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MINERALOGICAL STUDIES ON JAPANESE SPHALERITE

By

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I. Introduction

From various parts of the world, there are numerous reports of mineralogical studies on sphalerite; there are also one hundred and fifty or more from Japan.

Sphalerite is one of most well known minerals, and shows good crystalline state among natural minerals. It belongs to the cubic system hextetrahedral class and shows tetrahedral, dodecahedral, often distorted and near rhombohedral forms. There are three polymorphs in zinc sulphide. Among them sphalerite is lower temperature type, and inverts to wurtzite at 1020°C±5°, but the inversion temperature decreases with the increase in Fe content. Besides the high Fe content members approach

to black in colour.

The colour of sphalerite is white to nearly colorless when pure, but commonly yellow, brown, black, also red or green.

Some mineralogists and economic geologists, therefore, have been interested in the relation between Fe content in sphalerite and the change of physical properties.

At present it should seem, being three problems on sphalerite from the mineralogical standpoint, as follows:

(1) The relation between physical properties and Fe content, which substitutes for position of Zn atom in the chemical components, and also many minor elements in sphalerite.

(2) The relation between crystallized circumstances and trimorphs of zinc sulphide and these polytypes.

(3) The Change of physical properties in accordance with semiconductivity of sphalerite and its variation in colour and luminesence.

It was given on account that Fe atom substituting for position of Zn atom on crystal structure, was in a certain regular distribution. Besides it was not unlimited, but atomic ratio of iron to zinc was less than a half. In sphalerite, there is contained a minor amount of lead, cadmium, and manganese in addition to iron.

As to many kinds of minor elements, sphalerite is exceptional, although it contains not a small amount sometimes. Especially it has been an interesting problem that rare-earth elements are found in sphalerite and also hafnium, gallium and germanium were discovered by spectroscopic analyses. Almost always sphalerite is a mineral resource of cadmium and sometimes of rare-earth elements.

On the polymorphism of zinc sulphide, there are known with three polymorphs, α-zincsulphide of lower temperature type, β-zincsulphide of high temperature type, γ-zincsulphide between α- and β-type. The β-zincsulphide is sphalerite, while the α-zincsulphide is wurtzite in mineralogical name. In Japan the former is found almost always, but the latter rarely. The γ-zincsulphide has not yet been discovered.

Recently the phenomenon of polytype was discovered by development of crystalstructural studies. Frondel and Palache found that the 4H, 6H, and 15R polytypes of zincsulphide all had structures corresponding to previously known silicon carbide polytypes. It is important that the polytype phenomenon shows variation of habit as one of its characteristics. However polytypes of zincsulphide have not been discovered in Japan. The crystallization of sphalerite and wurtzite is changed by temperature

and chemical properties of solutions. Sphalerite is formed in alkaline solutions or under 1020°C±5° when pure. Wurtzite is the rarer and unstable form of zinc sulphide; it can be crystallized from acid solutions above 25°C or may be formed by heating sphalerite above inversion point and cooling with moderate rapidity. Therefore wurtzite often occurs intimately intergrown with sphalerite. Because of this fact mineralogists, economic geologists and geochemists take some interest in sphalerite as a geo-thermometer.

A number of studies on physical properties of sphalerite have been reported, but also change of colour is remarkable. The present writer has carried on some quantitative studies on the colour of sphalerite, on chromaticity, and on the connection between iron cotent and brilliance.

On the colour of sphalerite no experiments have been reported nor any discussions of brilliance and chromaticity, or of brilliance, hue and saturation.

Sphalerite was first discovered in Japan by J. MILNE (MILNE, 1879) "List of Japanese minerals, with note on species which are to be new", and by ZAPPE (ZAPPE, 1879) "Der Bergbau Japans und seine Haupterzeugnisse" also in 1879. Later sphalerite from Obira, Oita Prefecture; Uchinokuchi, Oita Prefecture; Kamioka, Gifu Prefecture; Aikawa, Niigata Prefecture; Ikuno, Hyogo Prefecture and Arakawa Akita Prefecture were found. Still later sphalerite as a mineral resource was first recovered at the Nakatatsu mine, Fukui Prefecture, in 1903, at the Kamioka mine in 1911.

The author has made researches on sphalerite from the mineralogical point of view since a decade ago. This report is a summary of studies on Japanese sphalerite from the first discovery to the present time.

II. Occurrences

Sphalerite and galena occur closely associated in one deposit; these chief lead producers, also zinc producers in Japan, are scattered throughout Honshu and to a certain extent in Hokkaido.

For the first time, sphalerite from Japan was reported by MILNE, (MILNE, 1879) and ZAPPE (ZAPPE, 1879) in 1879, but that as a mineral resources was first recovered at the Nakatatsu mine, Fukui Prefecture in 1903, at the Kamioka mine in 1906 and at the Hosokura mine in 1911, as above noted.

Sphalerite ad galena deposits of Japan are classified into three types (MURAKOSHI, et al., 1956) genetically.

