

**Distribution of Cobalt in Pyrites from Some Cupriferous
Pyrite Deposits, with Special Reference to Its
Relationship to Metamorphic Grade**

Shiro ITOH*

Abstract

The distribution of cobalt in ores from the typical cupriferous pyrite deposits in Japan has been investigated by the electron probe microanalyser. In the un- and low-metamorphosed deposits, cobalt in pyrites is distributed very heterogeneously. On the contrary, in the highest metamorphosed deposits of Japan, cobalt is sharply concentrated in the margin of pyrites and the content is homogeneous in the inner parts. In the deposits which underwent medium grade metamorphism, the distribution of cobalt shows transitional pattern. From these facts, it can be concluded that the migration of cobalt atoms within pyrite crystal took place during regional metamorphism.

A cobalt mineral, carrollite is found in the ore sample from the Shirataki mine which is one of the highest metamorphosed deposits in Japan. From the occurrence of carrollite, it is inferred that the mineral was formed by reaction between chalcopyrite and cobalt atoms migrated to the margin of pyrites.

In other ore forming minerals, such as chalcopyrite, sphalerite, bornite and gangue minerals, cobalt was not detected. This indicates clearly that during ore deposition almost all of cobalt ions entered into pyrite. The cobalt rich parts of some pyrites seem to agree with growth lines which become apparent by etching. At the places where a considerable amount of cobalt is concentrated, the iron content is evidently low compared with surrounding normal pyrites, which suggests the isomorphous substitution of cobalt for iron in pyrite lattice.

1. Introduction

It is well known that the sulfide ores from cupriferous pyrite deposits in Japan have characteristically high cobalt content in the range of 0.03 to 0.5% (ITO and KANEHIRA, 1967; ITO, 1971 a, b). In the Shimokawa deposit which has extremely high cobalt content up to about 2%, cobalt-pentrandite and cobalt-mackinawite had been found (KATO and SATO, 1963; NAKAMURA and MARIKO, 1967). Recently, KASE (1972) found cobaltite in the ores from the lower parts of Besshi deposit. Furthermore, the occurrence of carrollite in the ores from Sazare deposit was informed by NAKAYAMA (KANEHIRA and TATSUMI, 1970 a). However, except these few cases, no cobalt minerals had been found in the ores from cupriferous pyrite deposits, and it was believed that the cobalt substituted in pyrite crystals.

Recently, the results of interesting studies concerning the distribution of cobalt in pyrite crystals have been reported (VELIKOBORZ and LUKYANGHENKO, 1970; KASE, 1971; BARTHOLOME et al. 1971; BROWN and BARTHOLOME, 1972; RUDASHEVSKII, 1971). These reports show the heterogeneous distribution of cobalt in pyrite with the exception of VELIKOBORZ's study which was made by X-ray diffractometry.

* Geochemistry and Technical Service Department.

In Japan, the cupriferous pyrite deposits were metamorphosed to various grades up to epidote-amphybolite facies (KANEHIRA and TATSUMI, 1970 a). In highly metamorphosed cupriferous pyrite deposits in Japan, all pyrites are believed to have been thoroughly recrystallized. In deposits which underwent medium grade metamorphism, colloform textures are often found in pyrite and they are considered to be relict textures. The behaviour of minor elements during recrystallization of the host pyrite by metamorphism is geochemically interesting and important. Detailed investigation concerning these problems, however, has not yet been made.

The author has investigated the distribution of cobalt in pyrite crystals in relation to the metamorphic grade of the cupriferous pyrite deposits. The electron probe microanalyser (EPMA) was used in this study. The studied specimens were collected from the Yanahara, Tsuchikura, Imori, Okuki, Shingu, Sazare, Shirataki and Shimokawa mines, all of which are typical cupriferous pyrite deposits in Japan. The locations of these mines are shown in Fig. 1. Various types of cobalt distribution patterns were obtained. Some typical patterns and the correlation between the distribution of the metal and metamorphic grade will be presented in this paper.

In the sample from the Shirataki mine in Shikoku, which is one of the highest metamorphosed deposits in Japan, a cobalt mineral was found during the course of this study. The results of optical observations and quantitative analysis of this mineral will also be shown.

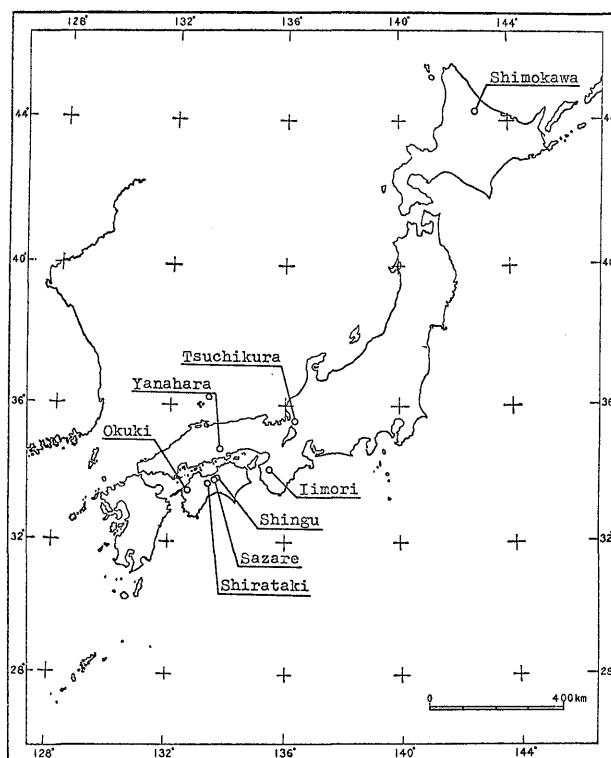


Fig. 1 Location map of mines.

2. Description of the samples studied

2.1 Shimokawa mine

The deposit of the Shimokawa mine, Hokkaido, occurs stratigraphically between slate and diabase of Hidaka Formation of pre-Cretaceous age (USHIZAWA, 1956 a; SAWA, 1958; MIYAKE, 1961; ISHIO and KUBOTA, 1969; BAMBA et al. 1970; IKEDA et al. 1971). The ores of this deposit are composed mainly of pyrite, chalcopyrite, pyrrhotite, and sphalerite. Valleriite, cubanite and cobalt minerals are often found as accessory minerals (USHIZAWA, 1956 b; MIYAKE, 1965). It is considered that this deposit is unmetamorphosed. The cobalt minerals found in this deposit are cobalt-pentlandite (KATO and SATO, 1963) and cobalt-makinawite (NAKAMURA and MARIKO, 1967).

The analysed sample, No. 1412, is a compact ore from No. 13S mining section of -2 sublevel, Honpi orebody. The sample occurred about 5 m from the foot wall which was diabase. The pyrite in the sample is xenomorphic. These pyrites can be classified into Py II of MIYAKE (1965) or Py Ic of BAMBA et al. (1970).

2.2 Yanahara mine

The deposits of the Yanahara mine, Okayama Prefecture, are enclosed between meta-diabase and slate of Permian age (OSHIMA, 1958, 1964; MAKI et al. 1961). The country rocks and probably the deposits suffered strong thermal metamorphism. The ores are composed almost solely of pyrite in the larger parts of the deposits and they become rich in pyrrhotite, magnetite and chalcopyrite in the outer parts. The relation between thermal metamorphism and the formation of pyrrhotite and magnetite of the deposits has been discussed (HIGASHIMOTO, 1958, 1962; TSUSUE, 1962; HAYASE and MARIKO, 1961; MUKAIYAMA et al. 1970). It is not clear whether the deposits underwent dynamic metamorphism and if they did suffer such metamorphism, it is considered that such metamorphism was very weak (MAKI et al. 1961).

Sample No. 1205 is a brecciated ore from the 21st level of the lower part of the Yanahara main orebody. Sample No. 1926 is a massive ore from the 27th level of the same orebody as No. 1205. From the spectrochemical data, both samples are classified into the highest cobalt content group in the deposits (cf. YAMAMOTO et al. 1968).

2.3 Tsuchikura mine

The deposits of the Tsuchikura mine in Shiga Prefecture, Central Japan, occur in the sheared zone of Paleozoic formations and consist of many orebodies of various sizes (HATANAKA, 1965; ITOH and KANEHIRA, 1967). The deposits were very weakly metamorphosed if at all. The ores of the deposits are generally compact and are mostly composed of pyrite and chalcopyrite with little amounts of sphalerite and bornite. The grain size of pyrite is commonly very fine.

Analysed sample, No. 23 is from Honpi orebody, +2nd level, 260 mining section. The sample was collected from the position in contact with the country rock which was black slate, and this is classified in higher cobalt content group (ITO and KANEHIRA, 1967).

