

Chemical Composition of Country Rocks and Minor Elements in Sulfide Minerals from Bedded Cupriferous Pyrite Deposits of Tenryu River Basin

By
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Abstract

The chemical properties of the country rocks and sulfide ores of the bedded cupriferous pyrite deposits in the Tenryu River basin were determined. Thirty-seven rock samples were chemically analyzed for major elements and 41 were spectrochemically determined for minor elements. In addition to these analyses, the minor elements in 125 sulfide ore samples were spectrochemically determined.

Comparison of chemical compositions and minor elements of the country rocks shows that the rock of Kunchonzan deposit which has been called metaporphyrite, is a basic rock similar to those of other deposits of the region. The contents of minor elements in pyrites from the deposits of the region show some differences in frequency pattern among the deposits in different formations.

It is noted that the high content of cobalt and high value of cobalt/nickel ratio in pyrite are characteristic features of the bedded cupriferous pyrite deposits in the region. The genesis of the deposits is briefly discussed on the basis of minor element distribution in sulfide ores.

1. Introduction

In the Sambagawa metamorphic zone which is distributed along the Tenryu River, there are many bedded cupriferous pyrite deposits. Some of them are shown in Fig. 1. It has been considered that these deposits were closely related to green schists which probably have been derived from basic tuffs or basic igneous rocks.

HORIKOSHI (1938) and KAMIYAMA (1959) concluded petrologically that the country rock of Kunchonzan deposit locating in the upper horizon of the stratigraphic formations of this region is metaporphyrite derived from porphyrite. Generally speaking, the porphyrite has intermediate silica content ranging from 55 to 65 per cent, whereas the basic tuffs or basic igneous rocks, the probable original rocks of common green schists, have lower silica content ranging from 45 to 55 per cent. The country rock of the Kunchonzan deposit has, therefore, a significant difference from those of other deposits. The chemical properties of this country rock, however, have not been clarified.

The main purpose of this paper is to clarify the chemical compositions of the representative rocks of the region including green schist, so-called metaporphyrite, black schist and chlorite schist. From the integrated data on country rocks will be solved some of the problems that only the Kunchonzan deposit shows the genetic relationship to comparative acidic igneous rocks or, like other deposits, this deposit also has the relationship to the country rocks derived from basic rocks.

As for the original rocks of the green schist related to the deposits, there are two contrasting

hypotheses. One holds them to be basic intrusive rocks, the other as basic tuffs or lavas which erupted into the sea bottom of geosynclinal region. The former postulates the deposits to be of epigenetic origin because the deposits were formed by activities related to the intrusion, the latter suggests syngenetic origin because the deposits seem to be concordant with the country rocks.

Since the investigations of SAGAWA (1910) and NISHIO (1910), the former hypothesis was predominant. Recently, however, some workers (WATANABE, 1957, 1965; MIYAKE, 1961, 1965; DOI, 1962) advocate syngenetic origin for bedded cupriferous pyrite deposits. It is one of the purposes of this paper to consider this problem from the standpoint of the distribution of minor elements in sulfide ores.

HEGEMANN (1943) concluded empirically that the genesis of deposits including pyrite can be determined by the bases of cobalt and nickel contents in pyrite. According to his conclusions, the high value of cobalt/nickel ratio of pyrite indicates hydrothermal origin and the homogeneities of cobalt and nickel contents in pyrite suggest the sedimentary origin.

The author (1967) showed in his previous work the pyrites from Tsuchikura mine, Shiga Pref., have higher content of cobalt than nickel and show high constancy in cobalt content. Comparison of these data on cobalt and nickel contents in pyrite with Hegemann's conclusions shows that the Tsuchikura deposit has both the hydrothermal and sedimentary characters in genesis.

Although both the Tsuchikura deposit and the deposits in Tenryu River basin are belonging to the bedded cupriferous pyrite deposits, the deposits in Tenryu River basin were suffered higher metamorphism than the Tsuchikura deposit. From these points of view, the author's attempts have been mainly made to clarify the geochemical characteristics of these deposits and to find the geochemical differences due to the difference of metamorphic grade.

2. Outline of geology and ore deposits

The geology of the region has been studied in detail by NAKAYAMA (1953, 1954) and the ore deposits were reported by HORIKOSHI (1938), HORIKOSHI and KATANO (1940), KAMIYAMA (1959) and TAKEDA (1959).

The Sambagawa crystalline schist of this region is located between two large tectonic lines, median tectonic line and Akaishi thrust, and is wedge-shaped (Fig. 1). In the western part of the region, black schist is dominant, while in the eastern part green schist is the major geological unit. The following is a brief description of stratigraphic formations of Sambagawa crystalline schist of the region.

Funayo formation: The lower limit of this formation is not clear because it is cut by Akaishi thrust. This formation is composed mainly of black schist with thickness of more than a kilometer. In this formation, mineralization has not been recognized.

Minenosawa formation: Green schist with intercalation of a few thin black schist beds is the main composite rock of the formation. It varies in thickness from 200 to 1,000 m. The facies changes to coarse-grained metadiabase or metagabbro in some parts. Minenosawa and Nako deposits occur in this formation.

Seziri formation: It consists of black schist and its thickness is about 200 to 800 m. Ore deposits have not been found.

