

Regional and temporal variation in FeS content of sphalerites from Japan and its relation to granitoids series

Katsuhiro TSUKIMURA*, Kohei SATO* and Shunso ISHIHARA*

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Abstract: Chemical compositions of sphalerites (Zn, Fe)S from 32 volcanogenic and plutogenic ore deposits in various metallogenic provinces of Japan were obtained with an electron probe microanalyser. The FeS content varies depending upon petrogenetic province, type of ore deposit, and mineral paragenesis (especially with iron sulfides). The sphalerites coexisting with iron sulfides show a narrow range of FeS variation within any single ore deposit, but yield a wide range of regional variation from 0.3 to 23.7 mole%. The mineral from vein-type deposits tends to be poor in FeS (less than 12%) in magnetite-series granitic terranes, whereas it has generally high FeS content (more than 14%) in ilmenite-series granitic terranes. The results indicate that f_{O_2} and f_{S_2} of ore solutions at the time of ore deposition were high in the magnetite-series terrane but low in the ilmenite-series terrane. Although no exceptions to the above systematics are found in the ilmenite-series, there exist some exceptions in the magnetite-series sphalerites, which may be explained by local reduction of the ore solution by carbon-bearing wall rocks. Regardless of the granitoids series sphalerites from skarn-type ore deposits generally have FeS content higher than 12 mole%. The high FeS content may indicate that skarn deposits were formed at high temperatures and/or in reduced chemical conditions influenced by carbonaceous host rock. On the contrary, Au-Ag and Mn veins in the magnetite-series granitic terranes have low FeS content, indicating that these ore deposits were formed under lower temperature and higher f_{S_2} environments than the base metal veins from the same terrane.

Introduction

Recent metallogenic discussion of the Japanese Islands has been focussed on the correlation between granitoids series and related ore deposits (ISHIHARA, 1978, 1981; SASAKI and ISHIHARA, 1980; SATO, 1980a, 1982; SHIMAZAKI, 1980). Originally, ISHIHARA (1977) classified the granitoids into two series, magnetite-series and ilmenite-series,

on the basis of the opaque mineralogy. As the two series differ in the assemblage and amount of opaque minerals, these series should differ in oxygen fugacity at the time of solidification of magmas. These differences are considered to have resulted from the origin and mode of emplacement of granitic magmas (ISHIHARA, 1977, 1984; SASAKI and ISHIHARA, 1979; SATO and ISHIHARA, 1983). The parallelism of oxidation status between ore deposits and proximate granitoids has been obtained for skarn type deposits. For example, SATO (1980b) indicated that tungsten skarn deposits related to the ilmenite-series granitoids formed in reduced condition compared with those related to magnetite-series granitoids. However, the parallelism has not

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been examined for the ore deposits distant from granitic bodies. Thus, we have studied the formation condition of those ore deposits by measuring the FeS content of sphalerite, and discussed the relation between the ore deposits and the related granitoids (TSUKIMURA *et al.*, 1982).

Sphalerite occurs commonly in ore deposits of both series of granitic terranes. FeS content of the mineral coexisting with iron sulfides provides a good parameter for estimating the

physicochemical condition during the ore formation. KULLERUD (1953) proposed on the basis of experimental study that FeS content of sphalerite coexisting with pyrrhotite could be used as geothermometer. It was, however, modified by the experimental study by BARTON and TOULMIN (1966). They found that FeS content in sphalerite coexisting with pyrite or pyrrhotite varies not only with temperature but also with sulfur fugacity. The FeS content in sphalerite also depends on

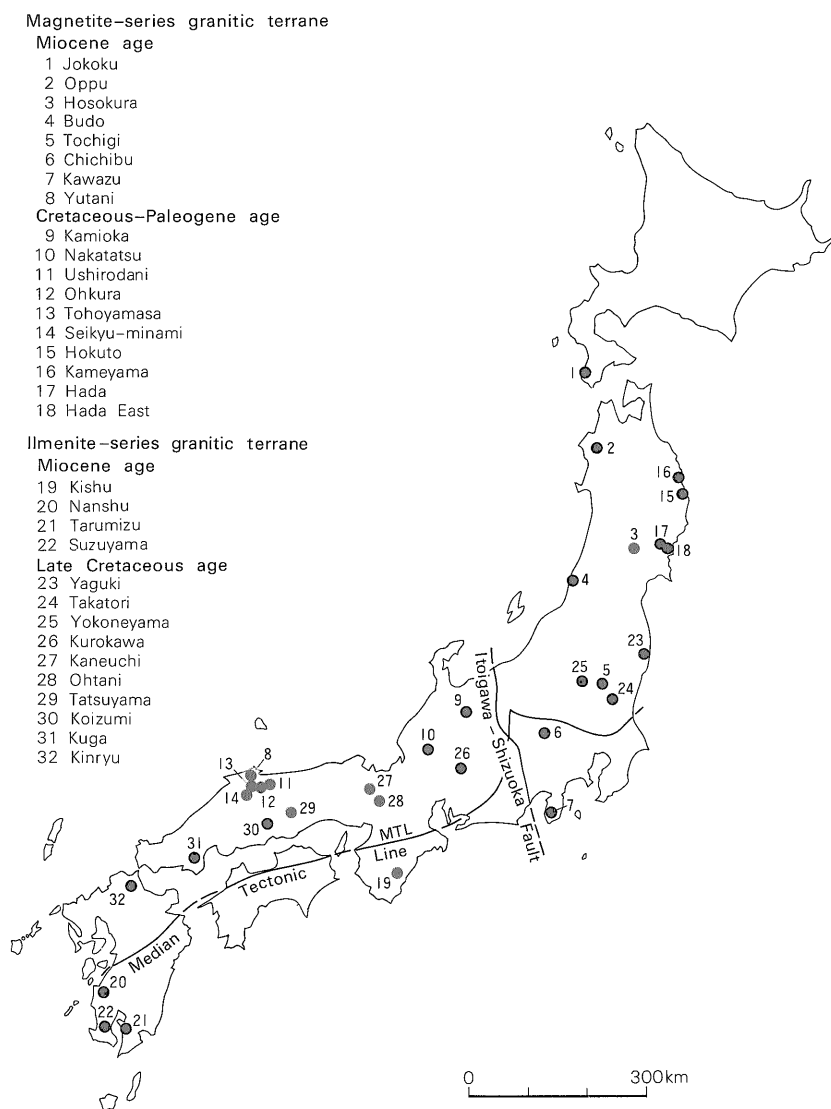


Fig. 1 Locality map of the studied ore deposits.

its forming pressure (SCOTT and BARNES, 1971; SCOTT, 1973), but its effect is rather small in low pressure condition common to hydrothermal ore deposits. SHIMIZU and SHIMAZAKI (1981) applied the geobarometer to 16 skarn deposits and determined pressures of all the deposits as below 2 Kb.

Sphalerite compositions of Japanese ore deposits have been reported by several authors (*e.g.* MUTA, 1958; TAKAHASHI, 1963). In particular, MUTA (1958) analysed many sphalerites from various types of zinc-rich ore deposits at 50 localities, and obtained a wide range of variation in the FeS content. The variation was explained by difference of formation temperature of the mineral. It appears, however, that MUTA's results need to be reevaluated from the view point of recent metallogenic discussion mentioned above, because most of the iron-rich sphalerites were collected from the ore deposits in ilmenite-series granitic terrane, while iron-poor sphalerites were mainly from magnetite-series terrane of the Green Tuff region.

Sphalerite compositions were discussed in terms of temperature and oxygen fugacity in the magnetite-series volcano-plutonic terrane of the Green Tuff region by several authors. URABE (1974) studied sphalerites from Kuroko deposits and found that the FeS content decreased within a narrow range up to 4 mole% from the lowest Keiko (siliceous ore) through Oko (yellow ore) to the uppermost Kuroko (black ore) bodies. In these deposits, the upward increasing of f_{O_2} and f_{S_2} , and upward decreasing of temperature were suggested by mineralogical and isotopic studies (KAJIWARA, 1971; SATO, 1973). SHIKAZONO (1974, 1975) observed a narrow range of FeS content (less than 1 mole%) in sphalerites from Ag-Au veins of the Seigoshi mine, and wide (up to 21 mole%) but relatively low FeS content of the mineral in Pb-Zn veins of the Toyoha mine, and discussed their results in terms of oxygen and sulfur fugacities during the ore formation.

In this paper, we examine the composition

of sphalerite from various but mainly vein types of both volcanogenic and plutogenic ore deposits of the magnetite-series and ilmenite-series metallogenic provinces in Japan (Fig. 1), and, in assembling all the previous data, discuss the regional and temporal variation of the FeS content with reference to the granitoid series terranes. For the more work on the skarn deposits, reader may refer to the recent paper by SHIMAZAKI and SHIMIZU (1984).

Analytical Procedure

Chemical composition of sphalerite was obtained by an electron microprobe analyser, JCSA-733, JEOL Co. Ltd. at the Geological Survey of Japan. One to three normally polished specimens were examined for each ore deposit. The following six elements, zinc, iron, cadmium, manganese, copper, and sulfur, were measured. Copper was measured to check the existence of chalcopyrite dots in sphalerite that influence the measurement of FeS content. Standard materials were synthetic ZnS for zinc and sulfur, natural chalcopyrite of known composition for iron and copper, synthetic CdS for cadmium, and synthetic MnS for manganese. Analytical conditions were as follows: (1) accelerating voltage: 25 kV, (2) beam current: 0.02 μ A, (3) beam diameter, ca. 5 μ m, (4) counting time: 50 sec. for Zn, Fe and S, 20 sec. for Cd, Mn and Cu. Intensities were corrected by ZAF method. The total contents were written in the range of 100.0 ± 0.8 weight per cent.

Studied Ore Deposits

Ore deposits studied here are mainly of vein-type and some skarn-type from 32 localities. Table 1 gives a list of studied ore deposits together with their recovered metal species and host rocks, and Fig. 1 illustrates their localities.

In the magnetite-series granitic terranes, eighteen deposits (nos. 1-18) are examined.