2.4 Okuki mine

The deposits of the Okuki mine of western Shikoku occur in the green rock formation which is a part of the upper Paleozoic Chichibu geosynclinal piles (WATANABE et al. 1970). The deposits were weakly metamorphosed (KANEHIRA, 1971). Ores from the deposits generally

consist of fine-grained pyrite and chalcopyrite with sphalerite and bornite.

Sample No. 1308 is a massive ore from West No. 2 mining section, the 2nd sublevel, Showa adit. This sample is relatively high in sphalerite content. Sample No. 1917 is from the 30th level of Odo adit and has relatively high chalcopyrite content.

2.5 Shingu mine

The deposits of the Shingu mine in central Shikoku are enclosed in green schist of the lowermost part of Minawa Formation, and consist mainly of three orebodies of pole-like form (MITSUNO, 1953). Because the country rocks of the deposits are of non-spotted zone and far from the spotted zone, it is considered that the metamorphic grade of the deposits is comparatively low.

Sample No. 3009 is a massive ore from No. 47 mining section, Daiichi-uwaban orebody. The sample occurred at 30 cm from the hanging wall, where the thickness of the orebody was about 2 m.

2.6 Iimori mine

The deposits of the Iimori mine on Kii Peninsula occur within Iimori Formation which is a part of Sambagawa crystalline schists and consist mainly of spotted green schists originated from basic pyroclastic rocks and volcanics. The ores from the deposits are classified into two types, massive and banded, and are thoroughly recrystallized (KANEHIRA, 1970b). The massive ore consists of pyrite with chalcopyrite, sphalerite and gangue minerals. The banded ore is composed of pyrite and gangue minerals and minor amounts of chalcopyrite and sphalerite. The metamorphic grade of country rocks of the deposits ranges from glaucophane-schist to epidote-amphibolite facies (KAMIYAMA et al. 1964; KANEHIRA, 1970b).

The sample No. 37 is a massive ore from No. 69 mining section of the 12th level. This sample was collected from the position in contact with the hanging wall.

2.7 Sazare mine

The deposits of the Sazare mine in central Shikoku occur in spotted green schist which constitutes either the upper part of middle Minawa Formation (KIKUCHI et al. 1967; DOI, 1959, 1962) or the lowermost part of upper Minawa Formation (KOJIMA et al. 1956). In the Sambagawa metamorphic terrain of Shikoku region, roughly speaking, the metamorphic grade increases successively from the lower to the upper formation (BANNO, 1964; TAKEDA, 1970). The metamorphic grade of the country rock of the Sazare deposits corresponds to glaucophanitic green-schist facies (TAKEDA, 1970) or transitional zone between glaucophane schist and epidote amphibolite facies (BANNO, 1964). As regards metamorphic grade, it is believed that the Sazare deposits are similar to the Iimori deposits described above.

Sample No. 3065 is a massive ore from E7 mining section of the 21st level, Kinsen orebody. The sample was collected from the central part of the orebody which thickness was about 40 cm. Sample No. 3067 is a massive ore with abundant chalcopyrite, which is from E9 mining section of the 21st level, Kinsen orebody. The thickness of the orebody at the sample No. 3067 occurred was 7 cm.

2.8 Shirataki mine

The deposits of the Shirataki mine in central Shikoku occur in spotted amphibolite schist of the upper part of Minawa Formation. The deposit is one of the highest metamorphosed

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deposits in Japan (TAKEDA, 1960, 1970; ITOH, 1971b). The metamorphic grade of the deposits corresponds to epidote amphibolite facies (TAKEDA, 1970; BANNO, 1964). The ores of the deposits consist of pyrite, chalcopyrite and sphalerite with minor amounts of bornite and chalcocite.

Sample No. 6044 with abundant chalcopyrite was collected from the position in contact with the hanging wall at No. 141 mining section of the 23rd level (see ITOH, 1971b). Sample No. 3012 is a massive ore with coarse-grained pyrites and is from No. 145 mining section of the 25th level.

3. Experiment

The many ore samples from the cupriferous pyrite deposits in Japan were spectrochemically analysed and those with higher cobalt content were selected for this study from each mine.

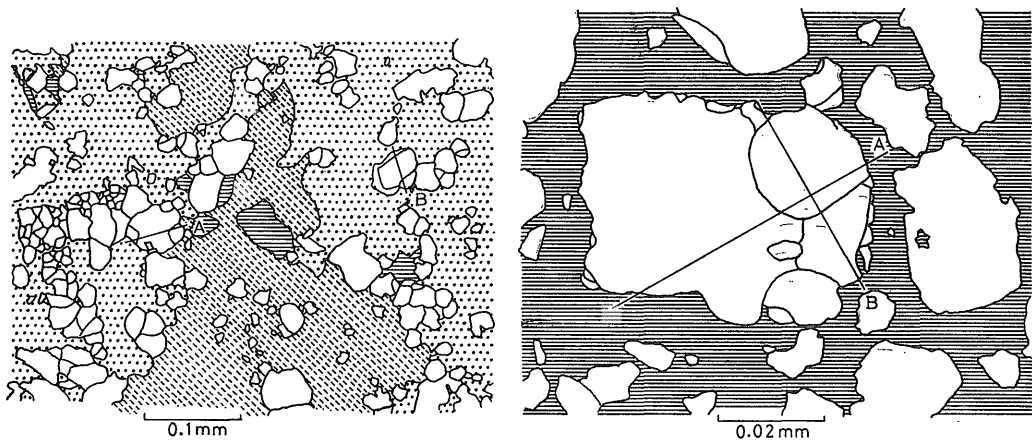
Model JXA-3A EPMA was used for the measurements. The conditions of measurement were as follows;

accelerating voltage	25 KV
electron beam diameter	2 microns
specimen current	0.1 μ A

After EPMA measurement, the samples were repolished and etched by HNO_3 solution. The grain boundaries and growth lines that appeared by etching were considered during the interpretation of EPMA data.

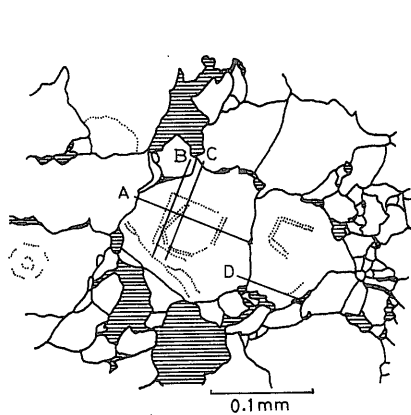
4. Results of experiment

The etched figures and analysed lines of the samples are shown in Fig. 2a-m. The EPMA line profiles which correspond to the lines shown in the etched figures are Fig. 3a-m. The values of vertical line (the Y axis) in Fig. 3 are from semiquantitative analyses with the error of about 15%.