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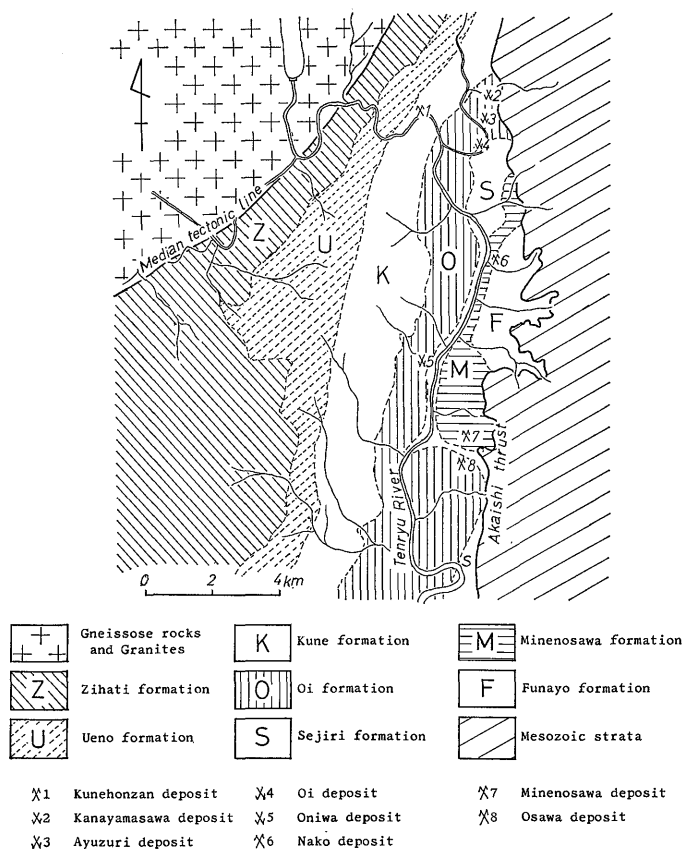


Fig. 1 Geological map of Sambagawa crystalline schist region and location of deposits in Tenryu River basin

Oi formation: The formation consists of alternating beds of green schist and black schist. Its thickness is about 400 to 1,500 m. In this formation, they occur in many small ore deposits such as Oi, Ayuzuri, Kanayama and Oniwa deposits. Facies of some parts of the green schist in this formation is metadiabase or metagabbro as in the case of Minenosawa formation.

Kune formation: The formation is composed mainly of black schist with metaporphyrite (by HORIKOSHI, 1938; KAMIYAMA, 1959), which is called "Shiroishi" by the mining engineers of Kune mine, in which Kunehonzan deposit have been discovered and developed. The estimated thickness is about a kilometer.

Ueno formation: It consists mainly of alternating beds of sericite schist and black schist, and in the lowest part, includes sandstone schist of several meters in thickness. The estimated thickness of this formation is about 350 m. Mineralization has not been recognized in the formation.

Zihati formation: This is the uppermost member of the metamorphic zone in the region. The formation is composed mainly of alternating beds of black schist and green schist which contain albite spots in some parts. In the lower part, it includes chert and crystalline limestone beds which can be used as key beds. The thickness of the formation is estimated at about 300 to 700 m. Several outcrops of ore deposit have been recognized, although they could not be developed.

There are some discrepancies concerning formation names, the following is the correlation of these names used by different authors.

Present work	Nakayama (1953)	Kamiyama (1959)
Zihati	Zihati	Kowaya
Ueno	Wasanma	Ueno
Kune	Shinkai (upper part)	Kune
Oi	Tatsuyama metadiabase (upper part)	Oi
Sejiri	Shinkai (lower part)	Owa
Minenosawa	Tatsuyama metadiabase (lower part)	Nako
Funayo	Funayo	Funayo

These formations, in general, have N40-60E strike and 30-50N dip. As a whole, they apparently have a monoclinic structure inclining to the west.

The deposits in each formation have characteristic features. The outstanding features are as follows:

- 1) The deposits in Minenosawa formation are composed mainly of banded ore and their constituent minerals are pyrite, chalcopyrite and magnetite with sphalerite. The deposits generally have larger amount of magnetite than those in other formations.
- 2) The deposits in Oi formation consist of several thin beds of sulfide ore and they are commonly small. Major ore minerals are pyrite, chalcopyrite and sphalerite with a small amount of pyrrhotite. The relative amounts of these ore minerals vary remarkably.
- 3) The deposits in Kune formation consist mainly of compact massive sulfide ore associated with a few banded ores. Constituent minerals of the deposits are pyrite, chalcopyrite, pyrrhotite and magnetite, and the deposits are characterized by high content of pyrrhotite compared with those

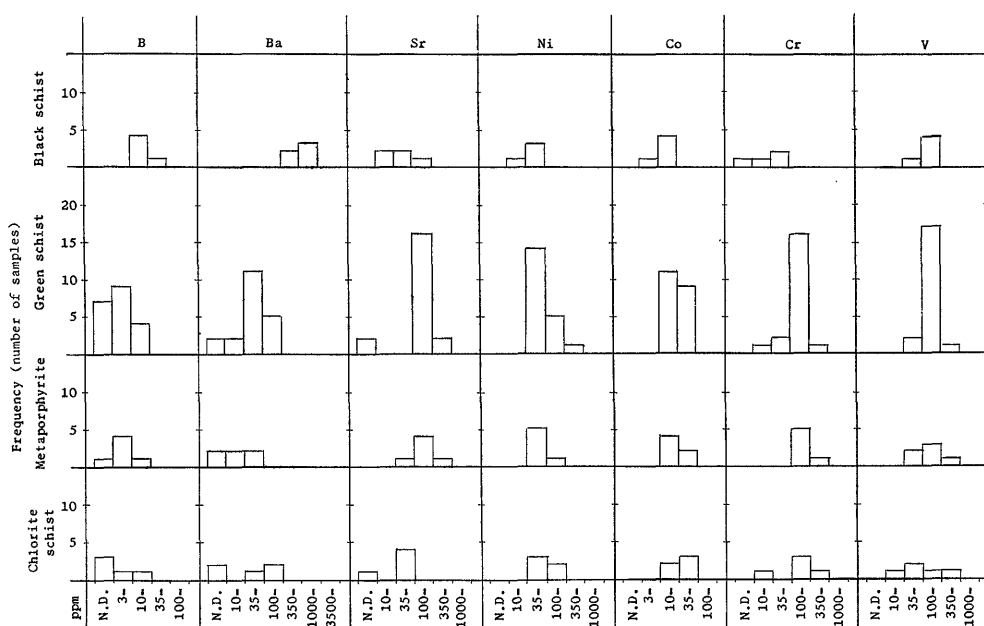


Fig. 2 Frequency diagram of minor elements in various metamorphic rocks from Tenryu River basin