(1) Contact metasomatic deposits

(2) Vein deposits
(3) Hydro-thermal replacement deposits

(1) *Contact metasomatic deposits*

Most of the contact metasomatic deposits (HORI, et al., 1942; HORIKOSCHI, et al., 1940; ITO, et al., 1947; MURAKOSCHI, et al., 1956; NAKANO, 1937; TOGARI, 1958; TOKUNAGA, 1958; 1959) are developed in the Mesozoic to Paleozoic limestones or other sediments which are usually metamorphosed by acidic to intermediate intrusive rocks. The deposits exist in skarn rocks. Ore bodies are mostly irregular chimney-like, steeply dipping to vertical in attitude, being formed along bedded planes, faults or some other structural lines.

Examples of contact metasomatic deposits in Japan are found at the Kamioka mine; the Tochibora deposit of this mine, which occurs in an injection gneiss is the largest example of this type, although the mineralization was repeated, and the deposit was enriched remarkably by later hydrothermal action.

Common accessories are pyrrhotite, pyrite, chalcopyrite, bornite, arsenopyrite, magnetite and hematite.

Of the skarn minerals which constitute most of the gangue, pyroxene of the diopside-hedenbergite series is predominant, with a minor amount of garnet, wollastonite and epidote.

It is assumed that this acid intrusion took place during earlier Cretaceous age in the outer Zone of Northwest Japan, while in the Inner Zone of Southwest Japan, the granitic batholith was emplaced in later Cretaceous age.

Then main localities for this type are Kamioka, Gifu Prefecture; Nakatatsu, Fukui Prefecture; Chichibu, Saitama Prefecture and so on.

(2) *Vein deposits*

Vein deposits are of hydrothermal origin; they occur mostly in Tertiary sediments, andesites or liparites (Geological Survey of Japan, 1959; HAMACHI, 1955; ITO, 1947; MURAKOSCHI, et al., 1956; TOGARI, 1959), exceptionally in granite porphyry such as at the Budô mine, Niigata Prefecture.

The late Tertiary age, especially the Miocene age, was characterized by most intensive and extensive volcanic activties. From this stage, base metal mineral deposits are grouped in three types, namely vein, network and replacement deposits which comprise "Kuroko" and "Kajika" deposits. In many deposits of each province, copper ore is closely associated with sphalerite-galena ore and sometimes they are called "complex ore".

The major mineralization provinces are Kitami Province,, Inner

Northeast Province including southwestern Hokkaido and Ashio Province, southern Fossa Magna Province, Ogoya Province, Kishû Province, Ikuno-Akenobe Province and Tsusima Province.

These deposits occur in various rocks, Miocene shale, sandstone, green tuff, tuff breccia, andesite, propylite and rhyolite. Some deposits are also found in clayslate, sandstone, chert, limestone and various igneous rocks of Paleozoic or Mesozoic age, as in the cases of the Akenobe and Ashio mines.

The chief ore minerals are sphalerite and galena. Accessory minerals are commonly pyrite, chalcopyrite, tetrahedrite, and other sulphides. In some instances a small quantity of argentite, stephanite, pyrargyrite and proustite are present.

Among gangue minerals, quartz is predominant, but is other cases various carbonates or barite are contained singly or mixed with one another. In some cases fluorite or chlorite is to a limited extent.

An excellent example is offered by the Hosokura mine, but the other main mines of this type are as follows: Toyoha, Hokkaido; Akenobe and Lkuno, Hyôgo Prefecture; Ôdomori, Miyagi Prefecture; Daira, Akita Prefecture; and Funauchi, Aomori Prefecture.

(3) *Hydrothermal replacement deposits*

Most of the hydrothermal replacement deposits of sphalerite and galena are so-called Kuroko deposits. These deposits are products of massive replacement of Tertiary tuff, tuff breccia or shale as a usual (Geological Survey of Japan, 1959; HAMACHI, 1955; HORI, 1940; ITO, 1947; KINOSHITA, 1930; MURAKOSCHI, et al., 1956). It is believed that this type of deposits is well developed only in Japan; most of them are found in the Inner Zone of Northeast Japan, San-in district and the southwestern part of Hokkaido.

Ore deposits of this type consist of "black ore" (Kuroko proper), "yellow ore", "silicious ore", white mass of gypsum or anhydrite and light gray clay, which are distinguished components of mineral assemblage.

Sphalerite is present only in "black ore"; it is attended by galena, barite and by more or less chalcopyrite and pyrite.

An example of this type of replacement deposit is seen in the Hanaoka mine, Akita Prefecture while the other chief localities are Yoichi, Hokkaido and so on.

III. Morphology of sphalerite

Sphalerite belongs to the cubic, hextetrahedral 4 3 m, a_0=5.400± 0.008 Å. It is very commonly found in massive cleavable, coarse to fine granular and compact, also floiated, sometimes fibrous and radiated or plumose, and also botryoidal and other imitative shapes. Sometimes well crystallized specimens of sphalerite have been found in Japan. For examples they are Ani, Arakawa, Ashia, Chichibu, Hosokura, Kamioka, Obira, Shiraita and so forth.