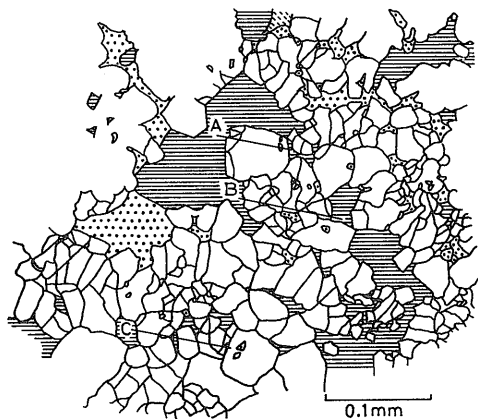


2a Shimokawa 1412

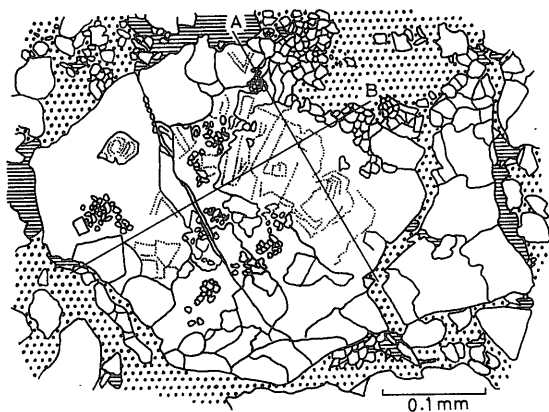
2b Yanahara 1205



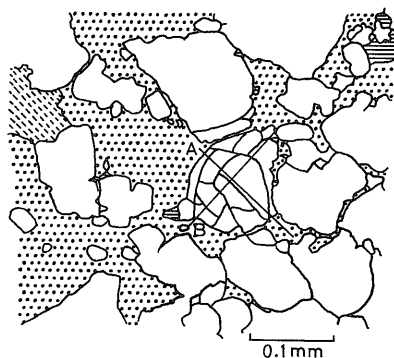
2c Yanahara 1926



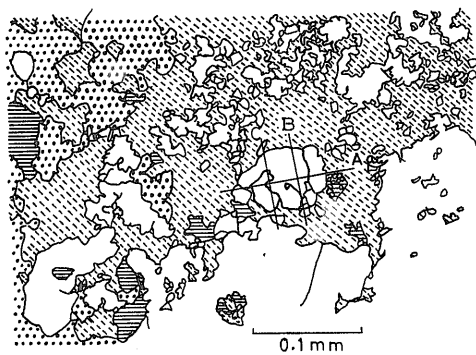
2f Okuki 1917



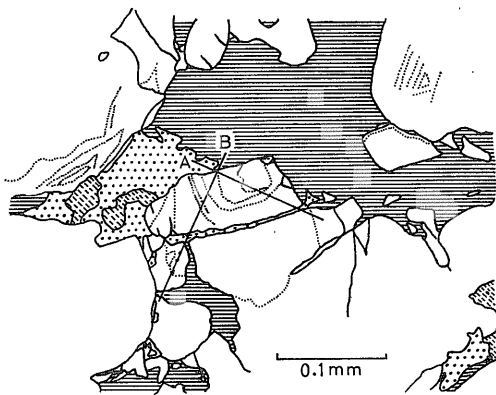
2d Tsuchikura 23



2g Shingu 3009

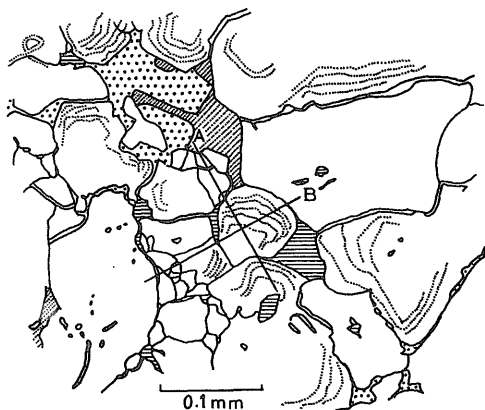


2e Okuki 1308

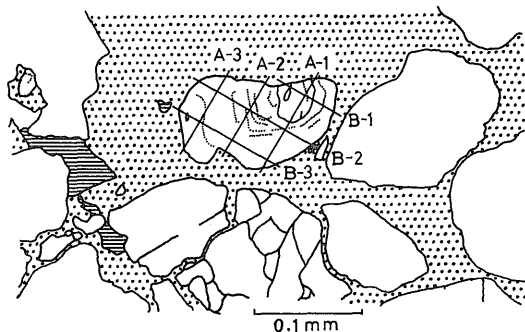


2h Iimori 37

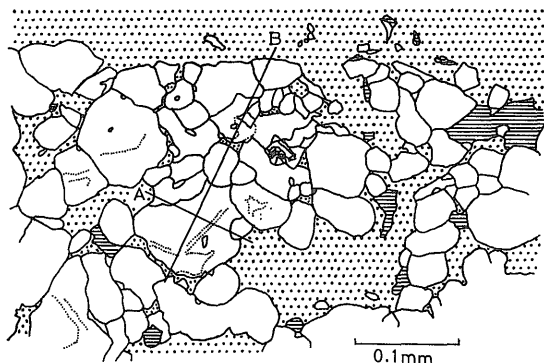
Distribution of Cobalt in Pyrites from Some Cupriferous Pyrite Deposits (ГРОН С.)



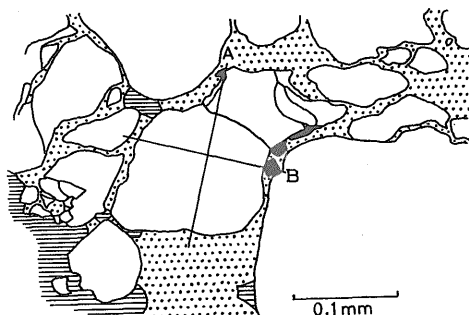
2i Sazare 3065



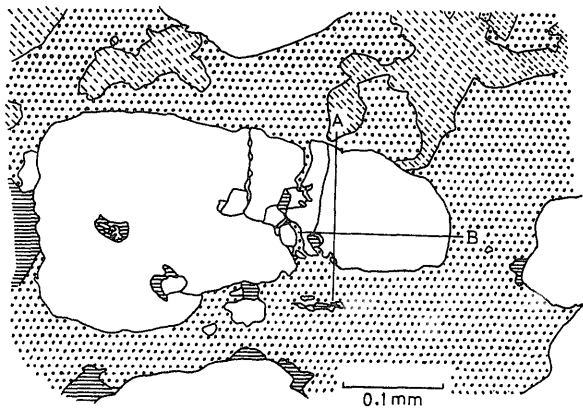
2l Shirataki 3012



2j Sazare 3067



2m Shirataki 3012



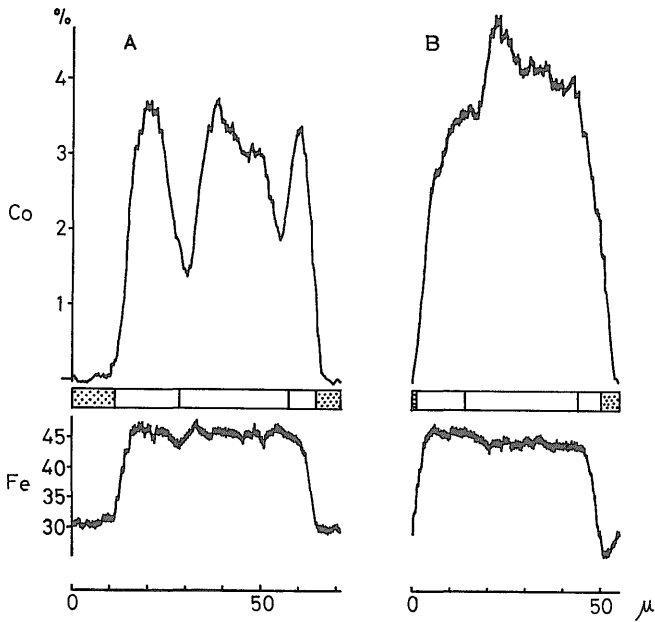
2k Shirataki 6044

LEGEND

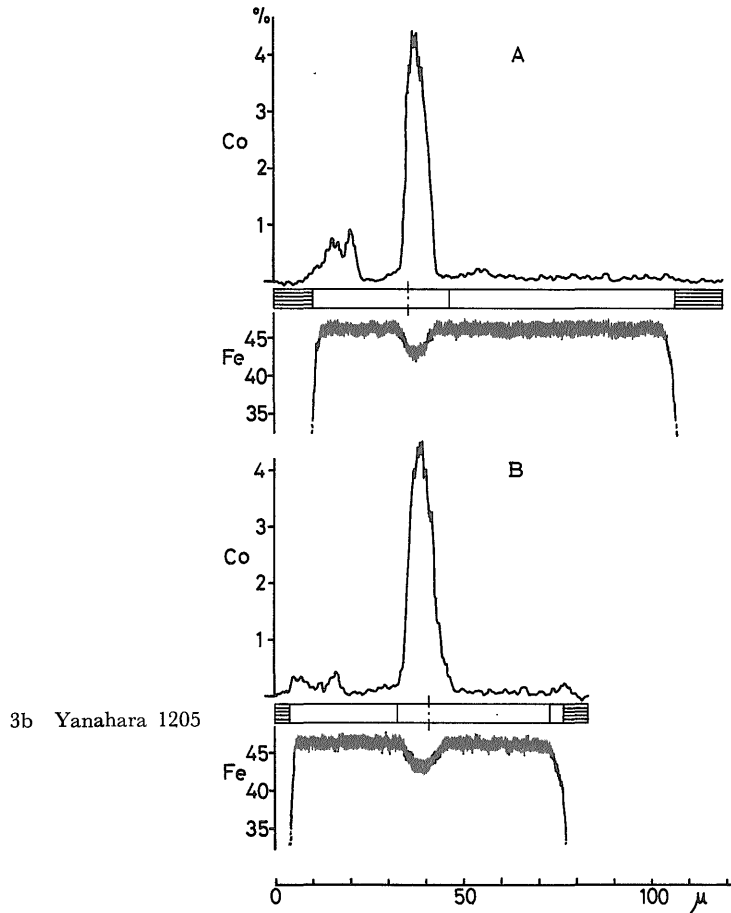
- Pyrite
- Chalcopyrite
- Sphalerite
- Gangue
- Bornite
- Carrollite
- Grain boundary
- Crystalline growth line
- Intersection of scanning line

This Legend has reference to Figs. 2a-m and Figs. 3a-m.

Figs. 2a-m Etched figures indicating EPMA scanning lines.