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Bedded Cupriferous Pyrite Deposits of Tenryu River Basin (S. Iron)

Table 1 Description of analysed samples and their localities

Sample	Location	Description
610801	-150 m L of Osawa deposit	Black schist of Sejiri formation.
610802	-150 m L of Osawa deposit	Green schist of Oi formation. Contact with black schist of Sejiri formation.
610803	-150m L of Osawa deposit	Metadiabase of Oi formation.
610804	-150m L of Osawa deposit	Green schist of Oi formation.
610805	-150m L of Osawa deposit	Green schist of Oi formation. Hanging wall rock of Osawa deposit. 20cm upper of ore body.
610806	-150m L of Osawa deposit	Green schist of Oi formation. Contact with magnetite ore.
610807	-15m L of Oi deposit	Green schist of Oi formation. Coarse grain.
610808	-15m L of Oi deposit	Green schist of Oi formation.
610809	-15m L of Oi deposit	Green schist of Oi formation. Sandwiched between ore bodies.
610810	-15m L of Oi deposit	Green schist of Oi formation. With impregnated pyrite
610811	-15m L of Oi deposit	Green schist of Oi formation.
610812	-15m L of Oi deposit	Green schist of Oi formation. Massive.
610813	-10th L of Kunehonzan deposit	Metaporphyrite of Kune formation. Typical.
610814	-10th L of Kunehonzan deposit	Chlorite schist of Kune formation. Contact with metaporphyrite.
610815	-10th L of Kunehonzan deposit	Chlorite schist of Kune formation. Contact with ore body.
610816	-10th L of Kunehonzan deposit	Ore. With gangue minerals.
610817	-10th L of Kunehonzan deposit	Sericite schist of Kune formation. Contact with ore body.
610818	-10th L of Kunehonzan deposit	Black schist of Kune formation.
610819	-8th L of Nako deposit	Green schist of Oi formation.
610820	0 L of Nako deposit	Metadiabase of Oi formation. Coarse grain.
610821	-8th L of Nako deposit	Green schist of Oi formation. Contact with ore body.
610822	0 L of Kunehonzan deposit	Metaporphyrite of Kune formation.
610823	0 L of Kunehonzan deposit	Black schist of Kune formation.
620101	-5th L of Nako deposit	Green schist of Oi formation. Hanging wall rock of Ebisu ore body.
620102	-5th L of Nako deposit	Green schist of Oi formation. Foot wall rock of Ebisu ore body.
620103	-8th L of Nako deposit	Green schist of Oi formation. Hanging wall rock of Daikoku ore body.
620104	-8th L of Nako deposit	Green schist of Oi formation.
620105	-8th L of Nako deposit	Green schist of Oi formation. Typical.
620106	-8th L of Nako deposit	Green schist of Oi formation. Typical.
620107	Outcrop	Quartz schist of Ueno formation.
620108	Outcrop	Sandstone schist of Ueno formation.
620109	Outcrop	Crystalline limestone of Zihati formation.

Sample	Location	Description
620110	-3th L of Kunchonzan deposit	Chlorite schist of Kune formation.
620111	-3th L of Kunchonzan deposit	Chlorite schist of Kune formation. 1.5 m distant from No. 620110 to upper horizon.
620112	-3th L of Kunchonzan deposit	Metaporphyrite of Kune formation. Slightly chloritized.
620113	-3th L of Kunchonzan deposit	Metaporphyrite of Kune formation.
620114	-3th L of Kunchonzan deposit	Chlorite schist of Kune formation. Foot wall rock of Otama ore body.
620115	-3th L of Kunchonzan deposit	Metaporphyrite of Kune formation. Hanging wall rock of Otama ore body.
620116	0 L of Kunchonzan deposit	Metaporphyrite of Kune formation. Typical.
620117	0 L of Kunchonzan deposit	Sericite-chlorite schist of Kune formation.
620118	0 L of Kunchonzan deposit	Black schist of Kune formation. Typical.

in other formations. Both hanging and foot walls of deposit are chlorite schist of about 1 meter in thickness, and this is rather unique for these deposits of the region.

3. Chemical composition and minor constituents of country rocks

3.1 Locality of samples and results of chemical analysis

Localities and brief descriptions of samples analysed are shown in Table 1. The majority of the samples were collected from underground and only three from outcrops. Conventional methods were used for chemical analysis. The results obtained are shown in Table 2.

3.2 Analytical results of minor elements

The spectrochemical method was used for determination of minor elements in country rocks. The spectrographic conditions and analytical lines of elements were the same as in the case of sulfide minerals which will be described later, except that sodium chloride was used as a buffer material. The results obtained are shown in Table 3 and summarized in Fig. 2 as frequency diagrams.

3.3 Discussion

It has been reported that the country rock of Kunchonzan deposit is metaporphyrite based mainly microscopic observation and is called "Shiroishi" due to its white colour in pulverised state.

Although the rock has apparent acidic features, the analytical results, especially SiO_2 content, are very similar to green schist. Both the "Shiroishi" and green schist also have similar value of the solidification index, $\text{MgO} \times 100 / \text{Fe}_2\text{O}_3 + \text{FeO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$, which was proposed by KUNO (1957) as a measure for magmatic differentiation, the values are about 35 to 40. This shows clearly that these rocks are classified in undifferentiated rock.