Table 1 List of the studied ore deposits

No.	Locality	Recovered Metal	Type	Host rocks
Magnetite-series granitic terranes				
Miocene age				
1	Jokoku	Mn, Zn, Pb	MnCO ₃ vein	Oligocene tuff breccia
2	Oppu	Zn, Pb, Cu	Quartz vein	Miocene dacitic tuff
3	Hosokura	Zn, Pb	ditto	Miocene andesite & pyroclastics
4	Budo	Zn, Pb	Carbonate-quartz vein	Cretaceous biotite granite
5	Tochigi	Cu, (Ag)	Quartz vein	Quartz porphyry & rhyolitic tuff
6	Chichibu	Zn, Pb	Skarn	Upper Paleozoic limestone
7	Kawazu	Ag, Au, (Cu, Mn)	Quartz vein	Miocene andesite & dacitic tuff
8	Yutani	Cu, Zn, Pb	ditto	Miocene andesite
Cretaceous Paleogene age				
9	Kamioka	Zn, Pb	Skarn	Limestone in Hida metamorphic rocks
10	Nakatatsu	Mo	Stockwork	Paleogene quartz porphyry
11	Ushirodani	Zn, Pb	Lens & Vein	Quartz schist (Sangun)
12	Ohkura	Zn, Pb	Vein	Biotite granite
13	Tohoyamasa	Mo	Quartz vein	ditto
14	Seikyū-minami	Mo	ditto	ditto
15	Hokuto	Mo	Vein	Biotite granite
16	Kameyama	Cu	Skarn	Mesozoic limestone
17	Hada	Mo, Cu	Vein	Granodiorite
18	Hada East	Cu, Pyrrhotite	Lens	Cretaceous andesite
Ilmenite-series granitic terranes				
Miocene age				
19	Kishu	Cu	Quartz-chl vein	Paleogene sedimentary rocks
20	Nanshu	Zn, Pb, (Cu)	Quartz vein	Cretaceous sedimentary rocks
21	Tarumizu	Sn	Quartz(-tour) vein	Biotite granite
22	Suzuyama	Sn	ditto	Cretaceous sedimentary rocks
Late Cretaceous age				
23	Yaŕuki	Cu, (W)	Skarn (Disseminated)	Upper Paleozoic limestone, (granodiorite)
24	Takatori	W, (Sn, Cu)	Quartz(-mus) vein	Upper Paleozoic sedimentary rocks
25	Yokoneyama	Mn	Stratiform	ditto
26	Kurokawa	Cu	Quartz-chl vein	Late Cretaceous felsic pyroclastics
27	Kaneuchi	W, (Sn, Cu)	Quartz(-mus, -Kf) vein	Upper Paleozoic sedimentary rocks
28	Ohtani	W, (Sn, Cu)	ditto	Biotite granodiorite
29	Tatsuyama	Cu	Vein & lens	Upper Paleozoic sedimentary & igneous metamorphic rocks
30	Koizumi	Pb, Zn	Lens & Pipe	Late Cretaceous andesites
31	Kuga	W, (Cu, Sn, Zn)	Skarn & vein	Triassic limestone
32	Kinryu	Cu, FeS	Skarn	Upper Paleozoic limestone

chl: chlorite, tour: tourmaline, mus: muscovite, Kf: K feldspar.

The samples nos. 15-18 are from early Cretaceous deposits in the Kitakami Mountains of Northeast Japan, where magnetite-series granitoids intrude into Paleozoic-Mesozoic sedimentary rocks and locally Cretaceous volcanic rocks, but the westernmost zone is composed of intermediate-series granitoids. Major commodities so far exploited in the Kitakami Mountains include iron (magnetite), copper, sulfur (pyrrhotite), tungsten and molybdenum.

The samples nos. 9-14 are from typical magnetite-series terrane of Paleogene age of the Sanin belt in Southwest Japan where granitoids intrude into Paleozoic-early Cenozoic metamorphic, sedimentary and volcanic

rocks. Main products from this belt are lead-zinc and molybdenum. Related igneous rocks to the Kamioka Pb-Zn deposit are still debatable, because igneous rocks of various ages are exposed in the mining area. Various genetic opinions as to the age and origin of the ore deposit have been proposed against the traditional view of pyrometasomatic and hydrothermal replacement type related to late Cretaceous felsic igneous activities (AKIYAMA, 1981). The granitic porphyries in the Kamioka and Nakatatsu mining areas are practically free from magnetite and more or less altered, although their hidden rocks have not been examined.

Miocene ore deposits (nos. 1-8) occur

mostly in Neogene volcanic rocks and partly in much older rocks in the Green Tuff region, which is a zone of the most fruitful sulfide mineralization in Japanese Islands including Au-Ag, Cu-Pb-Zn and manganese deposits (ISHIHARA, 1978). Besides the minerals of above metals, pyrite is most common and was mined for sulfur. Pyrrhotite and arsenopyrite are rare in these ore deposits. Miocene granitoids of this zone are composed of

magnetite-series rocks but locally converted to ilmenite-series by interaction with carbon-bearing sedimentary wall rocks (e.g., Chichibu and Kofu in the southern Fossa Magna, SASAKI and ISHIHARA, 1979; SATO and ISHIHARA, 1983; ISHIHARA et al., 1987).

In the ilmenite-series granitic terranes, fourteen ore deposits (nos. 19-32) of late Cretaceous and Miocene ages were examined. All the Cretaceous ones (nos. 23-32) but

Table 2 Associated minerals and chemical composition of sphalerite

No. Locality	Mineral Assemblage	Chemical Composition										
		(weight %)							(mole %)			
	sp py po asp cp gn	Zn	Fe	Cd	Mn	Cu	S	Total	(N)	FeS	CdS	MnS
Magnetite-series granitic terranes												
Miocene age												
1 Jokoku-1	++ +	64.55	1.18	0.10	0.12	0.09	33.39	99.43	(5)	2.06	0.08	0.22
Jokoku-2	++ -	66.24	0.65	0.18	0.03	0.00	33.50	100.60	(5)	1.12	0.16	0.06
2 Oppu	++	64.27	3.01	0.40	0.44	0.02	32.73	100.87	(3)	5.20	0.34	0.78
3 Hosokura-1	++ +	54.02	11.38	0.57	0.30	0.02	33.33	99.62	(3)	19.58	0.48	0.52
Hosokura-2	++ +	61.74	4.39	0.30	0.09	0.04	33.82	100.38	(30)	7.54	0.26	0.16
Hosokura-3	++ +	61.98	3.92	0.33	0.16	0.15	33.30	99.84	(11)	6.80	0.28	0.24
4 Budo	++	65.76	1.25	0.35	0.12	0.01	32.75	100.25	(9)	2.18	0.30	0.22
5 Tochigi	++	65.64	0.81	0.44	0.02	0.02	33.23	100.16	(3)	1.40	0.38	0.04
6 Chichibu-1	++	53.57	11.78	0.37	0.47	0.04	33.04	99.26	(3)	20.34	0.32	0.82
Chichibu-2	++	54.59	11.12	0.39	0.41	0.05	32.75	99.31	(3)	19.36	0.34	0.72
7 Kawazu	++	66.02	0.20	0.37	0.06	0.11	33.28	100.04	(5)	0.34	0.32	0.10
8 Yutani	+ ++	61.69	3.27	0.23	0.20	0.35	33.76	99.48	(7)	5.67	0.20	0.36
Cretaceous-Paleogene age												
9 Kamioka-1	++	62.11	3.55	0.24	0.06	0.02	33.41	99.39	(6)	6.18	0.20	0.10
Kamioka-2	++ ++	56.68	9.74	0.37	0.17	0.00	33.74	100.70	(7)	16.60	0.32	0.30
10 Nakatatsu	++ ++ ++	50.93	12.10	0.27	2.98	0.04	34.18	100.50	(5)	20.44	0.22	5.12
11 Ushirodani	+	60.96	4.35	0.46	0.15	0.02	33.38	99.32	(5)	7.56	0.40	0.26
12 Okurayama	++ -	59.14	6.33	0.39	0.23	0.29	33.84	100.22	(9)	10.87	0.34	0.40
13 Tohoyamasa	++ ++	62.51	3.43	0.23	0.18	0.16	33.63	100.14	(7)	5.92	0.20	0.32
14 Seikyū-minami	++ ++	65.94	1.31	0.21	0.06	0.02	32.93	100.47	(6)	2.27	0.18	0.10
15 Hokuto	- ++	54.70	9.23	2.05	0.06	0.77	32.85	99.65	(4)	16.06	1.78	0.10
16 Kameyama	++	61.52	4.50	0.80	0.35	0.05	32.79	100.02	(5)	7.82	0.70	0.62
17 Hada	- +	61.35	3.53	0.20	0.01	3.04	33.80	101.92	(4)	6.00	0.16	0.02
18 Hada East	- + -	55.70	9.99	0.42	0.11	0.46	32.77	99.45	(3)	17.32	0.36	0.20
Ilmenite-series granitic terranes												
Miocene age												
19 Kishu-1	++	61.80	4.58	0.16	0.07	0.07	33.54	100.22	(7)	7.90	0.14	0.12
Kishu-2	++	63.10	3.67	0.08	0.05	0.02	32.96	99.88	(9)	6.38	0.06	0.08
Kishu-3	++ +	58.02	8.16	0.17	0.09	0.25	33.21	99.91	(5)	14.08	0.14	0.16
20 Nanshu	++ +	56.64	9.22	0.81	0.23	0.07	32.97	99.94	(8)	15.94	0.70	0.40
21 Tarumizu	+ ++	49.60	12.21	1.83	1.78	0.56	33.56	99.55	(6)	21.00	1.56	3.12
22 Suzuyama	++ + ++	54.35	10.79	1.17	0.24	0.23	33.13	99.91	(8)	18.62	1.00	0.42
Cretaceous-Paleogene age												
23 Yaguki-1	+ ++	56.57	8.57	0.51	0.51	0.04	33.17	99.38	(7)	14.84	0.44	0.90
Yaguki-2	++ - +	57.03	8.13	0.21	0.09	0.39	33.37	99.22	(4)	14.08	0.18	0.16
Yaguki-3	++ - +	56.62	8.56	0.38	0.36	0.04	33.39	99.36	(6)	14.80	0.32	0.64
24 Takatori	- ++ - + ++ +	54.08	10.11	1.27	0.46	0.39	33.21	99.51	(8)	17.50	1.10	0.80
25 Yokoneyama	++ - +	51.18	10.49	0.92	2.56	0.08	34.28	99.51	(5)	17.92	0.78	4.44
26 Kurokawa-1	+ ++ -	51.32	13.84	0.56	0.28	0.11	33.46	99.57	(9)	23.74	0.48	0.48
Kurokawa-2	+ +	59.24	7.06	0.24	0.07	0.08	33.10	99.79	(9)	12.22	0.20	0.12
27 Kaneuchi	+ - ++ + -	54.80	9.36	3.03	0.30	0.05	32.64	100.18	(7)	16.30	2.62	0.54
28 Ohtani-1	+ - + ++	53.86	10.31	2.93	0.15	0.25	32.62	100.12	(6)	17.94	2.54	0.26
Ohtani-2	+ + ++ +	54.51	9.43	3.04	0.02	0.10	33.69	100.79	(5)	16.22	2.60	0.04
Ohtani-3	++ ++ +	53.56	10.36	2.76	0.17	0.17	33.23	100.25	(5)	17.92	2.38	0.30
29 Tatsuyama-1	+ + ++	56.37	9.11	0.43	0.40	0.17	33.31	99.79	(9)	15.70	0.36	0.70
Tatsuyama-2	++	56.45	9.01	0.45	0.25	0.08	34.02	100.26	(9)	15.40	0.38	0.44
30 Koizumi-1	++ +	56.33	9.40	0.44	0.21	0.10	33.16	99.64	(9)	16.24	0.38	0.36
Koizumi-2	++ + - + +	56.42	9.22	0.37	0.14	0.08	33.36	99.59	(9)	15.90	0.32	0.24
Koizumi-3	++ - + +	56.54	8.49	0.43	0.19	1.16	33.25	100.06	(9)	14.62	0.36	0.34
31 Kuga	++ +	53.06	10.77	0.58	1.03	0.04	33.83	99.31	(3)	18.50	0.50	1.80
32 Kinryu	++ - + -	56.69	9.31	0.49	0.07	0.02	33.20	99.78	(9)	16.07	0.42	0.12