In "Dana's System of Mineralogy" 7th edition it is reported that the number of crystal faces amount to ninety-six; ten faces are described as commonest, fifteen faces as common and 53 faces as an uncertain form. Twins are common, and crystals are often distorted or rounded.

III-1 *Forms and localities*

Commonly sphalerite from Japan shows simple form and few sorts of faces.

The number of crystal faces reported in Japan amounts to only eight. That is to say these are eight decided faces, as the result of goniometry of 41 specimens from 24 localities in Japan up to the present.

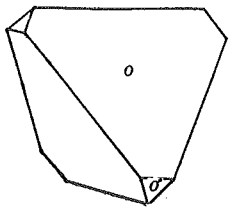
Commonest forms of sphalerite are a(001), d(011), o(111), m(113), m′($\bar{1}$13), n(112), n′($\bar{1}$12), p′($\bar{1}$22), and s′($\bar{1}$23), but the eight faces of appearance in Japan are o(111), o′($\bar{1}\bar{1}$1), a(100), d(110), m(311), T′(5$\bar{4}$2), S′(3$\bar{2}\bar{2}$) and n(211) alone (Fig. 1). The locality and the combination of them is shown in Table 1.

III-2 *H-, F-, and P-values*

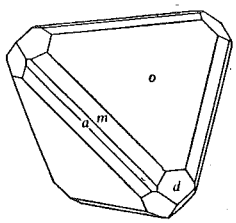
Two faces o(111) and o′($\bar{1}\bar{1}$1) are most frequent in appearance as the dominant face, and the two faces a(100) and d(110) also often appear, but m(311), T′(542), S′(3$\bar{2}\bar{2}$) and n(211) seldom. However, the frequency of appearance of faces under a(100) is much lower compared to the frequency of the first two faces.

The common crystals are combinations of o(111) and o′($\bar{1}\bar{1}$1) with one or both a(100) and d(110). Simple tetrahedral crystals and dodecahedral ones are rare; they sometimes have their edges truncated by the cube, and their corners by a complementary tetrahedron. Whenever the two tetrahedra occur together one is smooth and bright, while the other is striated or dull. These two forms may also be distinguished by etching with hydrochloric acid. The relative frequency of appearance in all Japanese sphalerite (H-value by P. NIGGLI) is shown in Table 2.

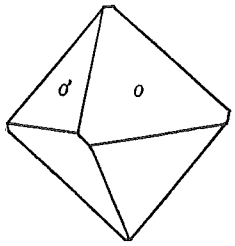
The change of appearance of faces about localities is described as



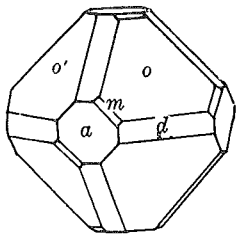
1. Kuratani mine



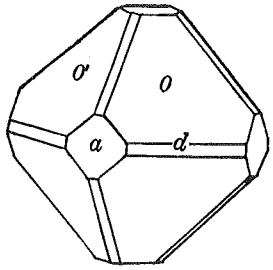
2. Kamioka mine



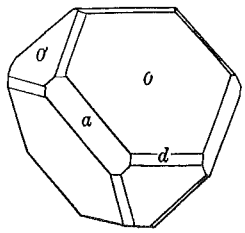
3. Arakawa mine



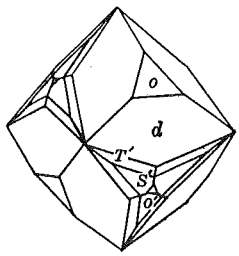
4. Arakawa mine



5. Daira mine



6. Hosokura mine



7. Shiraita mine

Fig. 1. Crystal forms of Japanese sphalerites.
2, 3—after Katayama N. (1933)
1, 4, 7—after Ito T. (1937)
5, 6—after Ito T. (1947)

TABLE 1. List of all Japanese sphalerite observed combinations.