In the total FeO-alkali-MgO diagram (Fig. 3) the green schists are distributed in the area which according to KUNO (1957) indicates the composition of primary magmas and the "Shiroishi" is also plotted within the area. Two samples isolated from the main trend in Fig. 3 are sample No. 610806 which may include magnetite and No. 620112 which is in contact with chlorite schist and is slightly chloritized. According to Kuno's classification the green schist of Oi formation and the "Shiroishi" can be considered as belonging to high alkali tholeiite rock series and can be

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Table 2 Chemical compositions of some metamorphic rocks from the Tenryu River basin

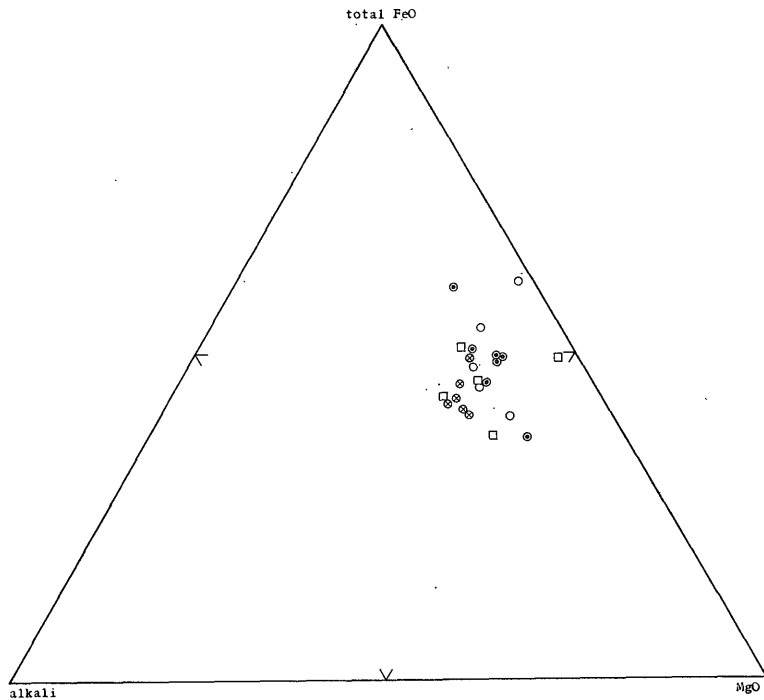
Sample	610801	610802	610803	610804	611805	610806	610807	610808	610809	610810	610811	610812	610813	610814
SiO ₂	52.38	41.23	44.74	43.85	39.51	29.69	47.20	48.67	51.79	48.67	49.55	47.65	43.60	39.66
TiO ₂	0.84	1.06	1.13	1.08	1.24	0.69	1.64	1.24	1.28	1.38	1.26	1.22	0.95	1.28
Al ₂ O ₃	21.17	14.30	18.06	14.42	15.03	13.05	14.42	14.35	13.37	14.89	14.32	14.75	16.36	17.32
Fe ₂ O ₃	1.65	0.83	4.90	2.07	3.86	3.77	4.36	2.62	2.82	3.27	3.85	4.14	2.65	1.36
FeO	5.73	8.24	4.78	5.91	7.63	14.55	6.55	7.71	6.46	6.64	5.47	5.91	5.41	11.41
MnO	0.23	0.24	0.19	0.16	0.78	1.09	0.20	0.19	0.20	0.18	0.18	0.17	0.19	0.16
MgO	5.07	7.77	7.16	8.67	7.24	10.84	7.78	9.52	8.72	8.33	7.88	7.84	9.41	15.77
CaO	0.40	9.75	11.94	10.25	12.18	11.18	11.93	7.27	9.35	8.76	11.30	12.33	10.27	0.80
Na ₂ O	3.30	1.52	2.44	2.02	1.35	0.16	2.74	4.10	3.98	4.10	3.56	2.99	2.72	2.74
K ₂ O	3.49	1.48	2.34	0.54	0.73	0.48	0.22	0.40	0.17	0.24	0.78	0.70	0.82	0.22
P ₂ O ₅	0.27	0.21	0.20	0.29	0.35	0.37	0.26	0.30	0.23	0.21	0.21	0.29	0.27	0.29
H ₂ O ⁺	4.86	5.60	3.15	5.13	4.94	6.62	2.19	3.04	2.44	3.18	1.83	1.99	4.44	9.06
H ₂ O ⁻	0.25	0.47	0.23	0.50	0.43	0.52	0.29	0.16	0.26	0.28	0.23	0.25	0.29	0.43
CO ₂	0.15	7.47	0.96	5.24	5.22	6.95	0.48	0.38	0.10	0.02	0.14	0.16	1.84	0.10
C	0.37	—	—	—	—	—	—	—	—	—	—	—	—	—
S	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Fe	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Total	100.16	100.17	100.22	100.13	100.49	100.23	100.26	99.95	100.67	100.15	100.56	100.39	99.24	100.60

(continuation)