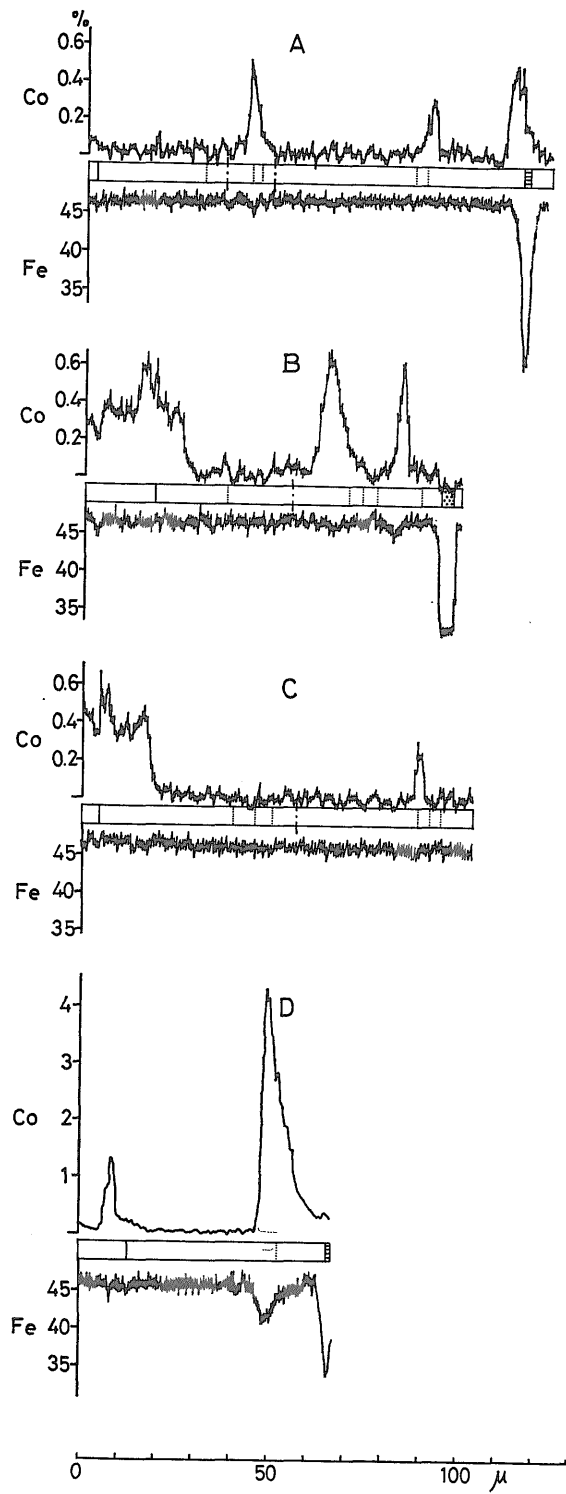


3a Shimokawa 1412

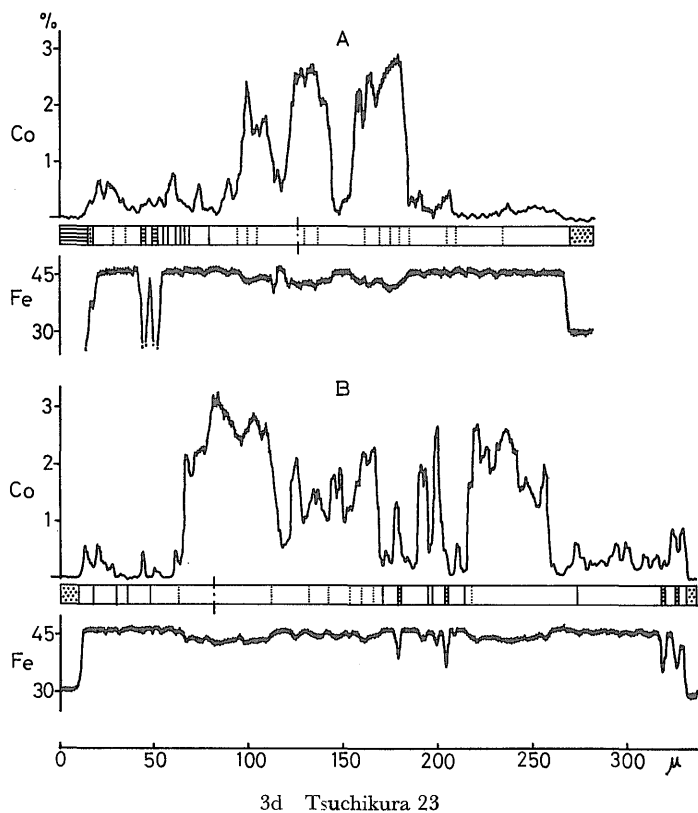


3b Yanahara 1205

Distribution of Cobalt in Pyrites from Some Cuprififerous Pyrite Deposits (Itoh S.)



3c Yanahara 1926



Shimokawa 1412

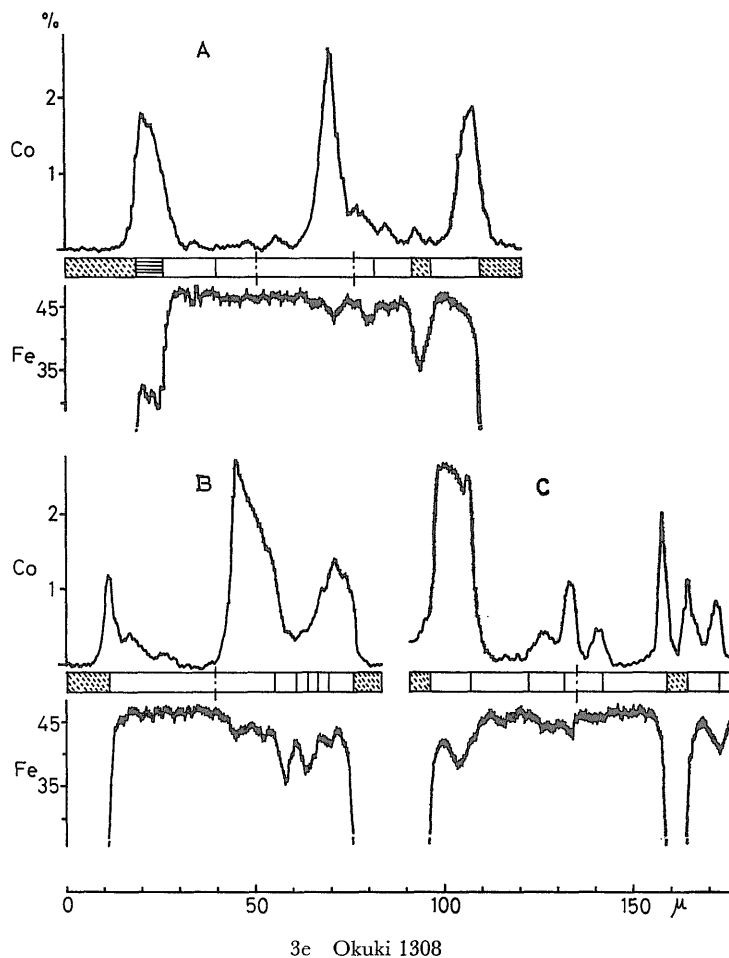
EPMA line profiles of the sample show sharp decrease in cobalt content at the grain boundaries which appeared by etching, resulting in the parabolic shape as in Fig. 3a A. The low cobalt content at the grain boundary of pyrites indicates that the rim of each pyrite of the Shimokawa mine is cobalt-poor. Such distribution of cobalt in pyrite consists with the theoretical consideration of SPRINGER et al. (1964) as will be discussed later.

Yanahara 1205

The etched figure, results of line scanning and EPMA X-ray image of this sample are shown in Figs. 2b, 3b and 4. The extremely localized concentration of cobalt as compared with the pyrite from Shimokawa is recognized in these figures. As shown in Fig. 3b, this point does not agree with the grain boundary, and the low iron content at this point is clearly seen. The high cobalt and low iron content at this point strongly suggest substitution of iron by cobalt in pyrite.