Yaguki (no. 23) are from the Sanyo belt of the Inner Zone of Southwest Japan. The Miocene ore deposits (nos. 19-22) are from the Outer Zone of Southwest Japan. The late Cretaceous and Miocene granitoids are generally of ilmenite-series, and intrude into Paleozoic to Mesozoic metamorphic, sedimentary and volcanic rocks. Recovered metals are dominantly tungsten, tin, and copper. Pyrrhotite is very common in these deposits and was mined at many places for sulfur; arsenopyrite is also common and was mined for arsenic in some deposits (TERASHIMA and ISHIHARA, 1976). The deposits studied here are of vein- and skarn-types except for one metamorphosed stratiform manganese deposit (Yokoneyama, no. 25).

Results and Discussion

Analytical results in averaging 3-9 measurements on each polished section are listed in Table 2. The results reveal a wide range of FeS content from nearly zero to 23 mole%.

Variation within a single ore deposit

The chemical heterogeneity of sphalerite within a given ore deposit is examined in a few deposits. Fig. 2 shows the variation in FeS content of sphalerites coexisting with iron sulfides from Ohtani, Koizumi and Hosokura deposits. The variation is less than 2.0 FeS mol% in the Ohtani and Koizumi deposits. Similar examinations are performed for some other ore deposits (*e.g.* Jokoku, Chichibu and Yaguki), and suggest that the FeS variation of sphalerite with a homogeneous appearance is small within a single vein or ore deposit in general.

However, a rather wide range of variation of FeS content within a single vein or ore deposit is also observed in some deposits. In some veins of the Hosokura Pb-Zn vein deposit, sphalerites are found to have distinct color banding within a single vein or one vein system, suggesting a wide compositional variation. The data for 30 grains in the mill head

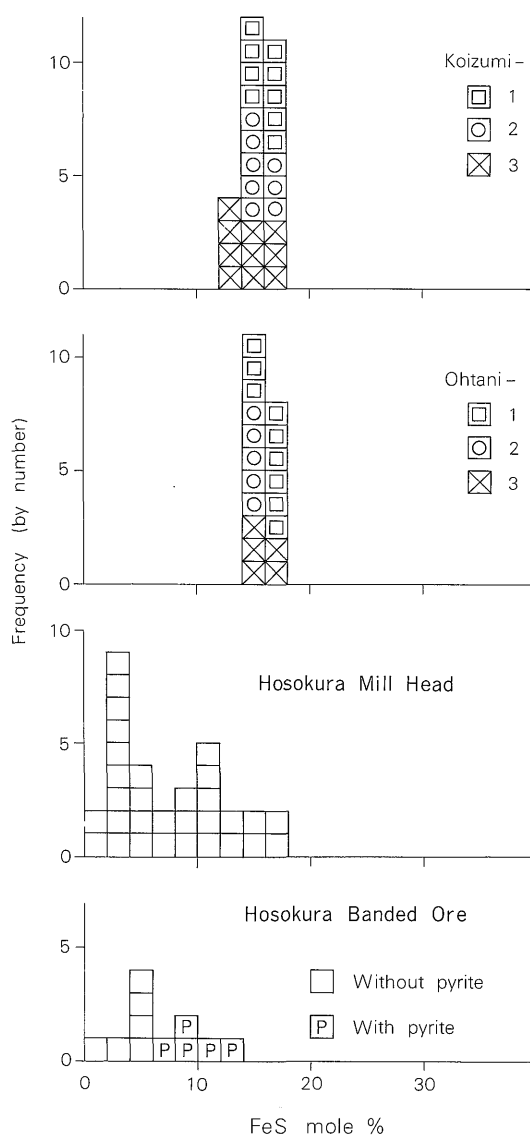


Fig. 2 Histograms of FeS contents in sphalerites from selected vein-type deposits. Koizumi 1-3 and Ohtani 1-3 imply specimen's number (See Table 2).

specimen are in the range from less than 2 mole% to 18 mole% with an average of 7.6 mole% FeS (Fig. 2). Analyses of the banded ore of 5 cm wide from Okubo West vein in the Hosokura deposit indicate that sphalerites occurring together with pyrite have high FeS content (more than 6 mole%), whereas those free from pyrite have low FeS content (less

FeS content of sphalerites from Japan (Tsukimura et al.)

Table 3 Chemical compositions of sphalerites occurring with or without pyrite in the banded ore of the Okubo West vein at -120 m level, Hosokura mine (80092203)

Sample No.	S	Zn	Fe	Cd	Mn	Cu	Total	FeS (mole%)
Without pyrite								
2	33.10	64.54	1.59	0.48	0.10	0.04	99.85	2.77
3	33.01	64.55	2.06	0.33	0.07	0.02	100.04	3.59
4	33.39	63.92	2.35	0.42	0.05	0.00	100.13	4.09
5	33.35	63.16	2.94	0.33	0.11	0.04	99.93	5.11
6	33.34	63.84	2.53	0.29	0.17	0.00	100.17	4.40
7	32.36	63.60	2.51	0.40	0.17	0.00	99.04	4.37
With pyrite								
9	33.47	57.79	7.88	0.28	0.35	0.06	99.83	13.57
10	33.58	59.31	5.50	0.29	0.20	1.42	100.30	9.51
11	33.50	59.27	5.67	0.49	0.12	0.03	99.08	9.82
12	33.51	62.67	3.63	0.21	0.17	0.03	100.22	6.30
13	33.66	59.14	6.52	0.15	0.21	0.05	99.73	11.25
Average	33.30	61.98	3.92	0.33	0.16	0.15	99.84	6.80
S.D.	0.37	2.55	2.11	0.11	0.09	0.42	0.43	3.66

Weight percent, unless otherwise noted. The total length from the sample no. 2 to no. 13 is 12 mm. S.D., standard deviation.

than 6 mole%, Fig. 2 and Table 3). The low FeS content is considered due to low FeS activity of ore solution. This can explain the wide variation of FeS content in the mill head specimen of this mine. The same tendency was observed on sphalerites from the Kamioka, Nakatatsu and Kishu mines.

SUGAKI *et al.* (1981) noted on sphalerites from tungsten-copper deposits at Tsumo that the FeS content varies systematically depending upon the kind of associated sulfide minerals as summarized in Table 4. The FeS content of sphalerite in varying mineral assemblages increases in the order of the sphalerite-bornite-chalcopyrite, the sphalerite-chalcopyrite and the sphalerite-chalcopyrite-pyrrhotite assemblages and pyrite is absent in the first two assemblages. This fact is also interpreted as the dependence of FeS content in sphalerite on the activity of FeS.

Magnetite-series granitic terranes

Sphalerites occurring in magnetite-series terranes have generally low FeS content (less than 12 mole%). In the typical magnetite-series terrane of the Sanin belt, FeS content is

Table 4 Averaged FeS contents in sphalerite from the Tsumo skarn deposits

Assemblage	FeS mole percent	
	Range	Average (n)
1) Sphalerite-bornite-chalcopyrite	0.7-3.0	1.7 (3)
2) Sphalerite-chalcopyrite	4.5-17.3	9.9 (22)
3) Sphalerite-chalcopyrite-monoclinic pyrrhotite	16.3-23.2	19.3 (13)
4) Sphalerite-chalcopyrite-monoclinic and hexagonal pyrrhotite	16.4-23.5	20.3 (20)

Data from SUGAKI *et al.* (1981)

always less than 12 mole%. In the Green Tuff region most of the ore deposits have low-FeS sphalerites (less than 12 mole%). Exceptionally, sphalerites containing high FeS content (more than 12 mole%) are found in the Kitakami Mountains.

In the typical magnetite-series terrane of the Sanin belt, where molybdenum mineralization is most representative, accessory sphalerites of the molybdenite-quartz vein from Tohoyamasa and Seikyu mines, which occur at the margins of related granitic masses, have low FeS content (less than 6

mole%). Fracture-filling type lead-zinc deposits at the Ushirodani and Ohkura mines have FeS content (5.9–10.9 mole%) higher than the molybdenum deposits, though the Ushirodani specimen does not contain Fe-sulfides. In the lead-zinc skarn deposits of the Kamioka mine, sphalerite in the Shiroji ore from Tochibora orebody, gave 6.2 mole% FeS. This low FeS content is consistent with the data of previous workers (SHIOBARA, 1961), who gave average values of 8.7 mole% and 4.7 mole% FeS for Tochibora and Maruyama orebodies, respectively. At the Nakatatsu deposit, sphalerite occurring along fractures in altered quartz porphyry was studied. This gives FeS content higher than 16 mole%. Sphalerites in major lead-zinc skarn ores of the Nakatatsu mine give an average of 10.0 mole% FeS (NZMC, 1984), although there occur sporadically iron-rich sphalerites (19.9–20.7 mole% FeS, SHIMAZAKI and SHIMIZU, 1984) which coexist with pyrite and pyrrhotite.

Sphalerites in the Green Tuff region have generally low FeS contents. The minerals from vein-type deposits of this region contain less than 6 mole% FeS, regardless of their associated minerals. Those in Kuroko deposits also show low (less than 4 mole%) FeS content (URABE, 1974). Sphalerites from the Daikoku orebody of the Chichibu skarn deposit gave exceptionally high FeS content (19–20 mole%), and similar values were also reported for the mineral from the Akaiwa (another major orebody of the same mine) by MIYAZAWA (1977). This skarn deposit was formed in limestone occurring with pelitic sediments, and sphalerites in this deposit commonly coexist with pyrrhotites (PARK and MIYAZAWA, 1971).