No.	occurrence	combination
1	Aikawa, Niigata Pref.	o, o′
2	Aikoku, Nagano Pref.	o, o′, d, a
3	〃 〃	o, o′
4	〃 〃	o, o′, a
5	Ani, Akita Pref.	o, o′
6	〃 〃	o, o′, d, a, m
7	〃 〃	o, o′, d, a, m
8	〃 〃	d,
9	〃 〃	o, o′
10	Arakawa, Akita Pref.	o, o′
11	〃 〃	o, o′, d, a, m
12	〃 〃	o, o′
13	〃 〃	o, o′, a
14	Ashio, Tochigi Pref.	o, o′, d, a
15	Bando, Fukui Pref.	o, o′, d, a
16	Chichibu, Saitama Pref.	o, o′, a
17	〃 〃	o, o′, d, a
18	〃 〃	o, o′, d, a
19	Daira, Akita Pref.	o, o′, d, a
20	〃 〃	o
21	Fumuro, Fukui Pre,	o, o′, a
22	Furôkura, Akita Pref.	o, a
23	Hosokura, Miyagi Pref.	o, o′, d, a
24	Hozawa, Yamagata Pref.	o, o′
25	Iomi, Fukui Pref.	o, o′, a
26	Kamioka, Gifu Pref.	o, d, a m
27	〃 〃	o, o′, d, a, m, T′, S′
28	〃 〃	o, o′, a, n
29	〃 〃	o, o′
30	Kamitaki, Tochigi Pref.	d
31	Kuratani, Ishikawa Pref.	o, o′
32	Kusakura, Niigata Pref.	o, o′, d
33	Mase, Niigata Pre.	o, o′, d, a
34	Obira, Oita Pref.	o, o′
35	Osarizawa, Akita Pref.	o, o′, d
36	Shimotugu, Aichi Pref.	o, o′, a
37	Shiraita, Niigata Pref.	o, o′, d, T′, S′
38	〃 〃	o, o′, d, a, T′, S′
39	Tomiyasu, Fukushima Pref.	o, o′, d
40	Uchinokuchi, Oita Pref.	o, o′

References

1; YAMADA, K., J. Geol. Soc. Jap., 3, 182 (1896).
2, 3; YAGI, T., J. Geol., Soc., Jap., 22, 132 (1915).
4; YAGI, T., J. GEOL, Soc. Jap., 22, 180 (1915).
5, 11, 31, 37; ITO, T., Japanese Minerals in Pictures (1937).
6, 7, 12, 13, 15, 16, 19, 21, 22, 23, 24, 27, 30, 32, 33, 34, 35, 38, 39, 40; ITO, T. and SAKURAI, K., Minerals of Japan (1947).
8, 9, 29; KO, S., J. Geol. Soc. Jap., 3, 86 (1895).
10; KATAYAMA, N., J. Geol. Soc. Jap., 40, 609 (1933).
11; KATAYAMA, N., J. Geol. Soc. Jap., 40, 610 (1933).
14; WATANABE, S. and KOIWAI, Y., J. Jap. Ass. Miner. Petr. Econ. Geol., 17, 38 (1937).
17, 18; SAKURAI, K. and FUJIYAMA, I., Bull. Chichibu Museum Natural History, 5, 39 (1955).
20; IGI, T., J. Geol. Soc. Jap., 3, 283 (1896).
25; ICHIKAWA, S., J. Geol. Soc. Jap., 17, 326 (1910).
26; KATAYAMA, N., J. Geol. Soc. Jap., 40, 610 (1933).
28; WATANABE, M., J. Jap. Ass. Miner. Petr. Econ. Geol. 3, 20 (1930).
36; S. D., J. Geol. Soc. Jap., 7, 31 (1900).
39; WATANABE, M., J. Jap. Ass. Miner. Petr. Econ. Geol., 26, 244; 282 (1941).
41; SCHINOMOTO, J., J. Geol. Soc. Jap., 1, 399 (1893).

TABLE 2. Relative frequency of appearance.
(H-value by P. Niggli)

Symbol	number of appearance	H in %
o (111)	39	95.12
o′ ($\bar{1}11$)	36	87.80
a (100)	23	56.09
d (110)	20	48.78
m (311)	5	12.19
T′ (5$\bar{4}$2)	3	7.32
S′ (3$\bar{2}$2)	3	7.32
n (211)	1	2.44

below. Already twenty-four localities in Japan are known, and all kinds of faces that appear in one locality, make up one combination.

From this combination, the frequency of appearance of faces is calculated in per cent, and it is the locality-percentage of indices (F-value by P. NIGGLI). According to this result, the faces o(111) and o′($\bar{1}$11) are high in grade of appearance, but the faces m(311), T′(5$\bar{4}$2), S′(3$\bar{2}$2) and n(211) are rare. A summary of this data is shown in Table 3.

TABLE 3. Locality-persentage of indices.
(F-Value by P. Niggli)

indices	F in %	Grades
o (111)	95.83	1st grade
o′ ($\bar{1}11$)	91.67	
a (110)	66.67	2nd grade
b (100)	62.50	
m (311)	12.50	3rd grade
T′ (542)	8.33	
S′ (3$\bar{2}$2)	8.33	
n (211)		

The total kinds of combinations from Japanese sphalerites is thirteen, and the highest frequency of appearance is that of face o(111). This face appears always except for simple dodecahedron.

