Sedimentary rocks are intruded here and there by Triassic meta-diorite and meta-gabbro. Granite porphyry of the same age is exposed in the western part of the area (KOJIMA and ASADA, 1973). Andesitic, rhyolitic, and breccia dikes also occur in the area. Recent age determinations of the rhyolitic dikes suggest that most dikes are of Late Cretaceous or Early Tertiary age (ISHIHARA and SHIBATA, 1972).

The deposits are of xenothermal type. They consist of about a hundred polymetallic composite veins traversing both sedimentary and igneous rocks. Main ore minerals are chalcopyrite, sphalerite, bornite, galena, magnetite, cassiterite and wolframite with subordinate amounts of pyrite, pyrrhotite and others (MURAOKA and IKEDA, 1968). Gangues are quartz, fluorite, siderite, calcite, chlorite and others (MURAOKA and IKEDA, 1968).

In recent years many workers have considered that the deposits are genetically related to Late Cretaceous or Early Tertiary granite which crops out to the northeast of the mining area (e.g. IMAI *et al.*, 1972; ISHIHARA and SHIBATA, 1972; KOJIMA and ASADA, 1973). NAKAMURA and HUNAHASHI (1970), however, has a different view that the mineralization is related to Neogene volcanic activities.

The Ryusei vein The Ryusei vein is located at the southern part of the mining area which belongs to the Cu-rich zone (IKEDA, 1970). Host rocks are diorite with some slate in the upper part of the vein and green rocks in the lower part (Fig. 1, after MURAOKA and IKEDA, 1968).

Main ore minerals are chalcopyrite, sphalerite, bornite, magnetite and cassiterite with minor amounts of wolframite, chalcocite, and other sulfides. Of these, chalcopyrite is by far the most abundant. Iron sulfides such as pyrite and pyrrhotite are absent or rare. Quartz is the principal gangue mineral with subordinate amounts of chlorite, siderite and others.

In most places the vein is composed of massive chalcopyrite in bands and irregular impregnations, associated with quartz, magnetite, sphalerite, bornite and others. Sphalerite occurs in rims around chalcopyrite grains, in aggregates intimately associated with chalcopyrite, or in separate bands. Sphalerite always has chalcopyrite blebs or veinlets in it. Bornite is found generally as sporadic fine inclusions in chalcopyrite, but in some places as massive aggregates associated with chalcopyrite and magnetite. Magnetite occurs mostly as fine granules in chalcopyrite and quartz,

or massive aggregates with laminated structure disseminated by chalcopyrite. Cassiterite occurs generally as fine granules in quartz and chalcopyrite. It is often concentrated around chalcopyrite and wall rock fragments in quartz veins.

Fig.1. Vertical section of the Ryusei vein (after MURAOKA and IKEDA, 1968).

EXPERIMENTAL

Samples Samples were collected from the levels of 1 to -6 of the Ryusei vein and their locations in the vein are shown in Fig.2. One sample each also was collected

Fig.2. Location of the Ryusei samples. Numbers in the figure must be prefixed by AR for the full sample Nos.

from the Shirogane and Ginsei veins. The Ginsei vein is located about 600m south of the Ryusei vein, and the Shirogane vein about 300m east of the Ginsei vein.

Sulfide minerals (chalcopyrite, bornite, sphalerite and galena) were separated from hand specimens by heavy liquid, hand picking and/or a hand magnet. When chalcopyrite and sphalerite coexist, chalcopyrite was purified by decomposing sphalerite in 4N HCl, H₂S from the sphalerite being collected for the isotopic analysis.

Isotope analysis of sulfur Sphalerite and galena were attacked by 4N HCl, the liberated H₂S was captured as CdS, then converted to Ag₂S. Chalcopyrite and bornite were decomposed by a HBr-HNO₃ mixture and the sulfate in solutions was precipitated as BaSO₄ which was converted to Ag₂S by the procedure described by THODE *et al.* (1961). Ag₂S obtained was combusted to SO₂ at 1,200°C in a stream of tank air for the mass spectrometry. The mass spectrometer used for the isotope analysis has been described by SAKAI (1966). The results of the isotope analysis are given in $\delta^{34}\text{S}$ value as defined by:

$$\delta^{34}\text{S}(\text{‰}) = [(^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{standard}} - 1] \times 1,000.$$

The standard is troilite sulfur from the Canyon Diablo meteorite. The uncertainty in $\delta^{34}\text{S}$ values is less than $\pm 0.2\text{‰}$ in most cases.