In the Kitakami Mountains, zinc mineralization is almost negligible and only minor sphalerite occurs in very limited portions of magnetite, copper, tungsten, molybdenum and gold deposits of granitic affinity. There are two groups in the FeS content of sphalerites. One with 6.0–7.8 mole% is seen

in vein-type molybdenum deposit (Hada) and copper skarn deposit (Kameyama), respectively. The other group of 16.1–17.3 mole% FeS is observed in molybdenite-quartz vein (Hokuto) and fracture-filling type copper deposit (Hada east), respectively.

Ilmenite-series granitic terranes

In ilmenite-series granitic terranes, sphalerites generally have FeS content higher than 12 mole%. In the Sanyo belt of Southwest Japan, sphalerites show high FeS contents (more than 12 mole%). Most of these deposits are of so called high-temperature type containing tungsten and tin. For example, oxygen isotope temperature of 450–540°C was reported for the Ohtani and Kaneuchi deposits (MORISHITA *et al.*, 1982). However, the Kurokawa chalcopyrite-pyrite vein is a low-temperature type, which occupies the outermost mineralized zone around the Naegi granite mass (SAKAMAKI *et al.*, 1961). Sphalerites from low-temperature type ore deposits also have high FeS contents.

Ore deposits in the Outer Zone of Southwest Japan have high FeS contents (more than 14 mole%), as long as sphalerite is associated with iron sulfides. The tendency is consistent with the results of MUTA (1958). At large vein-type copper deposits of Kishu mine, the mineralization is divided into four stages (ONO, 1969). Sphalerite in the first chalcopyrite-pyrite stage ore gives 14.1 mole% FeS (Kishu-3), but the mineral from the second stage yields less than 7.9 mole% FeS and is not associated with iron-sulfide (Kishu-1, -2, Table 2).

CdS and MnS contents

CdS and MnS contents of sphalerites are usually less than 1 mole%, but some sphalerites have high CdS and/or MnS contents (more than 1%). Sphalerites in ilmenite-series terranes occasionally have high contents of cadmium (up to 2.6 mole% CdS), especially in those associated with tin and tungsten mineralization. Manganese-rich sphalerites are found in a thermally metamor-

phosed stratiform Mn-deposit of the Yokoneyama mine (4.4% MnS), and the Kuga skarn deposit (1.8% MnS). The Kuga deposit has a Mn-rich feature resulted from the interaction of ore solution with manganese deposits in the Kuga group (SATO, 1980b). FUKUOKA and HIROWATARI (1981) also reported MnS contents up to 14 mole% in sphalerites from manganese deposits, and noted that manganese in sphalerite has no correlation with the FeS content, temperature and sulfur fugacity during the ore formation.

It is clear that these high MnS contents are resulted from the high Mn-content of ore solution. In the Takatori deposit, a high MnS content (4.4%) may also be interpreted with the similar reasoning. Indeed, the tungsten veins of this deposit occur crossing manganese chert beds. Another anomalous value at Nakatatsu suggests that manganese beds may occur at depth or in the surrounding sedimentary rocks, which could have been involved in the ore solution responsible for this ore deposit. The other anomaly is seen at Tatumizu where tin-quartz veins occur in S-type ilmenite-series granite in which manganese is concentrated in the latest crystallized mineral such as in garnet (ISHIHARA and KAWACHI, 1961).

Regional and temporal variation

FeS contents of sphalerites reported so far were summarized together with the present data in Appendices I and II, and are shown in Figs. 3-5. The ore deposits shown in Appendix I and Fig. 4 are Miocene-Pliocene, while those in Appendix II and Fig. 5 are Cretaceous-Paleogene in age. The regional and temporal classification of ore deposits in these Appendices and figures is based on the metallogenic provinces by ISHIHARA (1978). A representative value is shown for each locality in taking account of iron mineral assemblage in given ore deposit. For example, at Toyoha, the sphalerites coexisting with hematite and pyrite have 0.5-3.0 mole% FeS, and those coexisting with pyrite have all

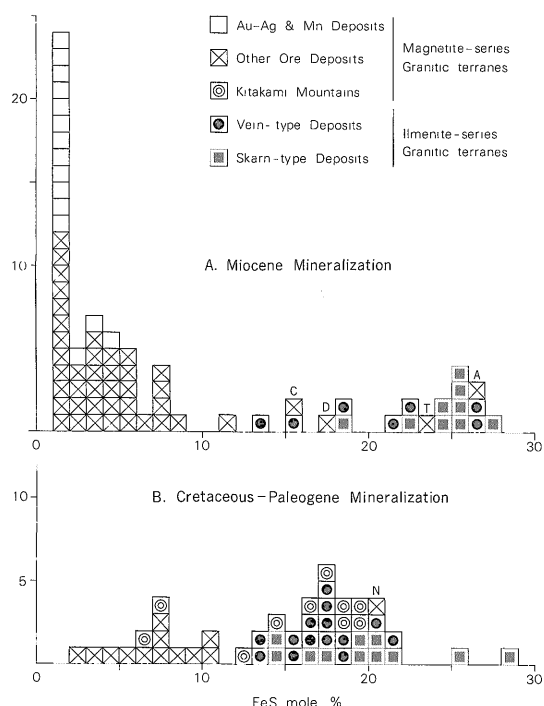


Fig. 3 Histograms of FeS contents in sphalerites. One box indicates one orebody or one ore deposit. C, Chichibu; D, Daira; T, Taishu; A, Ashio-Kajika; N, Nakatatsu-quartz porphyry (Mo).

range up to 20 mole% (SHIKAZONO, 1975). We consider that 7.7 mole% represents the ore deposit, because the sphalerite-pyrite assemblage is most common throughout the Toyoha vein system (YAJIMA and OHTA, 1979).

In the magnetite-series volcanic-plutonic terrane of the Green Tuff region, sphalerites of Au-Ag veins and of rhodochrosite vein deposits have low FeS values, up to 4.9 mole%, with a maximum concentration at 1-2 mole%. Sphalerites from base metal deposits in the same terrane range from 0.9 to 11 mole% in general, except for a few localities, which will be discussed later. In the Sanin belt, the FeS content ranges from 2.2 to 10.9 mole%, which is similar to that of the base metal deposits in the Green Tuff region. In the Kitakami area, however, the FeS value varies from 6.0 to 19.5 mole%, being intermediate between those of typical

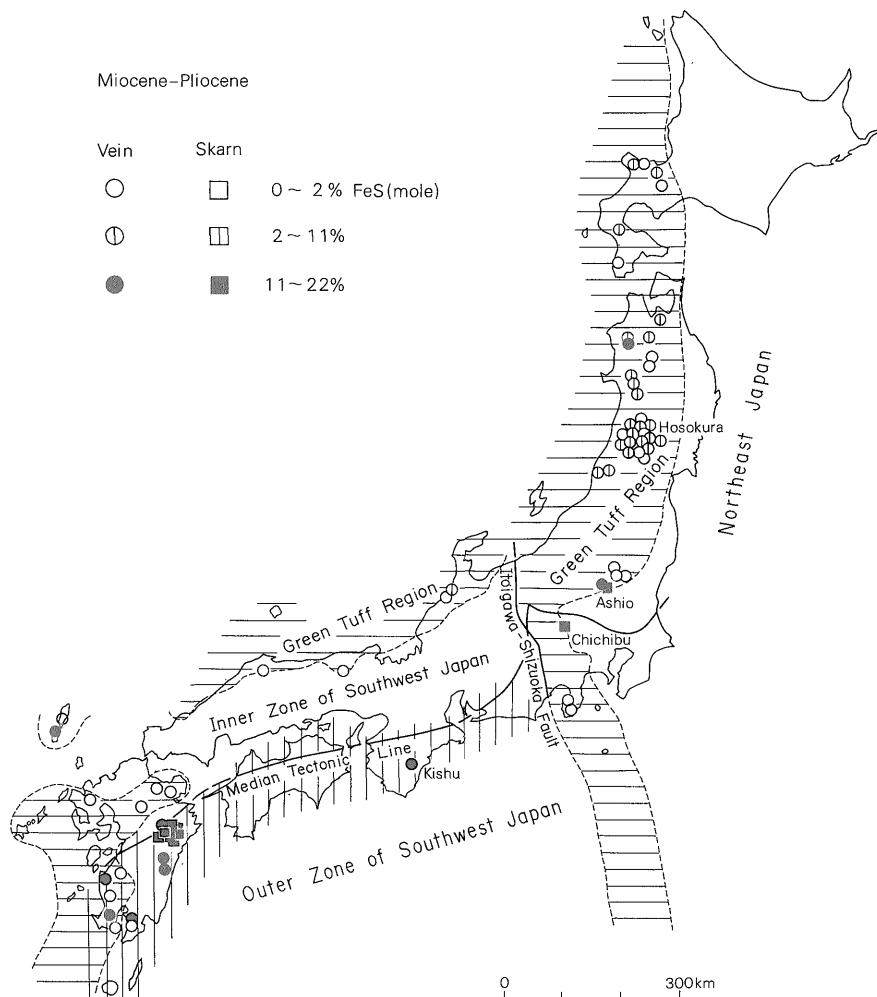


Fig. 4 Variation of FeS contents in sphalerites from the Late Cenozoic ore deposits.

magnetite-series and ilmenite-series granitic terranes (Fig. 3).

In the ilmenite-series granitic terranes, sphalerites from the Outer Zone of Southwest Japan are generally iron rich (14.1-27.7 mole% FeS but mostly 22-27 mole% FeS). Sphalerite samples in the Sanyo belt have the range of 13.7-28.8 mole% FeS but are generally 13-22 mole% FeS; thus contain less iron than in those of the Outer Zone ore deposits. There is a tendency that sphalerites of skarn-type ore deposits are slightly richer in FeS than those of vein-type ore deposits.

Genetic consideration

The granitoids series are beautifully correlated with FeS content of sphalerite from the related mineralizations (Fig. 3), including not only so-called high-temperature type deposits for tin, tungsten and molybdenum but also low-temperature type ores for base and precious metals. Sphalerites from the ore deposits of ilmenite-series granitic terranes have generally FeS content higher than 13 mole%, whereas those from the magnetite-series granitic terranes have the content generally less than 9 mole% when we consider the representative orebody value.

FeS content of sphalerites from Japan (Tsukimura et al.)