Three faces o′($\bar{1}$11), d(110) and a(100) also appear often, however are lower in frequency than the former face. This result of something preceding is so-called P-value by P. NIGGLI and shown in Table 4 as below:

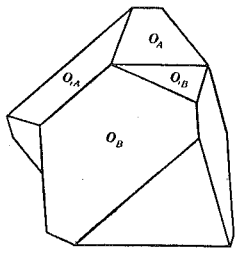
TABLE 4. Combination-percentage of Japanese sphalerites. (F-Value by P. Niggli)

	All Kinds of combinations							
1	o,							
2	o,			a				
3	o,		d,	a,	m			
4	o,	o′						
5	o,	o′,	d					
6	o,	o′,	d,	a				
7	o,	o′,	d,	a,	m			
8	o,	o′,	d,	a,	m,	T′,	S′	
9	o,	o′,	d,	a,		T′,	S′	
10	o,	o′,	d,			T′,	S′	
11	o,	o′,		a				
12	o,	o′,		a				n
13			d					

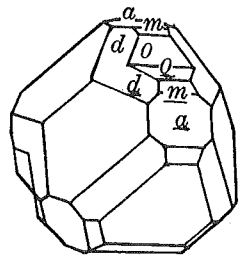
Form	P in %
o (111)	92.31
o′ ($\bar{1}$11)	69.23
d (110)	61.54
a (100)	61.54
m (311)	23.08
T′ (542)	23.08
S′ (3$\bar{2}$2)	23.08
n (211)	7.69

Table 5. H-, F- and P- value (by P. Niggli) of Japanes sphalerites (in Percentage)

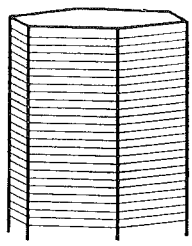
symbol	H	F	P
o (111)	95.12	95.83	92.31
o′ ($\bar{1}$11)	87.80	91.67	69.23
d (110)	48.78	62.50	61.54
a (100)	56.09	66.67	61.54
m (311)	12.19	12.50	23.08
T′ (542)	7.32	8.33	23.08
S′ (3$\bar{2}$2)	7.32	8.33	23.08
n (211)	2.44	4.17	7.69



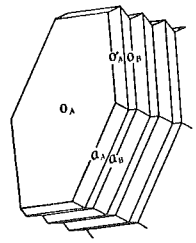
1. Arakawa mine



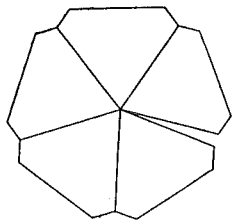
2. Ani mine



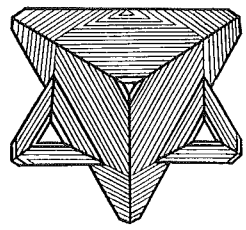
3. Ashio mine



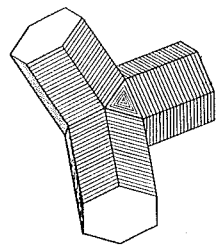
4. Ashio mine



5. Ashio mine



6. Kusakura mine



7. Ashio mine

Fig. 2. Twins of Japanese sphalerites.
6—after Kadokura M. (1915)
1—after Katayama N. (1933)
3, 4—after Ogawa U. (1933)
5—afthr Watanabe S. (1937)
2—after Ito T. (1947)

The summary of so-called "H-, F-, and P-value by P. NIGGLI" is in Table 5.

III-3 *Twinning*

Twins are common in sphalerite; they appear frequently in simple or multiple contact twins or in complicated lamellor intergrowths. Sometimes they appear in penetration fivelings for example Ashio mine (ITO, 1935; SUNAGAWA, 1954).

Twinning axis is [111]; composition surface may be parallel or perpendicular to [111]; it is not always planar. Sometimes simple twin crystals of the spinel type, of octahedral habit, are found. In these the bright faces of the tetrahedron o(111) on one individual are opposite to the dull faces of the other tetrahedron o'($\bar{1}\bar{1}1$), so that the twinning is to be described as due to hemitropy about the di-trigonal axis, and not to reflection over the tetrahedron-face to which that axis is perpendicular. Even in a spinel twin of this sort each individual is often traversed by twin-lamellae parallel to the other tetrahedron faces (Fig. 2).

In special case, a single, almost ideally developed penetration twin of tetrahedral sphalerite has been reported. This specimen, showing a very perfect form, has given a hint to decipher the faces in often imperfect and complex the "eared twin" (KADOKURA, 1915) of Japanese chalcopyrite, similar in character.

This crystal consists of one main crystal, carrying two smaller individuals, beside a very minute one (in Fig. 3). These three are the main ones, and each projects out of one of the tetrahedral faces of the latter, the two larger individuals in twinning position against the tetrahedron forming a continuous plane, piercd through by a ttrahedral edge of the main individual.

All the four individuals, forming the twin, are tetrahedral, with the quoin modified by subordinate faces of the opposite tetrahedron and rhombic dodecahedron. The prevailing tetrahedron is roughly striated parallel to the dodecahedral faces. However the other tetrahedron is entirely smooth.