Yanahara 1926

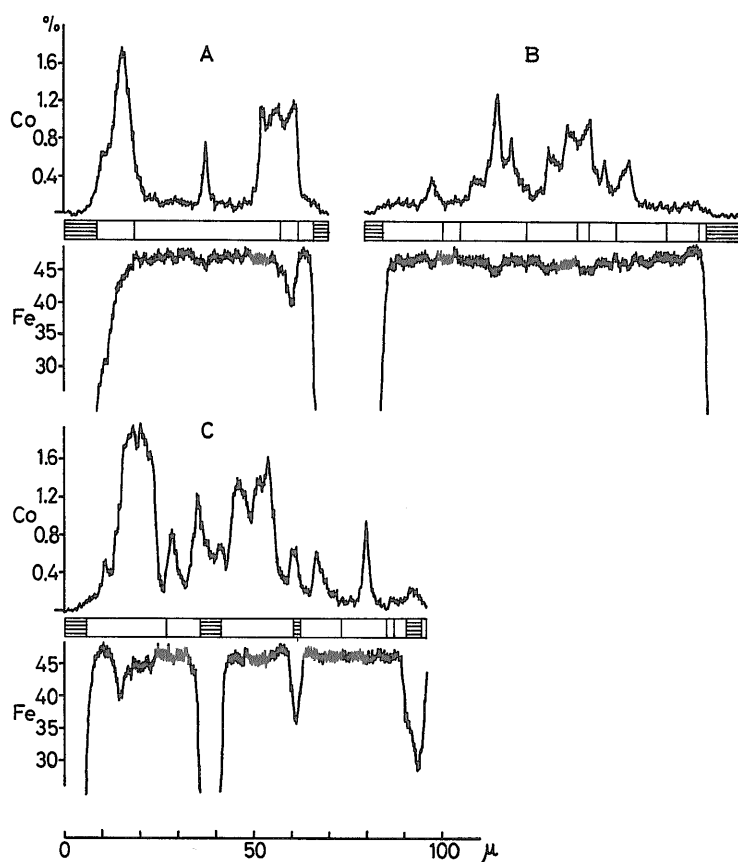
The absorbed electron image of the sample, Fig. 5, shows a pentagonal structure in the centre with heavier average atomic number than those of the surrounding normal pyrite. The structure can also be seen in the etched figure (Fig. 2c). The EPMA line profiles show the high



cobalt content at these positions (Fig. 3c). These facts suggest that at a certain stage of the growth of pyrite pentagonal dodecahedron, cobalt simultaneously deposited on the crystal surface. Besides these zonal distribution, cobalt is locally distributed about the grain boundaries, as seen in the left part of profiles B and C, and strongly concentrated at the points on line D, as in the case of No. 1205.

Tsuchikura 23

The etched figure of this sample shows complex grain boundaries and growth pattern (Fig. 2d). The results of EPMA line scanning also show irregular distribution of cobalt (Fig. 3d). However, some growth centres which can be inferred from the etched pattern seem to agree with cobalt concentration. Thus, it can be concluded from these results that the cobalt was enriched in the early stages of pyrite crystal growth in the case of pyrites of these deposits. This apparently agrees with the SPRINGER's consideration as same as the case of Shimokawa.



3f Okuki 1917

Okuki 1308

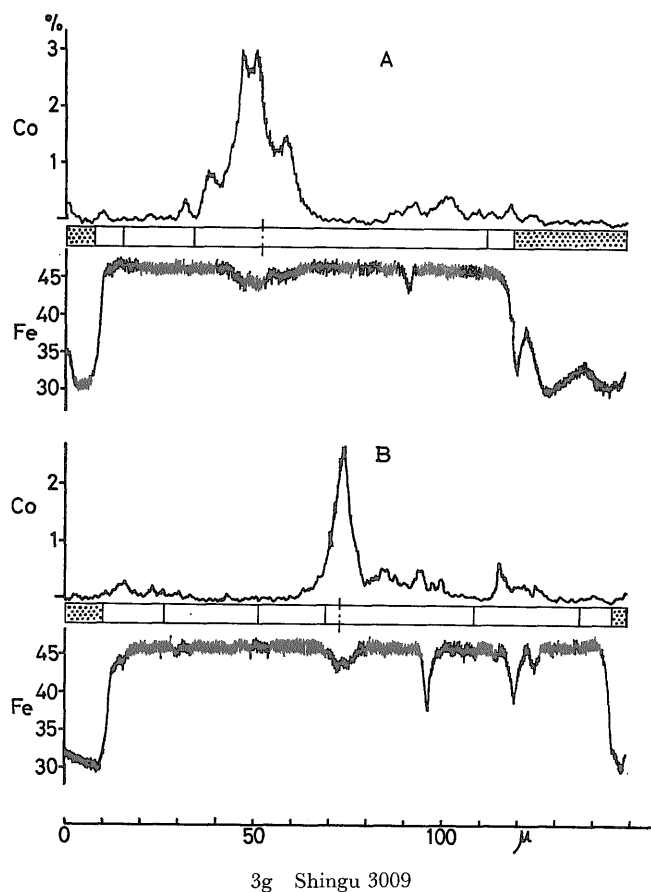
The cobalt distribution of the sample shows considerable variation (Fig. 3e), in spite of the small grain size of analysed pyrite as seen in Fig. 2e. The relationship between the cobalt distribution and grain boundaries is not clear. On the left side of EPMA profile of A line the amount of iron is abnormally low for pyrite, notwithstanding that the position concentrates cobalt. This anomaly in iron content is due to dilution by surrounding materials because of the fine grain size of pyrite.

Okuki 1917

The analysed part of this sample contains comparatively a large amount of gangue minerals (Fig. 2f). Although the cobalt content of the sample is less than that of No. 1308, the distribution shows similar variability in both samples. The relationship between this variation and grain boundaries seems to be obscure (Fig. 3f).

Shingu 3009

As seen in Fig. 3g, the results of measurement show that cobalt is distributed in a limited area around the intersection of scanning lines. Although grain boundary appeared in the



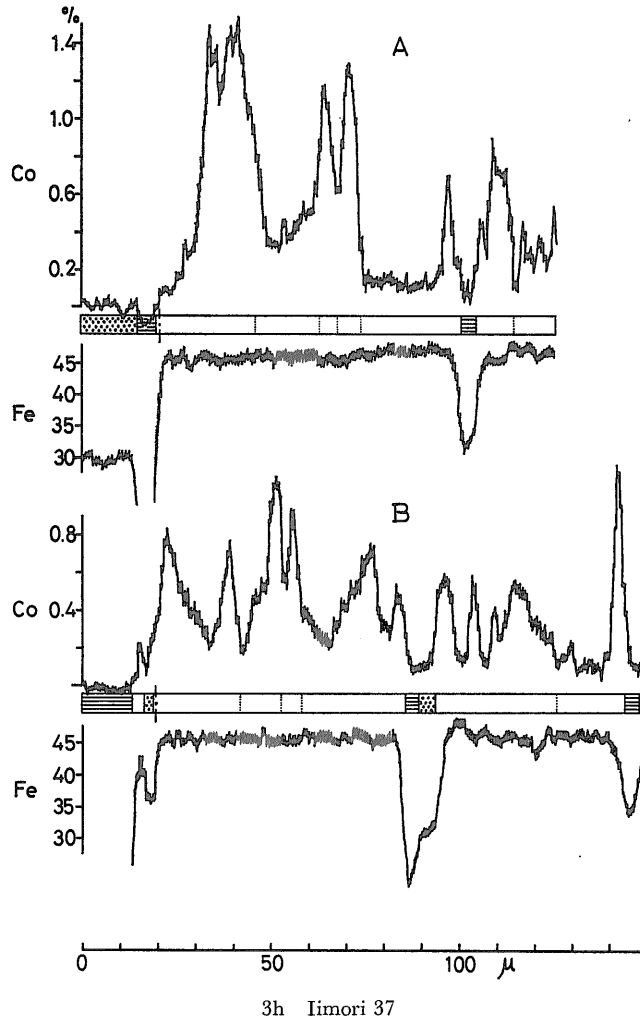
vicinity of this area (Fig. 2g), on the other boundaries in the pyrite the cobalt enrichment is not recognized. In addition, almost all of neighbouring pyrites show low cobalt content. From these observations, it can be suggested that the cobalt was concentrated in very localized positions.

Imori 37

The results of line analyses show that the cobalt distribution in pyrites of the sample differs somehow from those of the other samples described above (Figs. 2h and 3h). That is; 1) the relationship between cobalt distribution and grain boundaries (and/or growth lines) is clear, and 2) some peaks of cobalt in Fig. 3h have steep outside slope and slightly gentler inside one. These observations seem to indicate the direction of movement of cobalt atoms in pyrite during recrystallization. However, this tendency is not yet so clear, because probably of the weaker recrystallization of the sample than those of the Shirataki deposits as will be described later.