Sample	610815	610816	610817	610818	610819	610820	610821	610822	610823	620101	620102	620103	620106	620107
SiO ₂	36.54	37.53	67.34	66.19	48.28	44.37	40.73	42.59	68.22	41.07	45.40	52.47	46.58	74.75
TiO ₂	1.36	0.67	0.30	0.53	1.13	1.01	1.12	0.84	0.28	1.14	1.65	1.07	1.34	0.19
Al ₂ O ₃	14.78	6.12	11.43	12.70	15.87	16.42	16.11	18.17	15.23	16.80	15.37	11.55	15.83	12.47
Fe ₂ O ₃	6.18	0.45	0.82	1.33	3.71	2.76	5.11	2.86	0.79	2.81	4.92	3.10	3.66	1.31
FeO	13.09	3.67	2.33	3.23	5.33	6.25	6.93	4.21	2.99	11.86	6.21	5.42	6.53	1.09
MnO	0.06	0.05	0.38	0.14	0.17	0.16	0.20	0.18	0.05	0.15	0.23	0.17	0.16	0.03
MgO	16.54	6.01	2.41	1.79	7.71	7.31	8.12	5.51	1.42	6.92	8.52	11.13	8.03	0.43
CaO	0.69	0.08	3.97	3.37	10.79	11.10	6.93	15.19	0.93	5.28	9.55	6.63	11.17	0.65
Na ₂ O	0.04	0.08	0.34	1.62	2.32	1.75	1.47	2.92	2.35	1.23	1.87	2.77	1.68	3.29
K ₂ O	0.11	0.00	3.57	3.11	0.33	0.25	1.59	0.24	3.19	1.45	0.40	0.19	0.36	3.17
P ₂ O ₅	0.24	0.12	0.41	0.22	0.29	0.23	0.29	0.23	0.20	0.24	0.36	0.28	0.37	0.09
H ₂ O ⁺	9.78	(-2.0)	1.86	2.83	2.91	4.56	6.26	2.53	2.98	6.42	4.04	3.76	3.10	1.67
H ₂ O ⁻	0.44	0.42	0.38	0.40	0.32	0.41	0.56	0.43	0.49	0.47	0.49	0.56	0.16	0.23
CO ₂	0.15	—	3.43	2.17	0.21	2.80	4.33	4.07	0.10	4.04	0.62	0.45	0.24	0.41
C	—	—	—	0.40	—	—	—	—	0.45	—	—	—	—	—
S	—	21.34	—	—	—	—	—	—	—	—	—	—	—	—
Fe	—	18.59	—	—	—	—	—	—	—	—	—	—	—	—
Total	99.95	95.13 (97.13)	98.97	100.03	99.37	99.38	99.75	99.97	99.67	99.88	99.63	99.55	99.21	99.78

(continuation)

Sample	620108	620109	620110	620112	620114	620115	620116	620117	620118
SiO ₂	73.01	1.90	34.88	38.78	39.72	45.45	43.90	49.65	63.77
TiO ₂	0.28	0.00	1.27	1.03	1.06	1.00	0.93	1.01	0.68
Al ₂ O ₃	13.56	0.00	16.32	18.44	18.85	15.42	20.72	15.11	15.39
Fe ₂ O ₃	0.84	0.04	3.83	5.43	3.01	3.80	3.78	2.19	3.35
FeO	2.00	0.39	10.74	6.18	7.36	4.88	4.66	5.79	3.04
MnO	0.04	0.01	0.16	0.19	0.16	0.46	0.28	0.39	0.08
MgO	0.99	5.44	20.41	10.75	14.89	6.93	5.41	5.45	1.70
CaO	0.87	49.14	1.05	11.13	3.22	12.95	11.39	6.19	0.85
Na ₂ O	3.37	0.11	0.35	0.34	0.47	2.32	2.03	4.51	2.11
K ₂ O	1.81	0.22	0.27	0.25	1.10	0.34	0.23	0.05	3.19
P ₂ O ₅	0.14	0.05	0.14	0.10	0.15	0.10	0.13	0.08	0.16
H ₂ O ⁺	1.77	0.29	10.15	5.59	8.04	2.68	4.23	4.39	3.80
H ₂ O ⁻	0.16	0.21	0.29	0.62	0.87	0.49	0.54	0.58	0.55
CO ₂	0.56	42.54	0.32	1.59	0.70	2.98	1.48	4.34	0.37
C	—	—	—	—	—	—	—	—	0.64
S	—	—	—	—	—	—	—	—	—
Fe	—	—	—	—	—	—	—	—	—
Total	99.30	100.34	100.18	100.42	99.60	99.80	99.71	99.73	99.68



- Country rock of Osawa deposit, Minenosawa formation.
- Country rock of Nako deposit, Minenosawa formation.
- ⊙ Country rock of Oi deposit, Oi formation.
- Country rock of Kune deposit, Kune formation.

Fig. 3 The total FeO-alkali-MgO diagram of country rocks of some bedded cupriferous pyrite deposits in Tenryu River basin

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Table 3 Minor elements in some metamorphic rocks from the Tenryu River basin

Sample	B	Ba	Sr	Ga	Ni	Co	Cr	V	Cu	Pb	Zn
610801	20	800	25	30	50	10	40	150	250	—	250
610802	5	300	350	10	70	20	120	120	65	—	150
610803	—	40	300	15	80	25	150	200	150	—	200
610804	7	80	250	30	350	35	450	200	150	—	150
610805	3	80	300	10	100	45	100	120	150	40	600
610806	12	120	300	30	300	60	150	80	400	20	2,500
610807	—	25	200	25	80	20	70	150	100	—	150
610808	—	40	120	10	80	15	120	120	100	—	350
610809	—	40	120	10	40	20	25	80	1,500	—	500
610810	—	60	250	15	60	25	120	120	2,500	—	600
610811	—	150	300	20	100	30	200	150	400	40	500
610812	5	120	450	30	150	35	250	350	400	25	600
610813	3	60	300	12	70	30	150	150	150	—	200
610814	—	80	80	20	60	30	25	60	40	—	150
610815	—	200	80	20	60	45	550	400	80	—	200
610816	—	150	60	15	12	55	7	40	> 1%	—	250
610817	10	1,500	40	12	25	10	—	80	60	40	150
610818	20	1,200	25	25	40	12	25	120	100	—	200
610819	3	80	300	15	60	15	100	150	150	—	200
610820	—	60	250	25	120	25	220	250	120	—	250
610821	3	40	200	40	60	40	80	120	600	—	800
610822	5	80	350	30	120	30	400	350	65	—	120
610823	25	800	60	10	40	8	80	200	80	—	150
620101	10	100	—	12	40	30	120	100	60	20	400
620102	5	—	100	12	55	30	130	150	35	—	150
620103	10	—	—	10	60	35	150	130	25	—	100
620104	5	40	200	12	80	35	130	200	80	—	200
620105	10	20	200	12	80	35	150	150	120	10	200
620106	5	70	150	12	85	35	180	200	120	—	300
620107	20	1,000	120	15	30	—	60	5	30	20	100
620108	20	700	100	12	20	2	35	20	35	20	100
620109	—	—	8,000	—	—	—	—	—	15	—	—
620110	5	—	—	10	100	40	150	100	20	—	200
620111	—	—	50	10	100	35	180	50	12	—	200
620112	5	—	100	10	85	35	150	65	100	—	150
620113	10	—	35	12	80	35	150	60	20	—	150
620114	10	150	30	10	85	30	150	50	10	—	100
620115	8	20	120	10	90	30	150	120	100	—	250
620116	2	20	120	10	75	30	150	100	100	—	150
620117	6	—	25	10	90	45	180	120	300	—	500
620118	40	2,000	130	15	100	20	150	130	100	10	200