IV. Chemical composition of sphalerite

Sphalerite consists of zinc element and sulphur one; zinc contributes 67 percent sulphur 33 percent, when pure. But often it also contains iron and manganese, and sometimes cadmium, mercury and rarely lead and tin. Also sometimes sphalerite contains traces of indium, gallium and thallium and it may be argentiferous and auriferous.

Sphalerite nearly always contains iron, the maximum iron content being about 26 percent. Manganese, with a maximum of 5.81 percent, and cadmium, with a maximum of 1.66 percent, are usually present in small amount. Mercury has been reported in minor amounts in some of the older analyses. Traces of indium, gallium and thallium have been noted. Silver, gold and many other elements have been reported in traces, but these are possibly due to impurities. Especially it has been an interesting problem that rare-earth elements have been found in sphalerite, and also that hafnium, gallium and germanium have been discovered by spectroscopic analyses. Sometimes sphalerite is the mineral resource of rare-earth elements in foreign countries, but not in Japan.

IV-1 *Chemical analyses*

Up to the present quantitative chemical analyses of Japanese sphalerite have been made twenty five times. The data are shown in Table 6.

These assays indicate the presence of 67.46 to 37.60 precent zinc, 35.49 to 24.6 percent sulphur, 20.20 to 0.16 percent iron, 0.42 to 0.02 percent copper, 1.66 to 0.06 percent cadmium, 0.13 to 0.03 percent lead, and 1.40 percent tin.

Among all quantitative chemical analyses, three assays report an absence of iron, but each of nine assays report the absence of copper or

TABLE 6. Chemical compositions of Japanese sphalerites.

	1	2	3	4	5	6	7	8
Zn....	65.30	50.65	49.70	31.8	58.14	66.83	67.46	66.59
S....	32.56	32.54	34.64	24.6	32.33	32.52	32.22	33.60
Fe....	1.82	14.25	15.04	20.7	4.85	0.04		0.16
Cu....		0.35			0.30			
Cd....			0.22					0.06
Pb....								0.03
Sn....								
SiO_2....	0.32				4.42	0.04		
H_2O (−)						0.50		
Total	100.00	99.64	99.60	100.00	100.04	99.93	99.68	100.44

1. Hozawa mine, Yamagata Pref., Isiwara, T. and Hizioka, H. (1930).
2. Ashio mine, Totigi Pref., Isiwara, I. and Okada, M. (1930).
3. Ashio mine, Totigi Pref., Kisi, T. (1933).
4. Kaso mine, Totigi Pref., Yosimura, T. (1933).
5. Tomiho mine, Hukusima Pref., Watanabe, M. (1941).
6. Ainai mine, Akita Pref., Takeuchi, T. and Nanbu, M. (1950).
7, 8. Hosokura mine, Miyagi Pref., Togari, K. (1954).

	9	10	11	12	13	14	15	16
Zn....	65.44	64.52	65.61	53.58	37.60	65.84	65.74	64.80
S....	33.38	32.57	33.00	33.60	34.70	34.19	34.20	33.50
Fe....	0.40	0.57	0.21	10.44	26.20			0.20
Cu....		0.06		0.42				
Cd....		1.05	0.24					
Pb....		0.05	0.13					
Sn....					1.40			
SiO_2....			0.41					
H_2O (−)								
Total	99.67	99.56	99.47	100.34	99.90	100.03	99.94	98.50

9-16. Hosokura mine, Miyagi Pref., Togari, K. (1954).

	17	18	19	20	21	22	23	24	25
Zn....	61.71	56.21	54.10	52.02	65.84	65.40	66.75	55.86	65.90
S....	32.97	34.07	35.49	33.46	32.91	32.66	31.65	32.23	31.56
Fe....	3.84	9.25	10.31	12.17	1.21	1.33	0.40	7.85	0.09
Cu....					0.04	0.02	0.07	0.13	0.07
Cd....				1.66	0.18	n. d.	0.72	0.33	0.53
Pb....									
Sn....									
SiO_2....					0.20	0.38	0.14	2.70	1.26
H_2O (−)									
Total	98.52	99.53	100.02	99.31	100.23	99.79	99.73	99.33	99.41

17-20, Hosokura mine, Miyagi Pref., Togari, K. (1954).
21. Budo mine, Niigata Pref., Sato, M. (1959).
22. Budo mine, Niigata Pref., Sato, M. (1959).
23. Noto mine, Ishikawa Pref., Sato, M. (1959).
24. Nakatatsu mine, Fukui Pref., Sato, M. (1959).
25. Aomori mine, Aomoro Pref., Sato, M. (1959).

cadmium. Tin was found in only one assay and lead in three.

It must be examined in future, that copper, cadmium, lead, tin and so on for position of zinc atom on crystal structure substitute or not.

Galena occurs usually in close association with sphalerite in one ore mineral, therefore it seems that the latter includes a slight amount of the former sufficient to be revealed by X-ray analyses.

About the inclusion of copper, it is an important fact, that equilibrium relation exists between sphalerite and pyrrhotite, or chalcopyrite, and they show the phenomenon of so-called "Entmischung" in accordance with

lowering of temperature. Therefore copper may be present in sphalerite as chalcopyrite in microscopic amounts.