Sazare 3065

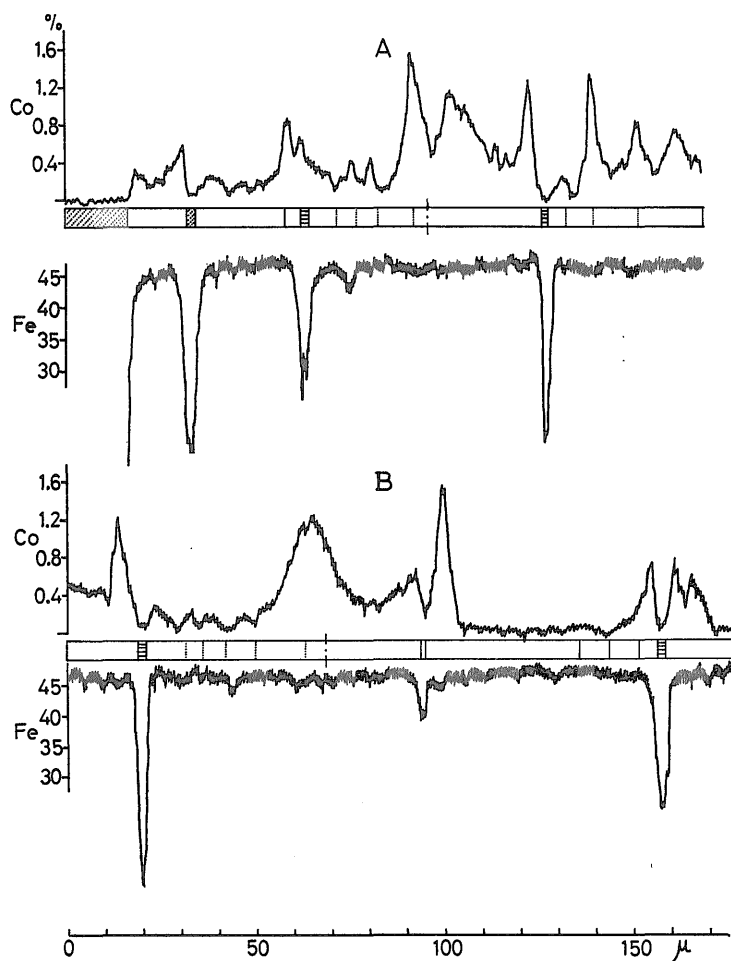
As seen in Fig. 2i, the concentric growth pattern is distinctly shown by etching. The



characteristics on the distribution of cobalt are similar to that of the Iimori 37.

Sazare 3067

This sample shows the mosaic etched figure and does not show the concentric growth pattern like the sample No. 3065 (Fig. 2j). The EPMA line scanning showed the relationship between the cobalt distribution pattern and the etched figure (Fig. 3j). Especially, the EPMA profile of B line is similar to that of Shirataki 3012. However, there are some cobalt peaks in the inner parts of pyrite crystals. They seem to indicate that the metamorphism of the Sazare deposits was not intense enough to form homogenized crystals in relation to cobalt content in the inner parts of pyrite.



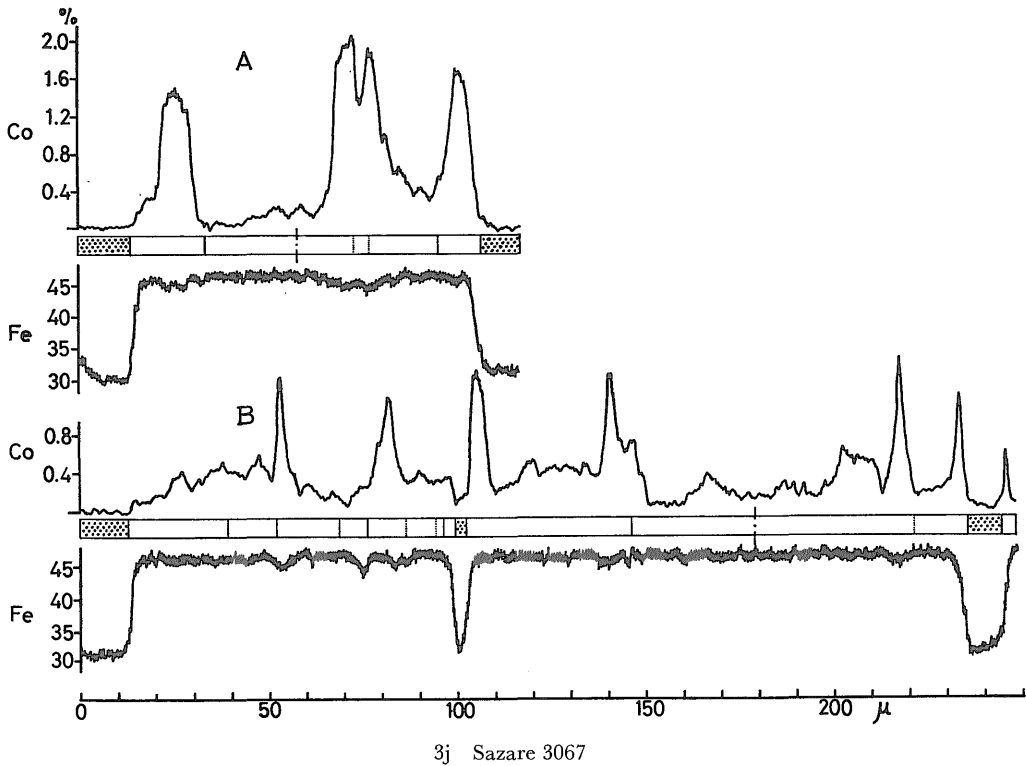
3i Sazare 3065

Shirataki 6044

As seen in Fig. 2k, the pyrites in this sample were resistant to etching. The distribution of cobalt in the pyrite is remarkably homogeneous in magnitude of about 0.4%, except the small pyrite grain at the right end of pyrites of line A in Fig. 3k. Such distribution is unique among the samples of the other deposits described above.

Shirataki 3012

Although the analysed pyrite of this specimen is a small grain, the concentric growth pattern and grain boundaries were clearly shown by etching as seen in Fig. 21. The results of EPMA line scanning show that cobalt is concentrated in very thin rims of the pyrite and the content is homogeneous in inner parts (Fig. 31). Both A-1 and B-1 line profiles cut across the enclosed pyrite and show the difference in cobalt content between the host and enclosed pyrite.



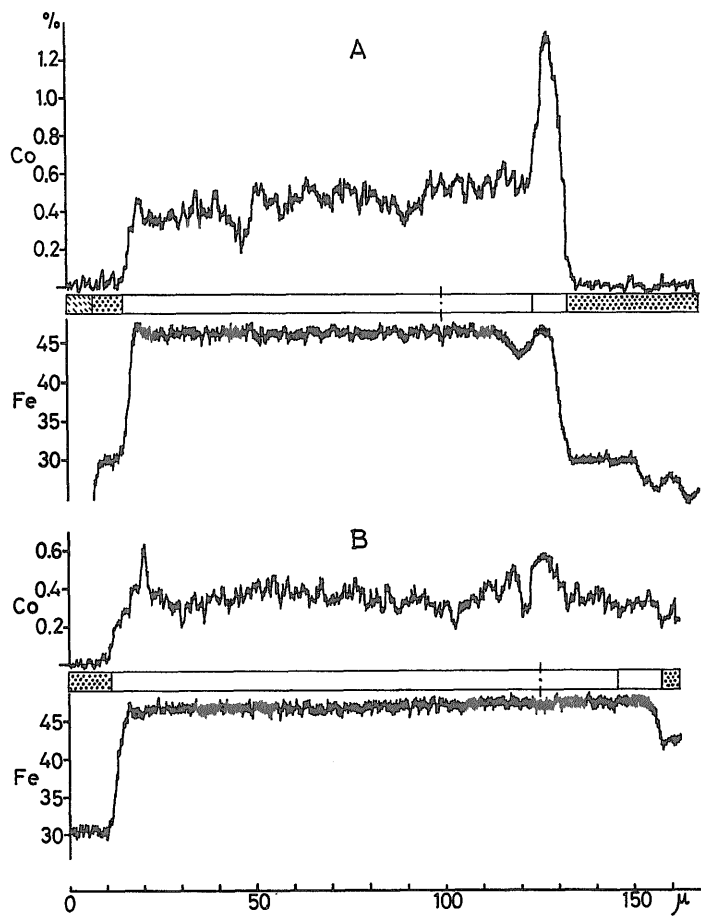
The cobalt mineral was found in this specimen, the details of which will be described in the following section.

5. Cobalt mineral in the Shirataki deposits

In the cupriferous pyrite deposits in Japan, with the exception of the Shimokawa and Besshi deposits, no cobalt minerals have been reported in spite of their high cobalt content. From microscopic observations and electron probe microanalyses of ores from the Shimokawa deposits, KATO and SATO (1963) found cobalt-pentlandite which occurs generally in pyrrhotite. NAKAMURA and MARIKO (1967) also reported that in the same deposits cobaltian mackinawite and un-identified cobalt mineral were detected by the electron probe microanalyser. KASE (1972) reported the occurrence of cobaltite in the ores from the lower parts of Besshi deposit, in which pyrrhotite was a predominant mineral and it was believed that the pyrrhotite was formed from pyrite by thermal metamorphism.