distinguished from those of Minenosawa formation which can be classified as alkali rock series.

In Fig. 4 the relationship diagram of mafic-alumina-alkali components is shown. In this diagram the green schists are plotted in the area of about 50 per cent mafic component and about 10 per cent alkali component. Although some of the "Shiroishi" are distributed in the same area, others considered as typical metaporphyrite show higher alumina content. This is interpreted as the result of higher plagioclase content than in ordinary green schist. The chlorite schist shows a trend of increase of mafic and decrease of alkali and alumina contents with increasing chlorite content. Some country rocks which are in contact with ore bodies can be included in the category of chlorite schist in this figure.

In Fig. 4 the Paleozoic muddy rocks of different provinces and metamorphic grades (the data from UNO, 1961, and HARAMURA, 1961) are plotted in the same region as black schist derived from mudstone. From this fact it can be concluded that the changes in chemical composition, at least regarding these three components, was negligible small during regional metamorphism. This inference can be extended to green schist which is sandwiched by the black schist. The chemical composition of the green schist, therefore, is believed to represent the range of the chemical composition of the original rocks.

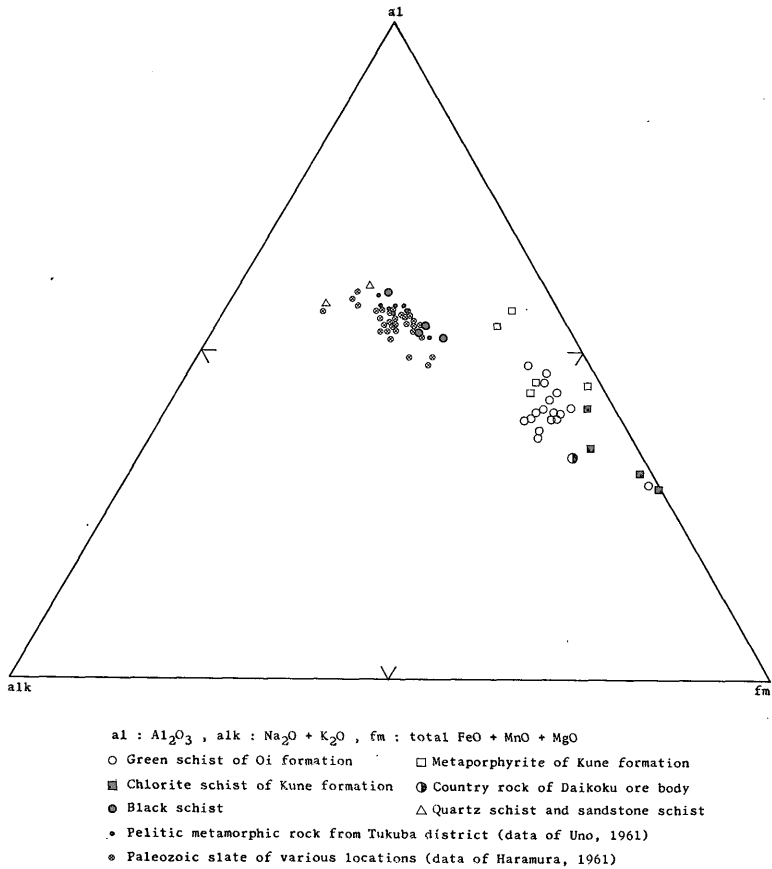


Fig. 4 The relationship diagram of alumina-alkali-mafic components of various metamorphic rocks from Tenryu River basin

Chemical Composition of Country Rocks and Minor Elements in Sulfide Minerals from
Bedded Cupriferous Pyrite Deposits of Tenryu River Basin (S. ITOH)

Table 4 Analytical lines of elements and its sensitivity

Element	Analytical line (Å)	Sensitivity (ppm)	Element	Analytical line (Å)	Sensitivity (ppm)
Ag	3,382.89	0.5		2,782.97	10
As	2,349.84	100	Mn	2,801.06	1
	2,780.20	200		2,939.30	5
B	2,496.78	5		2,799.84	100
Ba	4,554.04	50	Mo	3,158.17	3
	2,304.24	1,000		3,085.62	300
Bi	3,067.72	3	Ni	3,414.76	1
	2,897.98	50		3,050.82	5
Cd	3,261.06	3		3,037.93	20
Co	3,453.50	1	Pb	2,614.20	10
	3,395.38	50		2,577.28	100
	3,333.39	1,000	Sb	2,311.47	80
Cr	3,014.92	5		2,598.06	200
	3,013.71	30	Sn	3,034.12	3
Cu	3,273.96	0.5		3,330.59	30
	2,824.37	50	Tl	2,767.87	2
	3,036.10	300	V	3,202.38	10
Ga	2,943.64	2		3,183.41	1
	2,944.18	10	Zn	3,345.02	80
Ge	2,651.18	1		3,345.57	300
	2,651.58	50		3,345.93	500
Mg	2,779.83	1			

As is clear in Fig. 2, both green schist and the "Shiroishi" contain considerable amounts of the minor elements, such as Ni, Co, Cr and V, all of which are characteristically concentrated in basic rocks.