RESULTS AND DISCUSSION

All the sulfur isotope data obtained are tabulated in Table 1. The variation range of $\delta^{34}\text{S}$ values for sulfide minerals in the Ryusei vein is graphically shown in Fig.3, together with those for other Japanese sulfide deposits so far studied.

Distribution of $\delta^{34}\text{S}$ values for sulfide minerals in the Ryusei vein Sulfide minerals (mostly chalcopyrite) in the Ryusei vein exhibit a narrow spread in $\delta^{34}\text{S}$ value ranging from -4.4 to -0.4‰ (Fig.3). Although the spread in $\delta^{34}\text{S}$ value is similar to those in other Japanese sulfide deposits, the Ryusei sulfide minerals have characteristically lighter $\delta^{34}\text{S}$ values than others.

Although the over-all variation in $\delta^{34}\text{S}$ value for the Ryusei sulfide minerals is narrow, a comparison of the distribution of $\delta^{34}\text{S}$ values with the vein map does not indicate any relationships between $\delta^{34}\text{S}$ values of sulfide minerals and their horizontal or vertical distribution in the vein. Furthermore, it is notable that in the specimen, AR102, which is about 1kg in weight, chalcopyrite from one band (AR102-2) has a $\delta^{34}\text{S}$ value of -0.8‰ , which is distinctly higher than the values of chalcopyrite from another band, AR102-3 (-2.8‰), and coarse-grained impregnations with quartz, AR102-4 (-3.1‰). Similar difference is also observed between AR103-1 and AR103-3. These results indicate that the vein sulfide minerals are, though not so much, irregular and inhomogeneous in $\delta^{34}\text{S}$ value.

Table 1. $\delta^{34}\text{S}$ values of sulfide minerals from the Ryusei vein of the Akenobe mine

Sample No.	Mineral	$\delta^{34}\text{S}(\text{‰})$	Remarks
AR101	cp	-4.2	a discontinuous cp band (3~10mm wide)
	sp	-4.2	discontinuous rims (0.5~1mm thick) around the cp above
AR102-1	sp	-0.8	a sp band (3~5mm)
-2	cp	-0.8	a cp band (3~10mm) separated from the sp band above by a quartz band (3~5mm)
-3	cp	-2.8	a cp band (~20mm) separated from the cp band above by a quartz band (~15mm)
-4	cp	-3.1	coarse-grained impregnations in a quartz band adjacent to the cp band above
AR103-1	cp	-0.9	irregular disseminations in massive magnetite
-3	cp	-2.8	coarse-grained impregnations in a quartz band near the magnetite above
AR001	cp	-3.7	irregular impregnations with quartz
AR002-1	cp	-1.2	a cp band (~10mm)
-2	cp	-1.2	medium-grained impregnations in a quartz band adjacent to the cp band above
AR005	cp	-2.7	massive aggregate of cp and sp
	sp	-3.5	
AR006	cp	-1.7	massive aggregate of cp and sp
	sp	-4.4	
AR0102	cp	-1.6	irregular impregnations with quartz discontinuous rims (0.5~1mm) around, and irregular areas in, the cp above
	sp	-1.2	
AR0104	cp	-2.5	massive aggregate
AR0107	cp	-0.4	coarse-grained, near margin of the sp band below a sp band (~10mm)
	sp	-0.5	
AR0110	cp	-2.8	massive aggregate
AR0201	cp	-2.7	medium- to coarse-grained impregnations with quartz
AR0203	cp	-0.9	massive aggregate
AR0205	cp	-0.6	massive aggregate
AR0207	cp	-3.0	irregular impregnations with quartz
AR0208	cp	-2.2	massive aggregate irregular areas mostly near margin of the cp above
	sp	-3.8	
AR0303	cp	-1.3	a cp band (~20mm)
AR0305	bn	-0.8	massive aggregate with cp and magnetite
AR0307	cp	-2.1	a cp band (~20mm)
AR0310	cp	-2.5	coarse-grained impregnations with quartz
AR0402	bn	-2.4	massive aggregate with cp irregular veinlets in the bn above
	cp	-2.3	
AR0405	cp	-3.6	fine- to coarse-grained impregnations with quartz
AR0406	cp	-2.7	fine- to coarse-grained impregnations with quartz
AR0408	cp	-1.2	coarse-grained, at the margin of the sp below massive aggregate
	sp	-2.4	

(Continued)

Sample No.	Mineral	$\delta^{34}\text{S}(\text{‰})$	Remarks
AR0409	sp	-1.2	coarse-grained impregnations with quartz
AR0603	cp	-1.2	medium-grained impregnations with quartz
AG0202	cp	-2.3	from the Ginsei vein, massive aggregate of cp and sp
	sp	-3.0	
ASI201'	cp	-1.6	from the Shirogane vein, aggregate of gn with some cp and sp
	sp	-2.4	
	gn	-2.9	

cp : chalcopyrite, *sp* : sphalerite, *bn* : bornite and *gn* : galena.