The sample containing the cobalt mineral was collected from No. 145 mining section of the 25th level of the Shirataki deposits and is a massive ore with coarse pyrite grains. As shown in Fig. 2m, the cobalt mineral occurs in chalcopyrite filling the interstices of pyrites and usually is in contact with pyrite. All of the mineral grains in this specimen are less than 0.02 mm in diameter. Other observations of the mineral under the microscope are as follows:

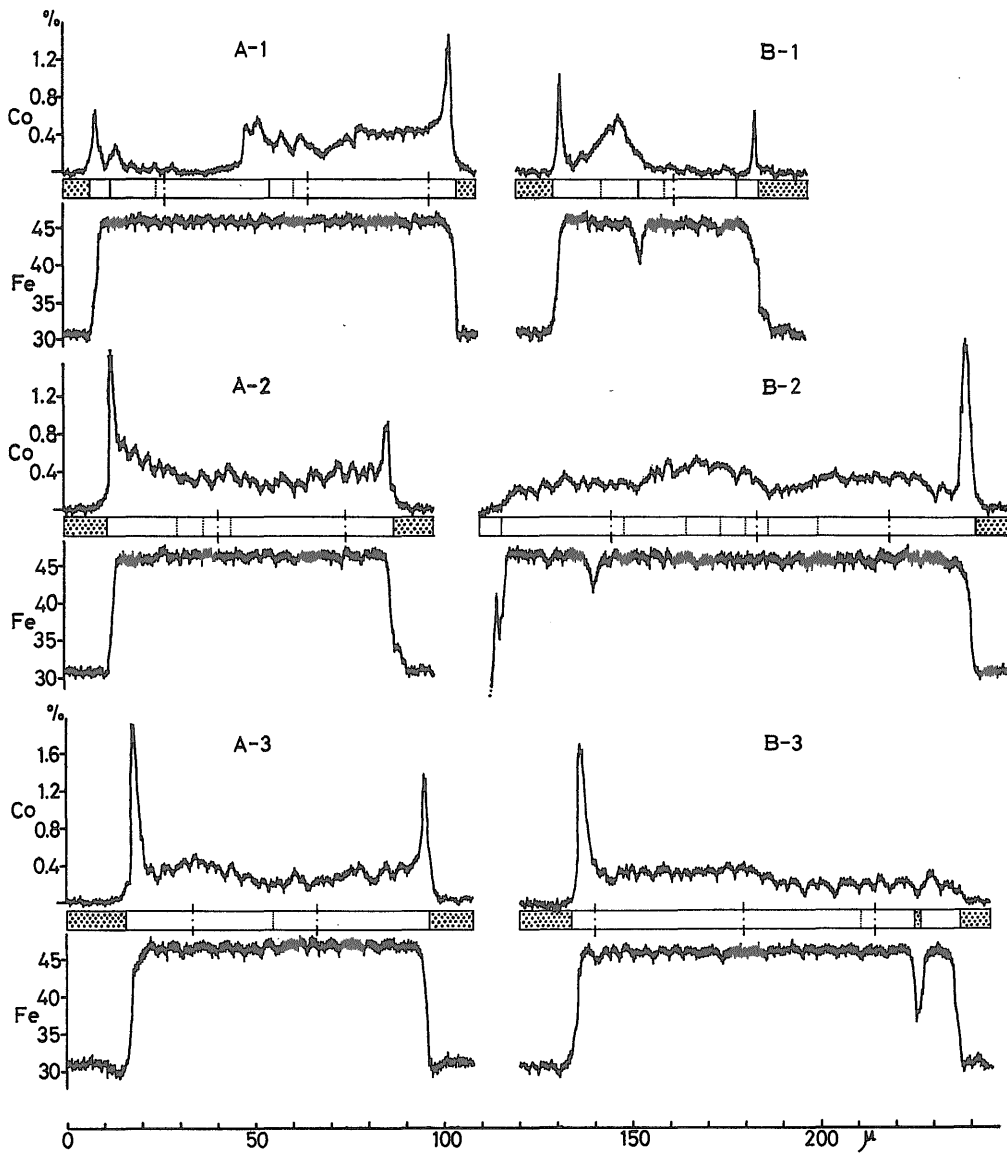
Distribution of Cobalt in Pyrites from Some Cupriferous Pyrite Deposits (Iron S.)



3k Shirataki 6044

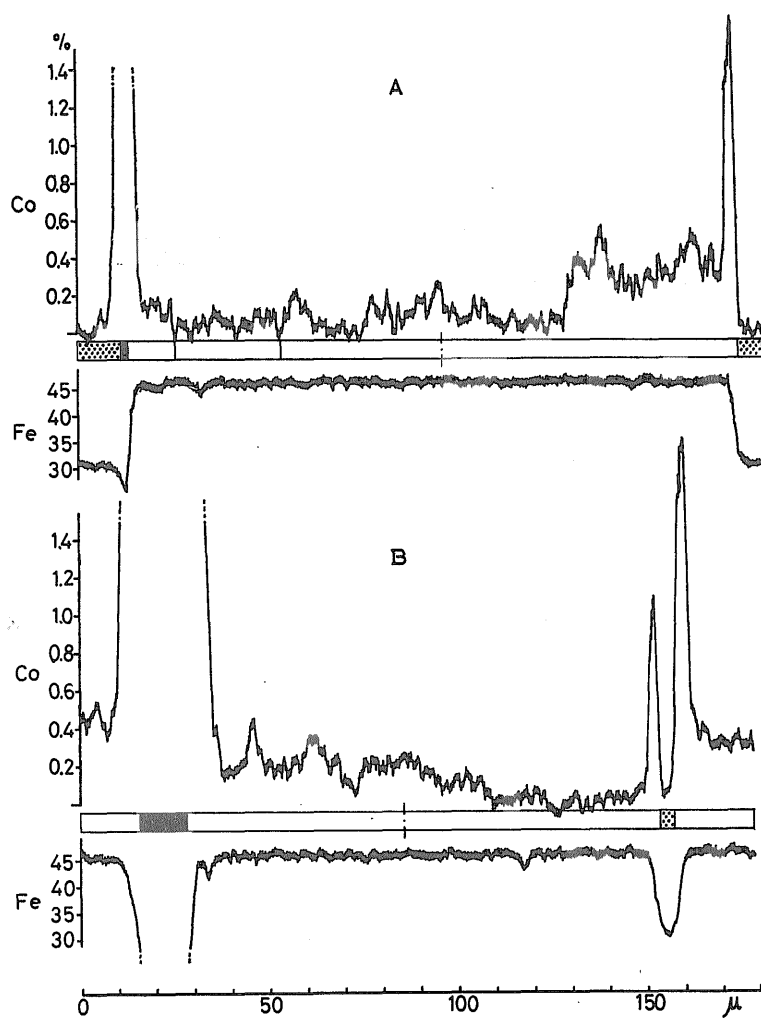
Colour:	Creamy white with slight pinkish tint.
Reflection pleochroism:	None.
Anisotropy:	None.
Internal reflection:	None.
Polishing hardness:	≥ chalcopyrite, < pyrite.

The quantitative analysis of this mineral was made by the electron probe microanalyser. The result of analysis is shown in Table 1. The atomic ratio indicates that this mineral is carrollite, Co_2CuS_4 , with small amounts of iron and nickel substituting copper. The optical natures of the mineral also agree with carrollite.



31 Shirataki 3012

Distribution of Cobalt in Pyrites from Some Cupriferous Pyrite Deposits (Itoh S.)



3m Shirataki 3012

Figs. 3a-m EPMA line profiles along the lines corresponding to those in Figs. 2a-m.

Table 1 Chemical composition of cobalt mineral,
(analyst: Y. SHIMAZAKI)

	Wt. %	Atm. ratio	
Co	39.9	0.677*	1.0
Cu	15.8	0.249	0.4
Ni	1.4	0.024	0.05
Fe	1.1	0.020	0.05
S	42.7	1.332	2.0
total	100.9		

Carrollite: Co_2CuS_4

* the value divided Wt.% by each atomic weight

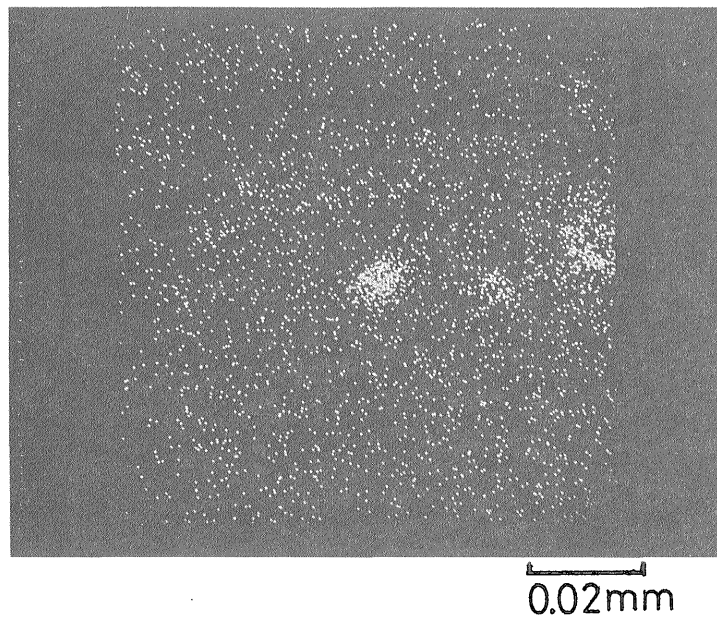


Fig. 4 Characteristic X-ray image by Co $K\alpha$ of sample "Yanahara 1205."