Sphalerite is almost always the ore mineral of cadmium, but it does not include solid-solution of greenockite, because greenockite belongs to the hexagonal system.

IV-2 *Sulphur component*

Sphalerite as mineral of many variable colours has seemed to change in accord with Fe-content variation, because a specimen of little Fe content is pale yellow and one of high content is brown or dark brown. Further the colour of sphalerite is white to nearly colourless, yellow, green, orange, and red, and the hue is light or deep, and also brilliance is pale or dark. The character of the colour is rich in variation. There are many reports as to the cause of colouring which the variation of colour (yellow, orange and brown) is due to difference of iron content in sphalerite.

But according to the character of the colour, no experiments have ever been made, nor has then been discussion of brilliance, hue, and saturation of sphalerite (TOGARI, 1954; 1958; 1959).

The brilliance, hue, and saturation are three properties of colour which are quite independent of each other (TOGARI, 1959). Therefore it is not always appropriate to say that phenomena showing three independent properties are due to the same cause.

On the other hand the ratio of metal to sulphur is not equal to one and almost always sulphur is in excess. And then if that ratio is equal or nearly to one, the colour is nearly pale and light.

Accordingly in order to analyse accurately the sulphur content, a new assey was attempted by the methods shown as Fig. 3.

Firstly the pure sample of sphalerite is put in quartz tube heated already to 1,500°C. Next into this tube oxygen gas is let flow at 600 cc per minute for about fifteen minutes.

Sulphur into sphalerite assumes the shape of SO_2, and then changes to H_2SO_4 in H_2O_2 solution. After that sulphur is determined throughout neutralization by normal NaOH solution.

B-F in Fig. 3 are washing apparatus of oxygen gas.

From the results of this analysis, excess of sulphur in sphalerite is calculated. Data obtained are shown in Fig. 7.

It seems that according to the increase of sulphur, colour of sphalerite changes from nearly colourless to yellow, orange, at last to red.

IV-3 *Minor elements*

Many kinds of minor elements were found in sphalerite. Semi-quantitative spectrum analyses on it were performed.

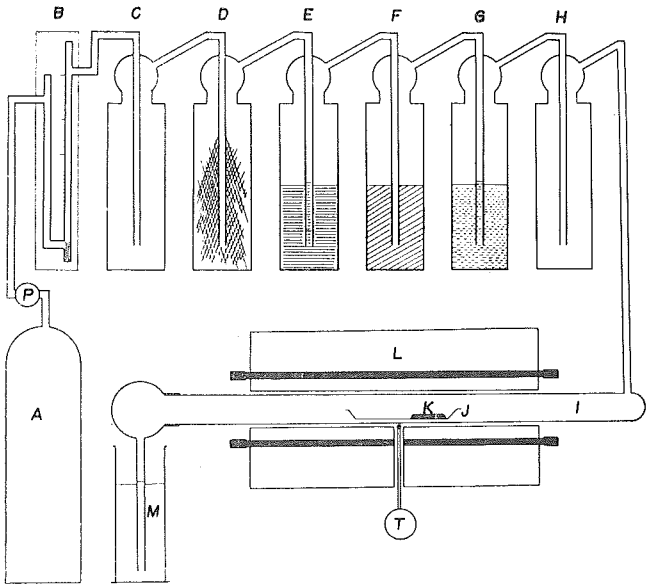


Fig. 3. Apparatus of sulphur analyses.

A Oxygen gass tank
B Flow meter
C, H Empty bottle
D Glass wool
E $K_2Cr_2O_7$ suturated solution
F Soda lime
G Conc. H_2SO_4
I Quartz tube
J Porcelain vessel
K Sample
L Electric furnace
M Absorption bottle
T Pyrometer

According to this experiment, the minor elements found in sphalerite are as follows: vanadium, chromium, manganese, iron, cobalt, nickel, copper, gallium, germanium, arsenic, selenium, columbium, molybdenum, samariu, rhodium, palladium, silver, cadmium, indium, tin, antimony, tellurium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, mercury thallium, lead and bismuth (FRONDEL, et al., 1950; Geological Survey of Japan, 1959; HENRIQUOS, 1957; ISCHIBASCHI, 1954; ITO, 1947; KINOSCHITA, 1930; KINOSCHITA, et al., 1950; MINO, 1957; MUTA, 1960; SAITO, 1953; STOIBER, 1940; TOGARI, 1954; 1958; 1959; TOKUNAGA, 1959; UMEMOTO, 1955).

Sometimes the locality or type of ore deposit made a difference in sort of minor elements. But generally cadmium, gallium, germanium, tin and manganese appear in first rank of frequency, and arsenic, antimony, bismuth, silver, thallium, cobalt and molybdenum in second rank.