Fig.3. Variation range of $\delta^{34}\text{S}$ values for sulfide minerals from the Ryusei vein and some other Japanese sulfide deposits. Numbers under bars showing the variation range are those of sulfide samples analyzed isotopically.

References: 1: this paper, 2: YAMAMOTO et al. (1968), 3: YAMAMOTO and KASE (1973), 4: KAJIWARA (1971), 5: YAMAMOTO (1974) and 6: KIYOSU and NAKAI (1971).

Abbreviations: *py*:pyrite, *po*: pyrrhotite, *cp*: chalcopyrite, *bn*: bornite, *sp*: sphalerite and *gn*: galena.

Figure 4 indicates that $\delta^{34}\text{S}$ values of chalcopyrite show a bimodal distribution, having one peak at -3.0 to -2.5‰ and the other at -1.5 to -0.5‰. Although the data are only a few, the distribution of $\delta^{34}\text{S}$ values of sphalerite and bornite may also be regarded as bimodal (Fig.4). A possible interpretation may be that chalcopyrite in the Ryusei vein represents at least two different stages of mineralization. It is generally accepted that the Ryusei vein as well as other veins in the Akenobe mine were formed by multiple-stage mineralization (e.g. SAIGUSA, 1958; ABE, 1963; MURAOKA and IKEDA, 1968). Then, the differences in $\delta^{34}\text{S}$ values between chalcopyrites of different bands and impregnations may reflect changes in the isotopic composition

of ore-forming solutions with time. Alternatively, such small variations as observed might have resulted from change in the temperature of deposition, the pH and f_{O_2} of ore-forming solutions, or relative proportion of sulfides precipitated to sulfur-bearing species in aqueous and other phases or combination of these, even if the sulfur isotopic composition of ore-forming solutions remained constant (SAKAI, 1968; KAJIWARA, 1971; OHMOTO, 1972).

Ore microscopic observations of more than half of the samples show that in most samples chalcopyrite is associated with magnetite, sphalerite and cassiterite in variable amounts and that in some samples chalcopyrite is associated with bornite, chalcocite and/or other Cu-S minerals. A comparison of $\delta^{34}S$ values of chalcopyrite with kinds and amounts of associated minerals, however, shows no distinct correlation between them.

This might suggest that the differences in $\delta^{34}S$ values of chalcopyrite are ascribed mainly to the variations of the sulfur isotopic ratios of ore-forming solutions.

Difference in $\delta^{34}S$ value between sphalerite and chalcopyrite within single hand specimens As is seen from Table 2, in nine samples in which sphalerite and chalcopyrite occur at least in close contact with each other, the difference in $\delta^{34}S$ value

Fig.4. Histograms showing the distribution of $\delta^{34}S$ values for the Ryusei chalcopyrite, bornite and sphalerite.

Table 2. Difference in $\delta^{34}S$ value between coexisting sphalerite and chalcopyrite

Sample No.	$\delta^{34}S_{sp}$ (‰)	$\delta^{34}S_{cp}$ (‰)	$\delta^{34}S_{sp} - \delta^{34}S_{cp}$ (‰)	Type*
AR0107	-0.5	-0.4	-0.1	I
AR0408	-1.2	-2.4	-1.2	I
AR005	-3.5	-2.7	-0.8	II
AR006	-4.4	-1.7	-2.7	II
AG0202	-3.0	-2.3	-0.7	II
ASI201	-2.4	-1.6	-0.8	II
AR101	-4.2	-4.2	0.0	III
AR0102	-1.2	-1.6	+0.4	III
AR0208	-3.8	-2.2	-1.6	III

* See text.

between two minerals ranges from +0.4 to -2.7‰. Only in a pair of AR0102, sphalerite is heavier than chalcopyrite in $\delta^{34}\text{S}$ value. In two pairs sphalerite is isotopically close to chalcopyrite, and in the remaining six pairs sphalerite is distinctly lighter than chalcopyrite.