From the evidences described above, it may be concluded that the original rock of the "Shiroishi" is not a porphyrite as considered hitherto, but the same as those of the country rocks of almost all bedded cupriferous pyrite deposits in this region.

4. Minor elements in sulfide minerals

4.1 Analytical method and results

The (-100~150) mesh fraction of crushed sulfide samples were used for separation of minerals. Silicate minerals were floated off by superpanner, and the magnetic minerals were then separated by means of an isodynamic separator. Further purification was carried out under a binocular microscope.

The purified samples were mixed 1:1 with graphite powder and crammed into the crater of anode electrode. A JACO 3.4 m Ebert Spectrograph with a 15,000 lines/inch grating was used to record first and second order spectra. The spectrographic conditions were as follows:

Discharge	d. c. arc
Amperes	8
Volts	220

Electrode gap	3 mm
Exposure time	90 secs.
Slit gap	20/1,000 mm
Plate	Kodak SA 1
Develop time	3 mins. at 20°C

Analytical curves were obtained from synthetic standards which were prepared by adding solutions of various concentration of each element to base of pyrite. The analytical lines used in the present work and its sensitivity are shown in Table 4. Co and Ni contents of some samples were checked with chemical analysis.

The results obtained are shown in Fig. 5 as frequency diagrams of different minerals.

4.2 Discussion

Because the constituent minerals of the ore are generally of very fine grain size, the separation of each mineral is difficult. Each mineral fraction obtained here, therefore, means only the concentrated fraction of each mineral. Therefore, the present results cannot be used as data for exact discussions such as those related to the partition coefficient of element among the minerals. Furthermore, the analytical precision and accuracy were not high enough for such discussions. These data, however, are of sufficient accuracy for consideration of the relationship between minerals and elements.

As is clearly evident from Fig. 5, the enrichment order of cobalt was pyrite>chalcopyrite, pyrrhotite>magnetite. Nickel did not show any clear tendency of preferential concentration. Silver was distinctly enriched in chalcopyrite and the order of enrichment was chalcopyrite>pyrite, magnetite. Bismuth and antimony had a similar tendency as silver. The distribution of both

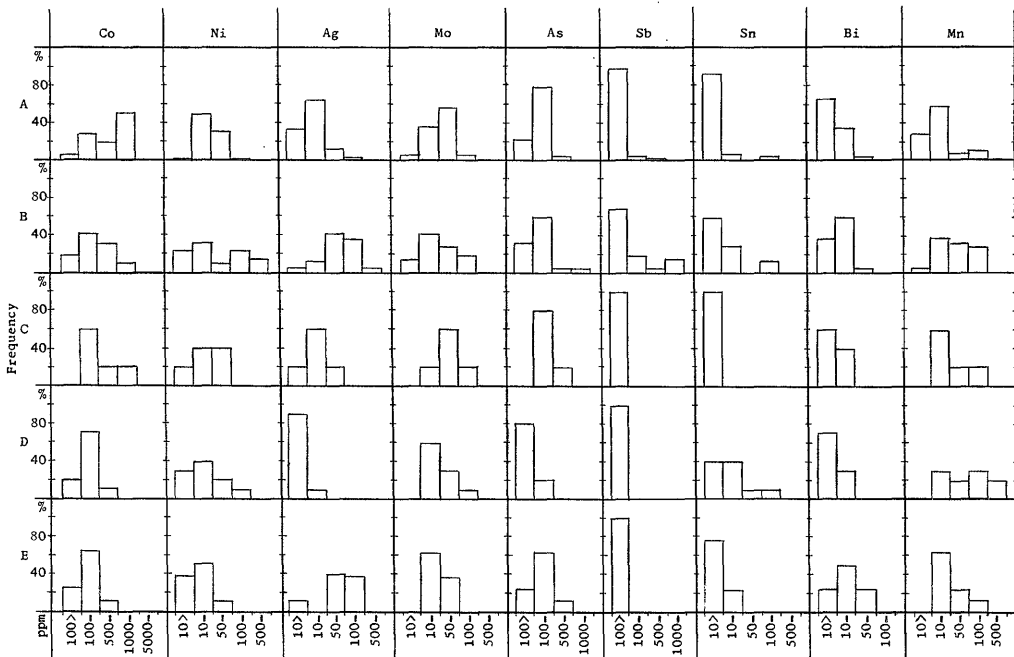


Fig. 5 Frequency diagram of minor elements in different minerals from bedded cupriferous pyrite deposits in Tenryu River basin
 A : Pyrite (90 samples) B : Chalcopyrite (22 samples) C : Pyrrhotite (5 samples)
 D : Magnetite (10 samples) E : Sphalerite (8 samples)

elements, however, probably is erratic because of the possibility of tetrahydrite mixture in chalcopyrite fraction. The order of decreasing manganese content was magnetite-chalcopyrite-pyrite, and as for molybdenum it was similar to cobalt.

The distribution of cobalt in sulfide minerals has been studied by some investigators. The result obtained here confirmed the conclusions of a study of various Canadian ore deposits by HAWLEY and NICHOL (1961) and of a study of Norwegian sulfide ore deposits by BJOLYKKE and JARP (1950). With regard to other elements analysed the tendencies of the distribution among co-existing minerals were in general agreement with those indicated by FLEISCHER (1955).