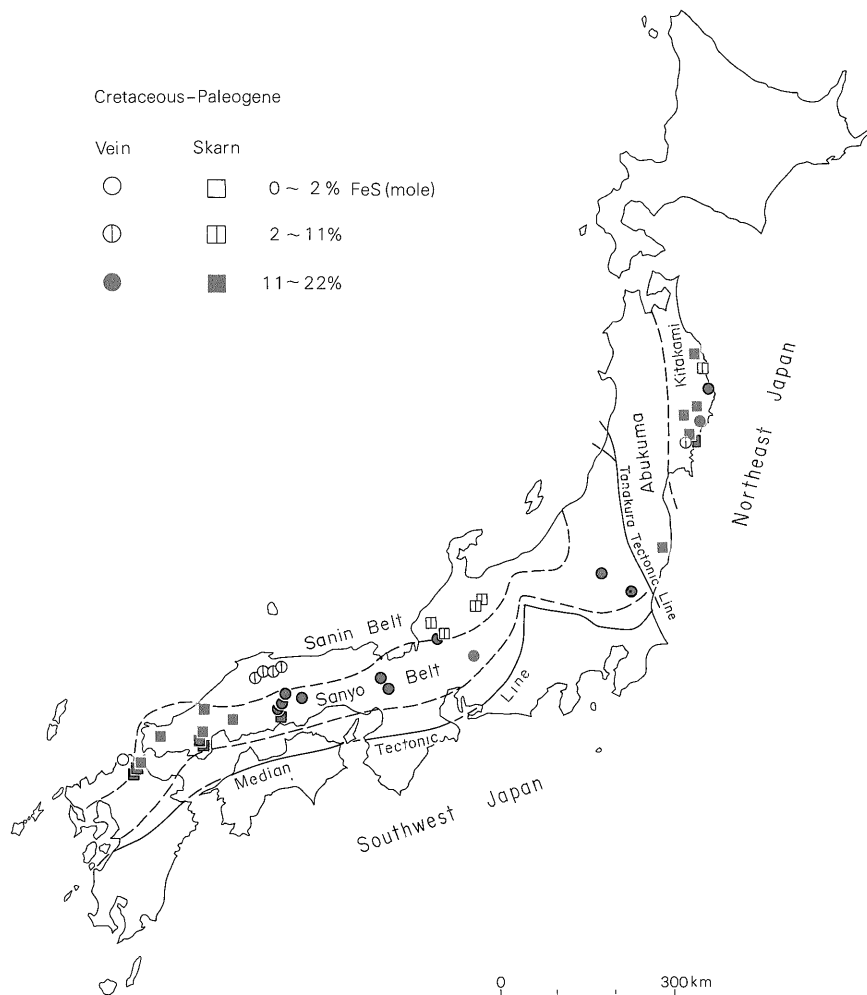


Fig. 5 Variation of FeS contents in sphalerites from the Cretaceous-Paleogene ore deposits.

Thus the sphalerite composition convinces us to have some genetic connection with the granitoid series.

The FeS content of sphalerite coexisting with iron sulfides depends on temperature and sulfur fugacity (f_{S_2}) (BARTON and TOULMIN, 1966). Fig. 6 illustrates such a relationship. The diagram shows that when the temperature is the same, Fe-rich sphalerites tend to be formed from low f_{S_2} ore solutions. In combining the FeS contents of sphalerite with the temperature data given by oxygen isotope and/or fluid inclusion, the ranges of sulfur fugacity of the studied ore deposits for

each series are obtained and shown in Fig. 6. Ore deposits are clearly divided into two groups, high f_{S_2} type (magnetite-series) and low f_{S_2} type (ilmenite-series). This suggests the genetic relation between high/low f_{S_2} and the oxidized/reduced conditions of related granitoids magmas.

Although the difference of sulfur fugacity is mainly responsible for that of the FeS content of sphalerite, the effect of temperature on FeS content of sphalerite is also observed (Fig. 6). If we compare the FeS contents in sphalerites from ore deposits in the same granitoids-series terrane, there is the tendency that the

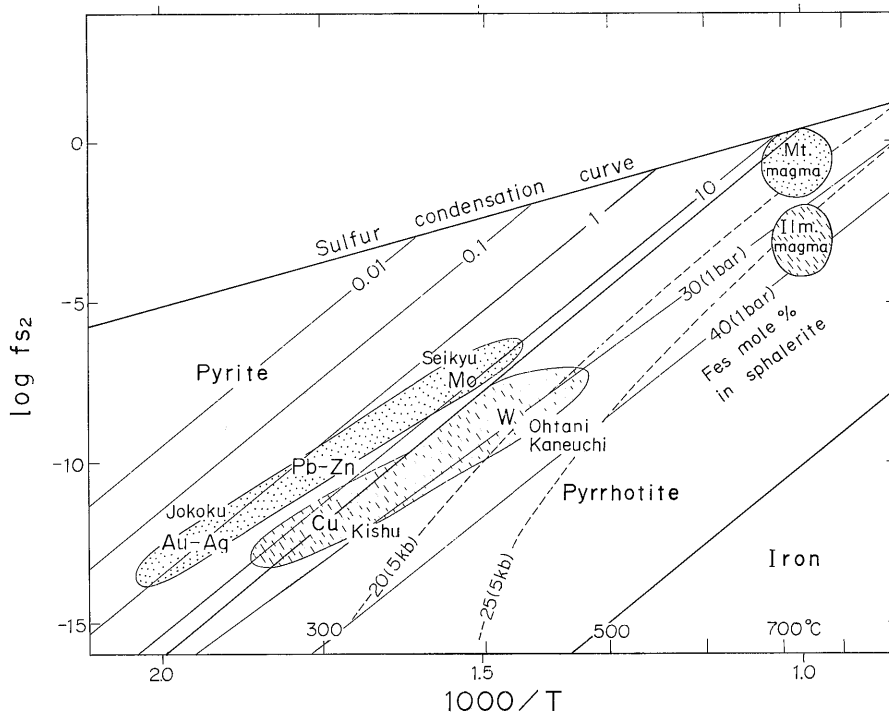


Fig. 6 The FeS contents in sphalerites as a function of temperature and sulfur fugacity. The FeS content is calculated by the method of HUTCHEON (1978) using the experimental data of BARTON and TOULMIN (1966). mt. magma, magnetite-series magma; ilm. magma, ilmenite-series magma.

low FeS content is observed in low temperature type ore deposits such as Au-Ag and Mn veins, and that the high FeS content is observed in high temperature type such as Mo veins. The effect of temperature on FeS content was also reported in the sphalerites from eastern China (SATO *et al.*, 1986).

Formation temperatures of ore deposits shown in Fig. 6 are estimated from oxygen isotope studies and fluid inclusion studies. Homogenization temperatures of fluid inclusion are available in many of the studied ore deposits (ENJOJI and TAKENOCHI, 1976). We have corrected those homogenization temperatures qualitatively, because homogenization temperature seems to be lower than the true formation temperature. Indeed, MORISHITA *et al.* (1982) and MORISHITA and MATSUHISA (1982) found the formation temperature up to 530°C by oxygen isotopic geothermometer on vein-forming minerals of

so called high-temperature type tungsten deposits at Ohtani, Takatori and Kaneuchi, where the homogenization temperatures of 350–200°C have been reported. They interpreted the discrepancy between two methods due to pressure effect, which is plausible from such geological view point as the tungsten deposits of the ilmenite-series are considered to have formed at place deeper than plutonic molybdenum deposits (ISHIHARA, 1973) and subvolcanic base metal and precious metal deposits of magnetite-series terranes.

Pressure effect on FeS content of sphalerite is notable when the mineral coexists with pyrrhotite, while it is negligible when the mineral coexists with pyrite. The FeS content of sphalerite coexisting with pyrrhotite at 5 Kbar is illustrated in Fig. 6. Although the FeS content of sphalerite coexisting with pyrrhotite is a function of so many parameters (pressure, temperature and f_{S_2}), it is certain

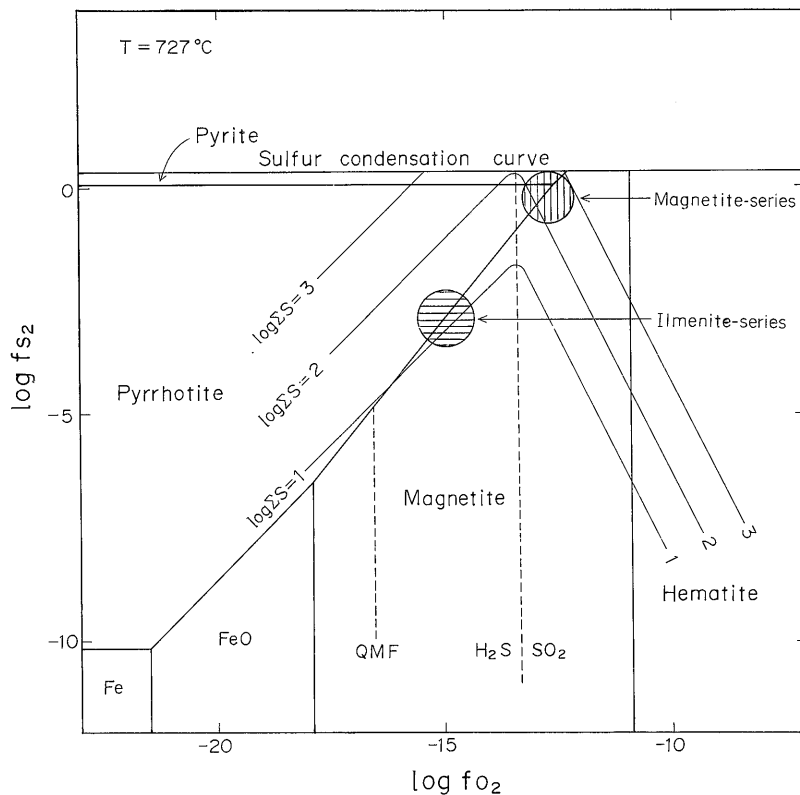


Fig. 7 The f_{O_2} and f_{S_2} diagram of Fe-S-O system at 1000 K (727°C). The thermodynamic data are based on ROBIE *et al.* (1977). When H_2S - SO_2 boundary and total sulfur are calculated, pressure of water is assumed as 1 kbar.

that FeS contents of sphalerites coexisting with pyrrhotite are always higher than 14 mole.% and indicate very low sulfur fugacities.