As is described in Table 1, textural relationship between sphalerite and chalcopyrite is not the same for all the samples, and may be classified into three types (Table 2): in type I, chalcopyrite occurs near margin of sphalerite bands or massive aggregates; in type II, sphalerite and chalcopyrite are intimately associated with each other, showing irregular boundaries between them; type III pairs are those in which sphalerite occurs as rims around, or near margin of, chalcopyrite. However, no definite correlation can be observed between the difference in $\delta^{34}\text{S}$ value and the textural relationship. Because sphalerite is heavier than chalcopyrite in equilibrium at all temperatures (SAKAI, 1968; KAJIWARA and KROUSE, 1971), the present results indicate that, except for AR0102, all the sphalerite-chalcopyrite pairs are not in the isotopic equilibrium. This is in accord with the mode of occurrence of types I and III pairs. But disequilibrium is rather surprising for type II pairs, because simultaneous precipitation of sphalerite and chalcopyrite is suggested from the texture of this type of samples. It may be that in type II pairs also deposition of two minerals was actually not simultaneous. Alternatively, it may be that a kinetic isotopic effect was more important than exchange equilibrium during the deposition of sulfide from sulfur-poor ore-forming solutions.

Speculation of the sulfur isotopic ratios of the ore-forming solutions From the examination of the stability relations among minerals in the Fe-S-O system in f_{O_2} -pH diagrams, OHMOTO (1972) has suggested that sulfide minerals which were precipitated in equilibrium with magnetite, hematite, or sulfate minerals could have $\delta^{34}\text{S}$ values markedly different from those of ore-forming solutions.

As mentioned previously, iron sulfides such as pyrite and pyrrhotite are absent and magnetite is the only mineral that occurs in the Fe-S-O system of the Ryusei vein. Most chalcopyrites are associated with magnetite; magnetite occurs as fine granules in chalcopyrite or massive aggregate disseminated by chalcopyrite.

Based on the assumption that the Ryusei chalcopyrite and magnetite were deposited simultaneously from ore-forming solutions in chemical and isotopic equilibrium, a similar examination as in OHMOTO (1972) of the stability field of the chalcopyrite-magnetite assemblage in the Cu-Fe-S-O system could place some limits to sulfur isotopic ratios of ore-forming solutions.

The stability relations of minerals in the Cu-Fe-S-O system in NaCl solution was recently studied thermodynamically by SATO (1972). Figures 5a and 5b are modifications of the f_{O_2} -pH diagram of the system constructed by SATO (1972) using the thermodynamic data of HELGESON (1969). Figure 5a shows stability relations among

Figs. 5a and 5b. Stability relations among minerals in the Cu-Fe-S-O system at 300°C. In Fig. 5a $\Sigma Cu = 10^{-2} m$, maximum $\Sigma Cu = 10^{-2} m$ and maximum $\Sigma Fe = 10^{-2} m$ and in Fig. 5b $\Sigma Cu = 10^{-3} m$, maximum $\Sigma Cu = 10^{-3} m$ and maximum $\Sigma Fe = 10^{-2} m$. The diagrams were constructed in a manner after SATO (1972). The equilibrium constants for the reactions considered are from HELGESON (1969). Activity coefficients for all the species are those in 3 molal NaCl solution given by HELGESON (1969). The lines between adjoining fields define the equal molality of the sulfur species of adjoining fields. The dashed lines define the neutral pH. The area between the dotted lines indicates the maximum stability field of K-feldspar and kaolinite calculated from the thermodynamic data of HELGESON (1969) and the numerical data given in the text. Abbreviations: ht: hematite, mt: magnetite, py: pyrite, po: pyrrhotite, Fe°: native iron, cp: chalcocopyrite, bn: bornite, cc: chalcocite and Cu°: native copper.

minerals in 3 molal NaCl solution at 300°C when total dissolved sulfur is 10^{-2} molal, and the maximum total dissolved copper and iron are $10^{-2}m$ each. In Fig.5b total dissolved sulfur is diminished to $10^{-3}m$, other variables holding the same values as those in Fig.5a. The molality of each dissolved species is chosen arbitrarily. The temperature, 300°C, at which the diagrams are constructed, is also rather arbitrary, since no data are available on the temperatures of mineralization for the Ryusei vein. However, in the Yonmyaku and Nanamyaku veins in the western area, TAKAHASHI *et al.* (1955) obtained 300 ~ 350°C for the temperatures of mineralization by the decrepitation method.

The diagrams show that when $\Sigma S = 10^{-2}m$ (Fig.5a) the chalcopyrite-magnetite assemblage is stable in the small area laid across the HSO_4^- , SO_4^{2-} and S^0 fields, while when $\Sigma S = 10^{-3}m$ (Fig.5b) the stability field of the assemblage expands into the H_2S field, covering small areas in the HSO_4^- , SO_4^{2-} and S^0 fields owing to the disappearance of the pyrite-pyrrhotite boundary. These features are, of course, pertinent to the particular set of variables as given above. However, from the diagrams at lower temperatures and varying molality of each dissolved species, it can be said, in general, that sulfur-poor chloride solutions have a much wider stability field for chalcopyrite-magnetite assemblage than sulfur-rich solutions, and the stability field lies mostly within the H_2S - HS^- fields.