In Fig. 6 data of pyrite from Tsuchikura mine (after ITOH and KANEHIRA, 1967) are shown for comparison with those from the deposits of Tenryu River basin. With the exception of thallium, the amounts of all elements in pyrites from Tenryu River basin have similar ranges to those from Tsuchikura mine. It has been known that the pyrite from Kuroko deposits generally has low cobalt and nickel contents in the same ranges as those of the vein type deposits in Inner Japan metallogenetic province (TAKAHASHI, 1961). The higher content of cobalt, common existence of nickel and higher value of cobalt/nickel ratio in pyrite from bedded cupriferous pyrite deposits, as indicating in Fig. 6, therefore, seem to be characteristic of these deposits. Thallium was not detected in pyrite from the region, while it was commonly found in pyrite from Tsuchikura mine. Such a difference in thallium content can be interpreted as difference of local geologic process.

In Fig. 6 the data on pyrite from the different formations are also summarized. The content of

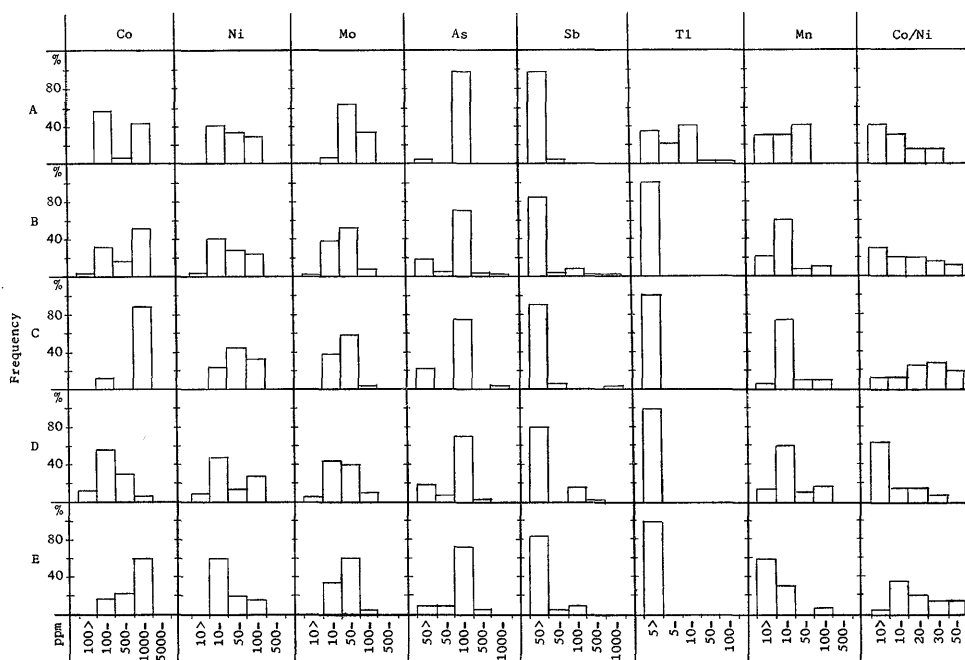


Fig. 6 Frequency diagram of elements in pyrites from the deposits in different formations
 A : Tsuchikura mine (41 samples) B : The mines of Tenryu River basin (76 samples)
 C : Deposits in Minenosawa formation (31 samples) D : Deposits in Oi formation (27 samples) E : Deposits in Kune formation (18 samples)

cobalt, nickel and manganese and cobalt/nickel ratio of pyrite from the deposits in different formations showed different patterns in frequency distribution from each other. These differences could be interpreted under the assumption that different mineralization took place in each formation and the sulfide ores had deposited syngenetically with their country rocks. From the geological and mineralogical field observations, the assumption described above has been proposed by some investigators who have considered a submarine exhalative or hydrothermal sedimentary origin for the genesis of such ore deposits.

HEGEMANN (1943) showed the following empirical conclusions in his investigation of the cobalt and nickel contents in pyrites from deposits of various types.

- 1) The sedimentary pyrite shows almost constant cobalt (10~30 ppm) and nickel (100~300 ppm) contents.
- 2) The contents of cobalt and nickel in magmatic and hydrothermal pyrite vary from sample to sample, and generally, have more cobalt than nickel.
- 3) In low grade regional metamorphic deposits, such as Meggen, Germany, the pyrite shows similar features in cobalt and nickel contents to sedimentary pyrite. The cobalt content and cobalt/nickel ratio of pyrite, however, increase with increasing grade of metamorphism.

As a whole, the variation of contents of minor elements in pyrites are comparatively large, which probably indicates that hydrothermal character is predominant in these deposits. The only sedimentary character of these deposits is the cobalt distribution in pyrite from deposits in Minenosawa formation, which is especially homogeneous. Therefore, it is not possible to conclude whether the deposits is hydrothermal sedimentary origin or not from these data alone. For this purpose further investigation including the study of possible movement of elements during regional metamorphism and detailed studies of distribution of elements in ore body and among co-existing minerals are required.

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天竜川流域の含銅硫化鉄鉱床の母岩の化学組成
および硫化鉱物中の微量成分元素

伊藤 司郎

要 旨

天竜川流域の含銅硫化鉄鉱床の母岩および周辺岩石の化学分析および発光分光分析を行なった。その結果、従来変珩岩とされてきた久根本山鉱床の母岩は、この地域のその他の鉱床の母岩と同様に、より塩基性の岩石であることが判明した。このことは鉱床の成因と関連するので重要である。

この地域の鉱床の鉱石 125 試料の発光分光分析結果を示した。その結果、一般に、黄鉄鉱は高 Co 含量および高 Co/Ni 比値を示し、このことはまた含銅硫化鉄鉱床の一般的な特長でもあることを指摘した。鉱床を胚胎する地層ごとに分類し、黄鉄鉱中の微量成分元素のデータを対比した結果、地層によってその頻度分布パターンが異なることが示された。

今なお議論の分かれているこの種の鉱床の成因について、微量成分元素上の特長に基づき、若干の考察を試みた。