We have shown that the sulfur fugacity (f_{S_2}) during ore formation is high in magnetite-series terranes and that it is low in ilmenite-series terranes. Such relation is expected to be held in the related granitoids as well as in ore deposits. On the basis of mineral assemblage of the granitoids (ISHIHARA *et al.*, 1983; 1985), the oxygen fugacity (f_{O_2}) and sulfur fugacity (f_{S_2}) of magnetite-series granitic magma are estimated as higher than those of ilmenite-series one. Fig. 7 shows the f_{O_2} - f_{S_2} diagram for Fe-S-O system. The f_{O_2} and f_{S_2} conditions for the magnetite-series granitoids magmas are schematically illustrated by the vertically shaded area in Fig. 7. The mineral assemblage of Fe-S-O system in magnetite-

series granitoids is generally magnetite-pyrite with or without pyrrhotite. The f_{O_2} and f_{S_2} conditions for the ilmenite-series granitoids are estimated as the area horizontally shaded in Fig. 7. The f_{O_2} of magnetite-series granitoid magmas was estimated as 2 to 3 orders of magnitude higher than that of ilmenite-series (CZAMANSKE *et al.*, 1981). There is pyrrhotite and may be very small amount of magnetite in ilmenite-series granitoids.

The magmas of magnetite-series and ilmenite-series differ in dominant sulfur species as shown in Fig. 7. H_2S is dominant in ilmenite-series magmas, while SO_2 is dominant in magnetite-series magmas. BURNHAM (1979) indicated that the solubility of oxidized sulfur species (SO_2) in granitic melts is very small. Then, most of the sulfur in magnetite-series magma is partitioned into fluid phase of magmas for magnetite-series.

This increase the f_{S_2} of the fluid phase. As a result of high f_{S_2} and high f_{O_2} , total abundance of sulfur in fluid phase of magmas for magnetite-series is much greater than that for ilmenite-series magmas (Fig. 7), which may be responsible for intensive sulfide mineralization in magnetite-series terranes.

A few exceptions to the correlation are observed in magnetite-series ore deposits. These are explained by the local reduction of ore solution by carbon-bearing wall rocks. Iron-rich sphalerites occur at several localities within magnetite-series granitic terranes of the Green-Tuff region such as Pb-Zn skarns at Chichibu, Pb-Zn veins at Taishu and Zn-rich "Kajika" orebody of the Ashio copper mines. In all the cases, pyrrhotite occurs abundantly. In the Chichibu mine, sphalerites of major orebodies, both Daikoku and Akaiwa, have generally 19-23 mole% FeS except for the upper most part of the Daikoku where the content decreases down to 2.3 mole% (MIYAZAWA, 1977). In the Taishu mine, the sphalerites have been known as dark-colored species which contain generally 21-25 mole% FeS but locally lower to 11 mole% FeS (MUTA, 1958). Granitic stocks related to these mineralizations are composed mainly of magnetite-series but are locally converted to ilmenite-series in contact with pelitic wall rocks (TERASHIMA and ISHIHARA, 1980). The Ashio deposits consist of vein-type mineralization occurring chiefly in the Ashio rhyolites and replacement type "Kajika" orebody occurring in the underlying chert beds (NAKAMURA, 1970). FeS-rich sphalerite is very common in the Kajika orebody where the mineral occurs with abundant pyrrhotite. This orebody may also have been reduced by sedimentary carbon during the ore formation. Sulfur isotope ratios of ore sulfur from these deposits show intermediate values between those of typical magnetite-series and ilmenite-series ore deposits (SASAKI and ISHIHARA, 1980). Thus sedimentary carbon and sulfur recycled through the magmatic and hydrothermal processes may have been responsible for

the reduced-type ore deposits in magnetite-series granitic terranes.

Several exceptions are also observed in the Kitakami Mountains area where the granitoids are generally of magnetite-series. Pyrrhotite is fairly common in the ore deposits of this area. The iron-rich sphalerites are found not only in skarn deposits but also in vein type ones. The sedimentary carbon may be responsible for the iron-rich sphalerites in the skarn deposits, because the sedimentary materials can reduce the contiguous magmas and ore solutions. However, iron-rich sphalerites (12-19 mole%) and pyrrhotites of the vein-type ore deposits indicate that the related granitoid magmas may have had somewhat low f_{O_2} and f_{S_2} compared with the typical magnetite-series magmas.

Concluding Remarks

The chemical composition of sphalerites revealed that the regional variation of FeS content is consistent with the theoretical considerations with respect to the granitoid-series terranes over the Japanese Islands. This characteristic is observed from low-temperature type to high-temperature type ore deposits. The ore fluids are concluded to have common background in terms of sulfur and oxygen fugacities to those of the related granitoids. The ore fluids liberated from the granitoids are locally modified by the wall rocks with respect to the oxidation/reduction status.

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References

- AKIYAMA, S. (1981) Recent information about the

FeS content of sphalerites from Japan (Tsukimura et al.)

- mineralization in the Kamioka mining area—Studies on regional geology and mineralization in the Kamioka district, No. 2. *Mining Geol.*, vol. 31, p. 157-168.
- BARTON, P. B. Jr. and TOULMIN, P., III (1966) Phase relations involving sphalerite in the Fe-Zn-S system. *Econ. Geol.*, vol. 61, p. 815-849.
- BURNHAM, C. W. (1979) Magmas and hydrothermal fluids, In *Geochemistry of Hydrothermal Ore Deposits, 2nd ed.* (H. L. BARNES, ed.). John Wiley & Sons, Inc., p. 71-136.
- CZAMANSKE, G. K., ISHIHARA, S. and ATKIN, S. A. (1981) Chemistry of rockforming minerals of the Cretaceous-Paleocene batholith in southwestern Japan and implications for magma genesis. *Jour. Geophys. Res.*, vol. 86, no. B11, p. 10431-10469.
- ENDO, M. (1963) Studies on the sphalerites from the Hitachi mine. *Jour. Japan. Assoc. Min. Petr. & Econ. Geol.*, vol. 50, p. 209-217.
- ENJOJI, M. and TAKENOUCI, S. (1976) Present and future researches of fluid inclusions from vein-type deposits. *Mining Geol. Spec. Issue*, no. 7, p. 85-100.
- FUKUOKA, M. and HIROWATARI, F. (1981) Manganese content of sphalerites from the manganese deposits in Japan, *Sci. Rept. Dept. Geol. Kyushu Univ.*, Geology, vol. 14, p. 1-12.
- HUTCHEON, I. (1978) Calculation of metamorphic pressure using the sphalerite-pyrrhotite-pyrite equilibrium. *Am. Mineral.*, vol. 63, p. 87-95.
- ISHIHARA, S. (1973) The Mo-W metallogenic provinces and related granitic provinces. *Mining Geol.*, vol. 23, p. 13-32.
- (1977) The magnetite-series and ilmenite-series granitic rocks. *Mining Geol.*, vol. 27, p. 293-305.
- (1978) Metallogenesis of Japanese island arc system. *Jour. Geol. Soc. London.*, vol. 135, p. 389-406.
- (1981) The granitoid series and mineralization. *Econ. Geol. 75th Anniv. Vol.*, p. 458-484.
- (1984) Granitoid series and Mo/W-Sn mineralization in East Asia. *Rept. Geol. Surv. Japan*, no. 263, p. 173-208.
- and KAWACHI, Y. (1961) On the Takakuma-yama granitic stock and related uraniferous ore deposit of Nagao-ko at Tarumizu mine, Kagoshima Prefecture. *Rept. Geol. Surv. Japan* no. 190, p. 333-348.
- , KANISAWA, S. and TERASHIMA, S. (1983) Sulfur and sulfides in the Cretaceous, magnetite-series granitoids of the Kitakami Mountains, Japan. *Jour. Japan. Assoc. Min. Petr. & Econ. Geol.* vol. 78, p. 1-10.
- , MATSUHISA, Y., SASAKI, A. and TERASHIMA, S. (1985) Wall rock assimilation by magnetite-series granitoid at the Miyako pluton, Kitakami, northeastern Japan. *J. Geol. Soc. Japan*, vol. 91, p. 679-690.
- , TERASHIMA, S. and TSUKIMURA, K. (1987) Spatial distribution of magnetic susceptibility and ore elements, and cause for the local reduction on magnetite-series granitoids and related ore deposits at Chichibu, central Japan. *Mining Geol.*, vol. 37, p. 15-28.
- KAJIWARA, K. (1971) Sulfur isotope study of the Kuroko-ores of the Shakanai No. 1 deposits, Akita Prefecture, Japan. *Geochem. J.*, vol. 4, p. 157-181.
- KULLERUD, G. (1953) The FeS-ZnS system, a geological thermometer, *Norsk. Geol. Tidsskr.*, vol. 32, p. 61-147.
- KUROSAWA, K. (1979) The chemical compositions of sphalerite and argentic tetrahedrite from Inakuraishi mine, Shiribeshi province, Hokkaido. *Rept. Geol. Surv. Hokkaido*, no. 51, p. 81-85.
- MIYAZAWA, T. (1977) *Contact metasomatic ore deposits in Japan and Korea*. Hakusuido, Tokyo, A3-A146.
- MORISHITA, Y., MATSUHISA, Y. and ISHIHARA, S. (1982) Oxygen isotopic compositions of minerals from Ohtani and Kaneuchi mines (abs.). *Mining Geol.*, vol. 32, p. 177.
- and ————— (1982) Oxygen isotopic composition of minerals from Takatori deposit (abs.). *Abstract Issue for Fall meeting, Soc. Mining Geol. Japan, Japan. Assoc. Pet. Min. Econ. Geol., and Soc. Mineral. Soc. Japan*, p. 41.
- MUTA, K. (1958) Variation of FeS solubility in sphalerite from Kyushu and its relation with minor elements. *Mem. Fac. Eng. Kyushu Univ.*, vol. 17, p. 139-162.
- NAKAMURA, T. (1970) Mineral zoning and characteristic minerals in the polymetallic veins of the Ashio copper mine. In *Volcanism and Ore Genesis*. (T. TATSUMI ed.), p. 231-246, Univ. Tokyo Press.
- NEDACHI, M. (1974) Mineralization of the Kohoku gold, silver and copper ore deposits, Miyagi Prefecture, Japan. *Sci. Rept. Tohoku Univ.*, Ser. III, vol. 12, p. 331-394.