Combining available equilibrium sulfur isotopic fractionation factors among various aqueous sulfur species and chalcopyrite (SAKAI, 1968; KAJIWARA and KROUSE, 1971) with the features of the stability field of the chalcopyrite-magnetite assemblage obtained above, we may state as follows:

(1) If chalcopyrite and magnetite were deposited from sulfur-rich ore-forming solutions in the HSO_4^- and SO_4^{2-} fields, the ore-forming solutions would have had $\delta^{34}\text{S}$ values markedly higher than those obtained for chalcopyrite. The difference in $\delta^{34}\text{S}$ value between ore-forming solutions and chalcopyrite would be, for example, up to 25‰ at 300°C.

(2) If chalcopyrite and magnetite were deposited from sulfur-rich solutions in the HS^- and S^0 fields, the ore-forming solutions would have had $\delta^{34}\text{S}$ values similar to or slightly lower than those for chalcopyrite. The difference would be, for example, in the range from 1 to -3‰ at 300°C.

(3) If chalcopyrite and magnetite were deposited from sulfur-poor solutions in the HSO_4^- and SO_4^{2-} fields, a situation similar to case (1) would be expected.

(4) If chalcopyrite and magnetite were deposited from sulfur-poor solutions in the H_2S and HS^- fields, the ore-forming solutions would have had $\delta^{34}\text{S}$ values slightly higher than those for chalcopyrite. The difference would be, for example, up to 2‰ at 300°C.

The author would choose case (4) in preference to any others as the plausible situation of deposition of the Ryusei chalcopyrite from the following reasons:

(1) The significant types of alteration of wall rocks in the Akenobe mine are silicification, chloritization and sericitization (IKEDA, 1970). The occurrence of sericite with quartz suggests that pH of the ore-forming solutions was in the range from weakly acid to neutral, if the salinity and K/Na ratio of the ore-forming solutions are assumed to have been in the range from 2 to 10 NaCleq. wt. % and in the range from 0.2 to 0.4, respectively (Figs. 5a and 5b). Both of the ranges are those observed for fluid inclusions in some Japanese plutonic vein deposits (ENJOI, 1972).

(2) If chalcopyrite had deposited with magnetite in the sulfate field, a slight variation in pH and/or f_{O_2} of the ore-forming solutions would have drastically affected the $\delta^{34}S$ value of sulfide (OHMOTO, 1972). On the contrary, $\delta^{34}S$ values of chalcopyrite are stable around 0~–5‰. In addition, a slight decrease in pH and/or f_{O_2} of the ore-forming solutions would have made the chalcopyrite-pyrite assemblage stable instead of the chalcopyrite-magnetite assemblage. The former assemblage is absent in the Ryusei vein.

CONCLUSIONS

1) Ryusei sulfide minerals (mostly chalcopyrite) exhibit a narrow spread in $\delta^{34}S$ value, which is comparable to those in other Japanese sulfide deposits so far studied. However, they are distinguished from others by their low $\delta^{34}S$ values (Fig. 3).

2) Any definite correlation cannot be observed between $\delta^{34}S$ values for sulfides and their locations in the vein.

3) $\delta^{34}S$ values for the Ryusei chalcopyrite show a bimodal distribution.

4) A possible interpretation of the features 2) and 3) may be that chalcopyrite was deposited in at least two different stages of mineralization in the Ryusei vein.

5) Most sphalerite-chalcopyrite pairs are isotopically in disequilibrium. This may be ascribed to non-simultaneous deposition of the two minerals.

6) The assumption that the Ryusei chalcopyrite plus magnetite were deposited in the chemical and isotopic equilibrium from the ore-forming solutions, coupled with some suggestive information on the depositional conditions, leads to the conclusion that the sulfur isotopic ratios of the ore-forming solutions were rather similar to those obtained for chalcopyrite.

ACKNOWLEDGMENTS

I am deeply indebted to Prof. H. SAKAI of the Thermal Spring Research Institute, Okayama University, for his critical reading of the manuscript and helpful advice in the mass spectrometry. Thanks are also due to Messrs. S. IKEDA and T. OHMAE of the Mitsubishi Metal Mining Co., Ltd. for their kind help in collecting samples, and Messrs. K. KASE and N. WADA of Okayama University for their kind guidance and help in microscopic observations of ore samples.

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