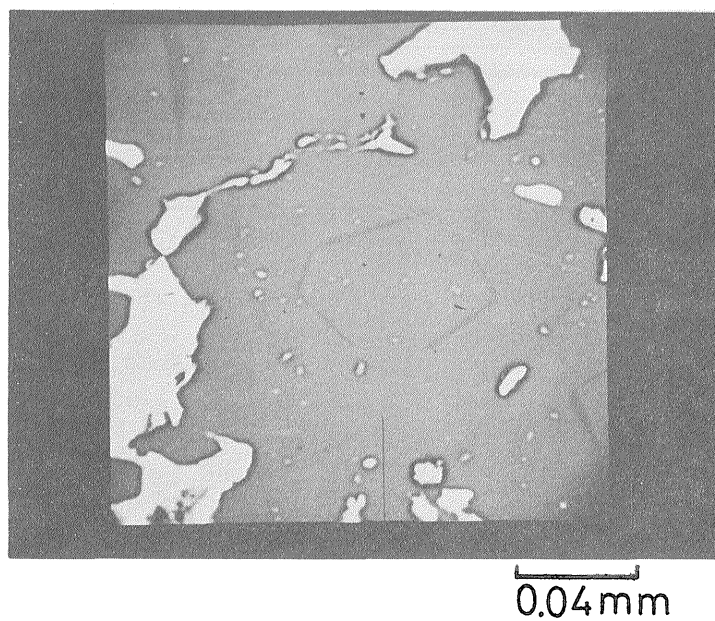


Fig. 5 Electron absorption image of sample "Yanahara 1926."

Carrollite is a member of linnaeite group together with siegenite. Carrollite is a very rare mineral reported only from some deposits of Central African copper-belt (e.g. Camoto mine by BARTHOLOME et al., 1971 and Chibuluma mine by DARNLEY and KILLINGWORTH, 1962), Raipas mine, Norway, (VOKES, 1956) and Carroll County of Maryland, U.S.A. (SHANNON, 1926).

KANEHIRA and TATSUMI (1970a) reported that they were informed of the occurrence of carrollite from the ores of the Sazare deposits by NAKAYAMA. ITOH and ENDO (1972) reported the occurrence and chemical composition of carrollite from the Shirataki mine. This was the first mineralogical report of the occurrence of this mineral in Japan. The details of this mineral will be reported in the near future by the writer.

It is seen from the examples of EPMA line profiles shown in Fig. 3 m that cobalt is evidently concentrated in the margin of pyrite grains. While it is not clear in the margin of the side of pyrite grain in contact with carrollite because it is hidden by the strong peaks of carrollite. However, from the consideration of relationships between distribution of cobalt and metamorphic grade the author believes that the cobalt mineral was formed by the reaction between chalcopyrite and cobalt migrated to the edge of pyrite during intense metamorphism. The small grain size of the mineral is also thus explained.

6. Discussion

As described in section 4, in the unmetamorphosed deposits, such as the Tsuchikura mine, cobalt in pyrite is distributed very heterogeneously. In the case of low-metamorphosed deposits, such as the Okuki mine, the distribution is again heterogeneous. In the relatively high-metamorphosed deposits, such as the Sazare mine, the cobalt atoms in pyrite seem to have migrated towards the margin of grains. Finally, in the highest metamorphosed deposit in Japan, the Shirataki mine, the marginal zone of pyrite is commonly enriched in cobalt and the inner zone is homogeneous with the content of about 0.4% Co. These facts indicate that cobalt atoms migrated within pyrite during regional metamorphism, and that the cobalt mineral carrollite found in the Shirataki mine was formed by neomineralization.

In the previous work the author (1971b) showed that the Co/Ni ratio in pyrites increased with the grade of metamorphism while that in co-existing Mg-silicate minerals (e.g. chlorite) had a tendency to decrease. From these facts the author inferred that nickel was expelled from pyrite and enriched in Mg-minerals by recrystallization, while cobalt remained in the pyrite lattice during metamorphism.

In this work the behaviour of nickel, unfortunately, could not be determined due to its insufficient content in pyrite for the electron probe microanalysis. However, from the results of both previous and present works, it is reasonable to infer that the nickel in pyrite can be moved more easily than cobalt by regional metamorphism.

Cobalt was not detected in other ore forming minerals, such as chalcopyrite, sphalerite, bornite and gangue minerals. This indicates that during ore deposition the majority of cobalt ions entered pyrite lattice. In many cases, the inverse relation is observed in iron and cobalt contents in the analysed pyrites. Although quantitative analyses have not been carried out, semi-quantitative works suggest that this fact shows isomorphous substitution of cobalt for

iron in pyrite. Thus these facts show strong crystal chemical similarity between cobalt and iron or cobalt disulfide and iron disulfide.

SPRINGER et al. (1964) investigated experimentally the $\text{FeS}_2\text{-CoS}_2\text{-NiS}_2$ system by hydrothermal method. They also considered theoretically the solid solution of Fe, Co and Ni disulfides. From these experiments and considerations, they concluded that complete solid solution between the three disulfides was probable, and that the zonal structure of natural bravoite, $(\text{Fe, Co, Ni})\text{S}_2$, could be explained on the basis of solubilities of the three disulfides. According to their results, cobalt disulfide crystallized earlier than iron disulfide and was therefore concentrated in the innermost part of pyrite. However, the cobalt distribution of unmetamorphosed pyrite in this work, with the exception of some cases of Shimokawa and Tsuchikura deposits, does not show such a pattern and is commonly irregular.

On the other hand, the size of un- and low-metamorphosed pyrites in cupriferous pyrite deposits is generally very small, and the pyrite grains become larger with the increase of metamorphic grade by recrystallization (KANEHIRA and TATSUMI, 1970a). These facts seem to indicate that the deposition of sulfide ores was very rapid under disequilibrium conditions and possibly both cobalt and iron sulfides precipitated simultaneously, in spite of some differences between two sulfides as indicated by SPRINGER et al. Also the rapid deposition could be one of the causes of the heterogeneous distribution of cobalt in pyrites.

During the recrystallization of ore minerals by regional metamorphism, cobalt atoms evidently migrated within pyrite crystals. It is believed that the migration is mostly due to the differences of ionic size between iron and cobalt, because it can be imagined that under high pressure the minor atoms of different sizes are expelled outward by major atoms.

The mechanism of recrystallization of ore minerals is still essentially unknown. MIYASHIRO (1965) mentioned the following three causes of recrystallization; 1) to reorganize distortion within the crystals, 2) to reduce the surface free energy of mineral grains, and 3) to form new stable minerals from the pre-existing minerals which became unstable due to the changes of external conditions.

The second of these three causes is important in regard to the fact that the pyrite grain size of cupriferous pyrite deposits increases with metamorphic grade. Under the condition of high stress of metamorphism, the fine-grained pyrites grow to larger crystals by the assimilation of surrounding pyrites, for which they reduce their total surface free energy. This is one of the reasons of coarse grain of high-metamorphosed pyrites.

In the case of such a mechanism of recrystallization, it can be inferred that the minor elements in pre-existing minerals are left out from the assimilation. The degree of the phenomenon may increase with differences of ionic radii between minor and major atoms and the grade of metamorphism. The distributions of cobalt in pyrites from high-metamorphosed deposits, which have been described above as a result of migration of atoms, may be interpreted by such a mechanism of recrystallization.

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含銅硫化鉄鉱床の黄鉄鉱におけるコバルトの分布

——とくに変成度との関連について——

伊藤 司郎

要 旨

わが国の含銅硫化鉄鉱床の黄鉄鉱中における Co の分布について EPMA を用いて検討した。その結果、未変成および低変成度の鉱石においては著しく不均質な分布を示した。もっとも変成度の高い鉱石では、Co は黄鉄鉱粒子の周縁に濃集し、黄鉄鉱粒子の内部で均質な分布形態を示した。中間の変成度の鉱石では、Co の分布形態も中間的であった。このような黄鉄鉱の Co の分布形態と変成度との関係は、変成作用によって黄鉄鉱が再結晶する際に、結晶内で Co 原子が移動することおよびその移動方向を暗示していると考えられる。

白滝鉱床の鉱石試料で Co 鉱物、カローライトの存在を記載し、その成因を上述の Co 分布の結果に基づいて考察した。

黄鉄鉱以外の鉱石鉱物の Co 含量は EPMA の検出限界以下であった。また、黄鉄鉱の高 Co 濃集部では明らかに Fe の量が低下することを示した。これらのことは、鉱床生成に際して、鉱液中の Co のほとんどは黄鉄鉱中に配分され、黄鉄鉱中の Fe を置換して存在することを示唆する。