- NZMC (Nippon Zinc Mining Co., 1984) Development of mineral exploration at the Nakatatsu mine. In *Mineral Exploration in Japan*, vol. 2, p. 79-112, Soc. Mining Geol. Japan.
- ONO, K. (1969) Structural features and their relation to metal quantities in ore deposits of the Kishu mine. *Mining Geol.*, vol. 19, p. 299-311.
- PARK, H. I. and MIYAZAWA, T. (1971) On the pyrrhotite from the Chichibu mine, Saitama Prefecture. *Mining Geol.*, vol. 21, p. 259-273.
- ROBIE, R. A., HEMINGWAY, B. S. and FISHER, J. R. (1977) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ Pascals) pressure and at higher temperatures. *U. S. Geol. Surv. Bull.* no. 1452, p. 1-456.
- SAKAMAKI, Y., IGARASHI, T. and SHIMAZU, M. (1961) Uraniferous ore deposits at Kurokawa mine, Gifu Prefecture. *Rept. Geol. Surv. Japan*, no. 190, p. 208-213.
- SASAKI, A. and ISHIHARA, S. (1979) Sulfur isotopic composition of the magnetite-series and ilmenite-series granitoids in Japan. *Contrib. Mineral. Petrol.*, vol. 68, p. 107-115.
- and ——— (1980) Sulfur isotope characteristics of granitoids and related mineral deposits in Japan. *Proc. 5th IAGOD Symp.*, E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany, p. 325-335.
- SATO, J., ENJOJI, M., OKEYA, M. and ONO, S. (1981) Black-colored ore of the Pifue-Honpi vein, the Chitose mine, Hokkaido, Japan. *Mining Geol. Spec. Issue*, no. 10, p. 127-142.
- SATO, K. (1980a) Distribution of flourite deposits in Japanese islands. *Mineral. Deposita*, vol. 15, p. 327-334.
- (1980b) Tungsten skarn deposit of the Fujigatani mine, Southwest Japan. *Econ. Geol.*, vol. 75, p. 1066-1082.
- (1982) Characteristics of tungsten skarns in Japan, two contrasting types. *Proc. Intern. Symp. Tungsten Geol.*, Jiangxi, China, 1981, p. 115-122.
- and ISHIHARA, S. (1983) Chemical composition and magnetic susceptibility of the Kofu granitic complex. *Bull. Geol. Surv. Japan*, vol. 34, p. 413-427.
- , NI, R., CHAO, F. and LI, W. (1986) Compositional variation of sphalerites from Cu and Pb-Zn deposits in the Lower Yangtze area, eastern China. *Bull. Geol. Surv. Japan*, vol. 37, p. 259-269.
- SATO, T. (1973) A chloride complex model for Kuroko mineralization. *Geochem. J.*, vol. 7, p. 245-270.
- SCOTT, S. D. (1973) Experimental calibration of the sphalerite geobarometer. *Econ. Geol.*, vol. 68, p. 466-474.
- and BURNES, H. L. (1971) Sphalerite geothermometry and geobarometry. *Econ. Geol.*, vol. 66, p. 653-669.
- SHIKAZONO, N. (1974) Physico-chemical environment and mechanism of volcanic hydrothermal ore deposition in Japan, with special reference to oxygen fugacity. *Jour. Fac. Sci., Univ. Tokyo*, Sec. II, vol. 19, p. 27-56.
- (1975) Mineralization and chemical environment of the Toyoha lead-zinc vein-type deposits, Hokkaido, Japan. *Econ. Geol.*, vol. 70, p. 694-705.
- SHIMAZAKI, H. (1980) Characteristics of skarn deposits and related acid magmatism in Japan. *Econ. Geol.*, vol. 75, p. 173-183.
- and SHIMIZU, M. (1984) Compositional variation of sphalerites from skarn deposits in Japan. *Jour. Fac. Sci. Univ. Tokyo*, Sec. II, vol. 21, p. 51-66.
- SHIMIZU, M. and SHIMAZAKI, H. (1981) Application of the sphalerite geobarometer to some skarn-type ore deposits. *Mineral. Deposita*, vol. 16, p. 45-50.
- SHIOBARA, K. (1961) Decrepitation temperature and chemical characteristics of the mineral species from the Kamioka mine. *Mining Geol.*, vol. 11, p. 344-349.
- SUGAKI, A., SOEDA, A., SHIMA, H., KITAKAZE, A., HIROWATARI, F., MARIKO, T. and TAKENO, S. (1981) Ore, deposits and minerals of the pyrometamorphic deposit of the Tsumo mine, with special reference to Maruyama deposit. *Mining, Geol. Spec. Issue*, no. 9, p. 89-144.
- TAGUCHI, S. and HIROWATARI, F. (1981) Chemical composition of sphalerite associated with gold mineralization at the Fuke mine, Kagoshima Prefecture. *Mining Geol. Spec. Issue*, no. 10, p. 35-42.
- TAKAHASHI, K. (1963) Geochemical study on minor elements in sulfide minerals. *Rept. Geol. Surv. Japan*, no. 199, p. 1-67.
- TERASHIMA, S. and ISHIHARA, S. (1976) Contents of arsenic in granitoids and their relation to mineralization. *Mining Geol.*, vol. 26, p. 327-339.
- and ——— (1980) Anomalous chlorine contents of Miocene granitoids from Tsushima, Japan. *Jour. Japan. Assoc. Min. Pet. Econ. Geol.*, vol. 75, p. 62-67.

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- TSUKIMURA, K., SATO, K. and ISHIHARA, S. (1982) The granitoid series and iron content of sphalerite. *Abstract Issue for Fall meeting, Soc. Mining Geol. Japan, Japan. Assoc. Pet. Min. Econ. Geol., and Mineral. Soc. Japan*, p. 25.
- URABE, T. (1974) Iron content of sphalerite coexisting with pyrite from some Kuroko deposits. *Mining Geol. Spec. Issue*, no. 6, p. 377-384.
- URASHIMA, Y., SOEDA, A., TSUKAHARA, N., MATSUGI, M. and SANJO, K. (1981) The Sakoshi-Odomari gold-silver deposits, Hyogo Prefecture, Japan. *Mining Geol. Spec. Issue*, no. 10, p. 53-73.
- YAJIMA, J. and OHTA, E. (1979) Two-stage mineralization and formation process of the Toyoha deposits, Hokkaido, Japan. *Mining Geol.*, vol. 29, p. 291-306.
- YAMAOKA, K. (1981) Native gold from Omine (Nippo), Oya, and Owashi mines—On the composition of gold from the contact-metasomatic and the fissure filling ore deposits in the Kitakami Mountains. *Mining Geol. Spec. Issue*, no. 10, p. 151-158.

日本における閃亜鉛鉱の鉄含量の時空変化と花崗岩系列との関係

月村勝宏・佐藤興平・石原舜三

要 旨

我が国の各地質区の32鉱床から得られた閃亜鉛鉱の化学組成を Zn, Fe, Cd, Mn, S につき EPMA により定量分析した。この結果、FeS 含量は、共生鉱物(特に、鉄硫化物)、岩石生成区、鉱床の型により大きく変化することが明らかになった。ひとつの鉱床内でも鉄硫化物の有無により鉄含量が大きく変動する場合もあるが、鉄硫化物と共生している閃亜鉛鉱の FeS 含量は、ひとつの鉱床内で比較する限り変動は少ない。そこで、鉄硫化物と共存する閃亜鉛鉱の FeS 含量の各鉱床の値を求め、既発表資料をも合せて、岩石生成区および鉱床の種類と FeS 含量との関係を考察した。

検討対象となった閃亜鉛鉱の FeS 含量は0.3-23.7モル%の变化幅をもつが、磁鉄鉱系花崗岩帯の鉱脈型鉱床では FeS 含量が一般に低い(12モル%以下)。他方、チタン鉄鉱系花崗岩帯の鉱脈型鉱床では鉄に富んでいる(14モル%以上)。この事実は、鉱床を形成した鉱液が磁鉄鉱系花崗岩では相対的に f_{O_2} と f_{S_2} が高く、チタン鉄鉱系では低かったことを示している、磁鉄鉱系地帯でも局部的に鉄に富む閃亜鉛鉱がみられるが、これは鉱液が周辺の堆積岩と反応することにより還元されたためと考えられる。北上山地の鉱床は火成岩母岩の閃亜鉛鉱でも鉄に富むものがあり、典型的な磁鉄鉱系地帯より全般に還元的であったものと思われる。

スカルン型鉱床中の閃亜鉛鉱は鉱脈型鉱床のそれより鉄を多く(12モル%FeS以上)含む。この事実はスカルン型鉱床が鉱脈型鉱床よりも高温で生成したか、母岩との反応により還元されやすかったかを示している。逆に、磁鉄鉱系地帯の金銀あるいはマンガンの鉱脈型鉱床は、他の鉱脈型鉱床に比べて鉄含量が低い。これは金銀あるいはマンガン鉱床が低温かつ酸化的環境で生成したことを示している。

(受付: 1986年9月10日; 受理: 1987年1月22日)

Appendix I List of FeS content of sphalerites in Japan (Miocene-Pliocene)

No.	Locality	Type	Recovered metal	FeS mole % (number)	coexisting Fe sulfide	Reference
Au-Ag veins						
1	Chitose, Hokkaido	V	Au-Ag	1.1 (3)	py	J.Sato et al.(1981)
				1.2	py	Shikazono(1974)
2	Kotoku, Tochigi	V	Au-Ag	1.6 (2)	py	Muta(1958)
3	Kidogasawa, Tochigi	V	Au-Ag	1.9 (1)	py	Muta(1958)
4	Seigoshi, Shizuoka	V	Au-Ag	0.6 (13)	?	Shikazono(1974)
5	Kawazu, Shizuoka	V	Au-Ag	0.3 (1)	?	This study
6	Yamaura, Oita	V	Au-Ag	1.6 (1)	?	Muta(1958)
7	Taio, Oita	V	Au-Ag	1.8 (1)	py	Muta(1958)
8	Asahi, (Yamakuni), Oita	V	Au-Ag	3.1 (2)	py	Muta(1958)
9	Gochoda, Saga	V	Au-Ag	1.7 (1)	?	Muta(1958)
10	Ohtani, Kagoshima	V	Au-Ag	2.3 (2)	?	Muta(1958)
11	Fuke, Kagoshima	V	Au-Ag	1.8 (1)	py	Muta(1958)
				1.4 (25)	py	Taguchi & Hirowatari(1981)
12	Iriki, Kagoshima	V	Au-Ag	1.4 (1)	?	Muta(1958)
Rhodochrosite vein						
13	Inakuraishi, Hokkaido	V	Mn	4.9 (10)	py	Kurosawa(1979), Fukuoka & Hirowatari(1981)
14	Yamanaka, Hyogo	V	Mn	1.8 (4)	py	Fukuoka & Hirowatari(1981)
15	Jokoku, Hokkaido	V	Mn	1.6 (2)	py	This study
Base metal vein						
16	Yoichi, Hokkaido	V	Pb-Zn	1.8 (1)	py	Muta(1958)
17	Toyoha, Hokkaido	V	Pb-Zn	7.7 (173)	py	Shikazono(1974)
18	Yakumo, Hokkaido	V	Cu	4.5 (1)	py	Muta(1958)
19	Kanahorizawa, Aomori	V	Cu	2.5 (1)	py	Muta(1958)
20	Oppu, Akita	V	Pb-Zn	5.2 (1)	?	This study
21	Akitsu, Akita	V	Pb-Zn	4.2 (1)	py	Muta(1958)
22	Daira, Akita	V	Pb-Zn	17.7 (1)	py	Muta(1958)
23	Osarizawa, Akita	V	Cu	1.2 (1)	py	Muta(1958)
24	Ohtsuta, Akita	V	Pb-Zn	1.7 (2)	py	Muta(1958)
25	Ani, Akita	V	Cu	8.6 (1)	py	Muta(1958)
26	Sayama, Akita	V	Cu	5.7 (1)	py	Muta(1958)
27	Hata, Akita	V	Pb-Zn	2.8 (2)	py	Muta(1958)
28	Innai, Akita	V	Cu, Ag	7.8 (1)	?	Takahashi(1963)
29	Murayama, Yamagata	V	Cu	2.7 (2)	py	Muta(1958)
30	Mutsuai, Yamagata	V	Pb-Zn	1.8 (2)	py	Muta(1958)
31	Ooizumi, Yamagata	V	Pb-Zn	5.3 (2)	py	Muta(1958)
32	Nissho, Yamagata	V	Pb-Zn	6.0 (11)	?	Takahashi(1963)
33	Kamuro, Yamagata	V	Cu	3.5 (1)	py	Takahashi(1963)
34	Tengumori, Yamagata	V	Cu	4.2 (2)	py	Takahashi(1963)
35	Daiyama, Yamagata	V	Cu	5.0 (2)	?	Takahashi(1963)
36	Shirakawa, Yamagata	V	Cu	1.4 (1)	?	Takahashi(1963)
37	Oohori, Yamagata	V	Pb-Zn	3.7 (4)	?	Takahashi(1963)
38	Tsuboge, Miyagi	V	Cu	1.4 (1)	?	Takahashi(1963)
39	Suginomori, Miyagi	V	Pb-Zn	3.3 (2)	py	Takahashi(1963)
40	Hosokura, Miyagi	V	Pb-Zn	7.3 (42)	py	This study
41	Oohira, Miyagi	V	Cu	0.9 (2)	?	Takahashi(1963)
42	Kusakizawa, Miyagi	V	Cu	4.8 (1)	?	Takahashi(1963)
43	Togisawa, Miyagi	V	Cu	1.7 (1)	py	Takahashi(1963)
44	Hananoyama, Miyagi	V	Pb-Zn	5.7 (2)	?	Takahashi(1963)
45	Oodomori, Miyagi	V	Pb-Zn	3.1 (6)	py	Takahashi(1963)
46	Ikezuki, Miyagi	V	Pb-Zn	3.1 (13)	py	Takahashi(1963)
47	Budo, Niigata	V	Pb-Zn	2.2 (1)	?	This study
48	Ashio, Tochigi (Cu vein)	V	Cu	11.0 (4)	py	Takahashi(1963)
	(Kajika)	V	Pb-Zn	26.5 (1)	po	Takahashi(1963)
49	Tochigi, Tochigi	V	Cu	1.4 (1)	py	This study
50	Chichibu, Saitama (Akaiwa)	S	Pb-Zn	20.9 (16)	po	Miyazawa(1977)
	(Daikoku, upper)	S	Pb-Zn	7.4 (3)	py	Miyazawa(1977)
	(Daikoku, lower)	S	Pb-Zn	18.7 (9)	py	Miyazawa(1977)
51	Nabeto, Ishikawa	V	Cu	1.1 (1)	py	Takahashi(1963)
52	Kanehira, Ishikawa	V	Cu	4.3 (1)	py	Muta(1958)
53	Yutani, Shimane	V	Pb-Zn	5.6 (1)	?	This study
54	Taishu, Nagasaki	V	Pb-Zn	3.3 (8)	py	Muta(1958)
	(Kamiagata)	V	Pb-Zn	23.1 (many)	po	Muta(1958)
	(Misoge vein)	V	Pb-Zn			

V: Vein, S: Skarn, K: Kieslager

FeS content of sphalerites from Japan (Tsukimura et al.)

Appendix II List of FeS content of sphalerites in Japan (Cretaceous-Paleogene)

No.	Locality	Type	Main recovered metal	FeS mole % (number)	coexisting Fe sulfide	Reference
Sanin Belt						
55	Kamioka, Gifu (Tochibora)	S	Pb-Zn	6.7	py	Shiobara(1961)
	(Maruyama)	V?	Pb-Zn	3.6	py	Shiobara(1961)
	(Mozumi)	S	Pb-Zn	10.0	py	Shiobara(1961)
56	Nakatatsu, Fukui	S	Pb-Zn	9.1 (1)	?	Muta(1958)
	(Mo in Quartz Porphyry)	V	Mo	20.4 (1)	po py	This study
57	Kutani, Fukui	S	Pb-Zn	4.6 (1)	?	Muta(1958)
58	Ushirodani, Tottori	S	Pb-Zn	7.6 (1)	py	This study
59	Ohkura, Tottori	V	Pb-Zn	10.9 (1)	py	This study
60	Tohoyama, Shimane	V	Mo	5.9 (1)	py	This study
61	Seikyu Minami, Shimane	V	Mo	2.2 (1)	py	This study
62	Katou, Fukuoka	V	Pb-Zn	7.1 (1)	py	Muta(1958)
Kitakami Mountains						
63	Ohkawame, Iwate	S	Mo	18.8 (3)	po py	Shimizu & Shimazaki(1981)
64	Kamaishi, Iwate	S	Fe, Cu	19.0 (3)	po py	Shimizu & Shimazaki(1981)
65	Akagane, Iwate	S	Cu	19.5 (1)	po py	Shimizu & Shimazaki(1981)
66	Owashi, Iwate	V	Au-Ag	12.3 (4)	po py	Yamaoka(1981)
67	Hokuto, Iwate	V	Mo	16.1 (1)	py	This study
68	Kameyama, Iwate	S	Cu	7.8 (1)	py	This study
69	Kouhoku, Miyagi	V	Au-Ag	14.2 (20)	po py	Nedachi(1974)
70	Hada, Miyagi	V	Cu	6.0 (1)	py	This study
71	Hada East, Miyagi	V	Cu	17.3 (1)	po py	This study
Outer Zone						
72	Kishu, Mie	V	Cu	14.1 (1)	py	This study
73	Obira, Oita	S	Sn, Cu, As	19.8 (10)	po py	Muta(1958)
74	Hoei, Oita	S	Sn, Zn	22.2 (6)	po py	Muta(1958)
75	Shinkura, Oita	S	Sn	24.6 (3)	po	Muta(1958)
76	Kannondai, Oita	S	Sn	18.3 (2)	? ?	Muta(1958)
77	Mitate, Miyazaki	S	Sn	25.5 (2)	po	Muta(1958)
78	Toroku, Miyazaki	S	Sn	24.0 (1)	po	Muta(1958)
79	Hase, Miyazaki	S?	Pb-Zn, Sb	25.7 (1)	? ?	Muta(1958)
80	Otagabuchi, Miyazaki	S	W	27.7 (1)	? ?	Muta(1958)
81	Matsuo, Miyazaki	V	As, Au	26.1 (1)	po py	Muta(1958)
82	Kuratani, Miyazaki	?	?	25.2 (1)	? ?	Muta(1958)
83	Onouchi, Miyazaki	?	?	25.4 (1)	? ?	Muta(1958)
84	Higashitani, Miyazaki	K?	Pb-Zn	22.0 (1)	? ?	Muta(1958)
85	Ino, Miyazaki	V	?	26.2 (1)	? ?	Muta(1958)
86	Nanshu, Kagoshima	V	Cu	15.9 (1)	py	This study
87	Tarumizu, Kagoshima	V	Sn	21.0 (1)	py	This study
88	Shinjo, Kagoshima	V	Pb-Zn	25.7 (1)	po py	Muta(1958)
89	Suzuyama, Kagoshima	V	Sn	18.6 (1)	po py	This study
90	Nishisuzuyama, Kagoshima	V	Sn	25.1 (1)	po	Muta(1958)
Inner Zone						
91	Yakuki, Fukushima	S	Cu, W	14.6 (3)	po py	This study
92	Takatori, Ibaraki	V	W	17.5 (1)	po py	This study
93	Hitachi, Ibaraki	K	Cu	14.8 (38)	po py	Endo(1963)
94	Yokoneyama, Tochigi	S	Mn	17.9 (1)	po py	This study
95	Kurokawa, Gifu	V	Cu	18.0 (2)	po py	This study
96	Kaneuchi, Kyoto	V	W	16.3 (1)	py	This study
97	Ohtani, Kyoto	V	W	17.4 (3)	po py	This study
98	Sakoshi-Odomari, Hyogo	V	Au-Ag	13.7 (2)	py	Urashima et al.(1981)
99	Tatsuyama, Okayama (Lens)	V	Cu	15.6 (2)	po	This study
100	Koizumi, Okayama	V	Pb-Zn	15.6 (3)	po py	This study
101	Mihara, Okayama	S	Cu, Zn	20.6 (6)	po py	Shimizu & Shimazaki(1981)
102	Yoshioka, Okayama	S	Cu	19.2 (3)	po py	Shimizu & Shimazaki(1981)
103	Nagusa, Okayama	V	Cu	18.5 (2)	po py	Shimizu & Shimazaki(1981)
104	Kinmei, Hiroshima	S	Cu	20.3 (1)	po py	Shimizu & Shimazaki(1981)
105	Kiwada, Yamaguchi	S	W	19.3 (4)	po py	Shimizu & Shimazaki(1981)
106	Kawayama, Yamaguchi	S	Cu	28.8 (1)	po	Muta(1958)
107	Ofuku, Yamaguchi	S	Cu	20.1 (1)	? ?	Muta(1958)
108	Tsumo, Shimane (Maruyama)	S	Cu, W	16.3 (29)	po ?	Sugaki et al.(1981)
	(Kanayama)	S	Cu, W	17.4 (11)	po ?	Sugaki et al.(1981)
109	Yoshiwara, Fukuoka	S	Cu	14.3 (1)	po py	Muta(1958)
110	Kinryu, Fukuoka	S, V	Cu	21.9 (1)	? py	Muta(1958)
111	Hiraodai, Fukuoka	?	Cu	21.7 (1)	? ?	Muta(1958)
112	Ryuo, Fukuoka	?	Cu	17.6 (1)	? ?	Muta(1958)
113	Higashitani, Fukuoka	?	Cu	13.9 (1)	? ?	Muta(1958)
114	Zurine, Fukuoka	?	Cu	17.0 (1)	? ?	Muta(1958)