For example a spectrum analysis by the present writer is shown in Table 7. In this table the symbol of S means sample from the Shimokawa Mine, Hokkaido; H is the Hosokura Mine, Miyagi Prefecture, and O is the Oizumi Mine, Yamagata Prefecture. All these mines are types of epithremal ore deposit.

Nickel and cobalt contents are large in so-called "Kies largar" type, but absent in hydrothermal type. Platinum and indium are remarkable in early stage, but on the other hand, silver and antimony are characteristic in latter stage in the same epithermal deposit.

The summary of above-mentioned data is as follows:

a) Many kinds of minor elements are contained in sphalerite, but

TABLE 7. Minor elements in sphalerites.

Sample no.	Mg	Al	Si	Ca	Mn	Co	Ni	Cu	Ga	Ge	Zr	Nb	Mo	Pd	Ag
S-1a	tr	+	+	tr	++	++			+						
S-1b	tr	+	+	tr	+				tr						
S-16	tr	tr	+	+	tr	++								tr	
S-17	tr	tr	tr			+								+	tr
S-21a	tr	+	+	tr					tr				tr	+	+
S-21b	tr	+	+	+		tr			tr					+	tr
S-21c	tr	+	+		+										
S-24a	tr	+	tr	+	+	tr									
S-24b	tr	tr	tr		+				tr						
H-1							+	++							
H-2						+	+	+	++						tr
H-3						+	tr	++	+						tr
H-4						+		+							+
H-5						+		+							+
H-6								+							+++
H-7						+	tr	+							++
O-1			tr		tr	tr		+	+	tr			+	tr	
O-2	tr		tr		+	+	+	++		+			+	tr	+
O-3			+		tr	tr		+	+	+		tr	+	+	
O-4	tr		+			tr		tr							
O-5	tr	tr	tr			tr		+							
O-6	tr		+			tr		++		++				tr	+

Sample no.	Cd	In	Sn	Sb	Te	Cs	La	Ce	Gd	Tb	Ta	Ir	Pt	Pb	Bi
S-1a		+				tr									+
S-1b		tr			+	tr								+	+
S-16		++				tr							+	+	
S-17		tr				tr								++	
S-21a		tr	++			tr		tr						tr	
S-21b		tr	+			tr								+	
S-21c		tr				tr								tr	
S-24a		+			tr	tr							tr	+	
S-24b		+	tr			tr								+	
H-1	+	+	+										+		
H-2	++	+		tr									+		
H-3	+	tr		+									+		
H-4	+	tr		++											
H-5	+			+++											
H-6	+	+		+++	+										
H-7	+	++		++	++				?						
O-1		tr			+										
O-2		tr			+		tr			?		+			
O-3	tr	+	+		+						+				
O-4	++	tr		tr	++									tr	
O-5	tr	tr												tr	tr
O-6		+	tr												tr

those are likely to chief elements from the view point of geochemistry.

b) According to the type of ore deposit, minor elements are characteristic such as high Ni- and Co-contents in so-called "Kieslagar" type.

c) According to the ore deposit province, minor elements are remarkable such as comparatively high content of As, Sb, Ag and Ge and low content of Ni, Co, Sn, and Mo in the Inner Northeast Province.

d) Some certain minor element is found concentrated in a specifically coloured sphalerite specimen such as high gallium content in pale brown specimen.

V. Problem on structure of sphalerite

On the crystal structure, these seem to be two problems in sphalerite.

The one is the three polymorphs of α-zinc sulphide, β-zinc sulphide and γ-zinc sulphide, and several polytypes; these phenomena are closely related with the circumstances of crystallization. The other problem is the relation between iron content substituting in the position of the zinc atom in crystal structure and lattice constant or interplaner spacings; these facts are concerned with crystallized conditions and iron content, but the crystal structure does not change.

V-1 *Variation of lattice constant*

Zinc-sulphide, ZnS, crystallises in two forms, as cubic sphalerite and as hexagonal wurtzite (WARREN, et al., 1954). The structures are essentially the same in principle, each atom being surrounded symmetrically by four of other kind. These structures resemble that of the diamond, and are called "adamantine." Now the diamond structure is typically homo polar, and the constancy of the interatomic distance in each column is such that the distance is determined rather by a bonded electronic structure than by a packing of ions.

The lattice of sphalerite itself has four points in each cell, it is a necessary consequence that the atoms of zinc lie on one face-centered cubic lattice inter penetrating the first. Then the lattice constant of sphalerite is determined as $a_0=5.400\pm0.008$ Å.

It is known that lattice constant changes in keeping with variation

TABLE 8a. Variation of interplanor-spacings.

Sample no.	d(Å) (531)
H-1	0.9149
H-7	0.9150
H-3	0.9150
H-4	0.9151
H-8	0.9150
H-1	0.9156
H-14	0.9150
H-12	0.9192
H-5	0.9154
H-13	0.9155
H-9	0.9151
V-1	0.9149
V-2	0.9150
V-3	0.9154
V-4	0.9155
V-5	0.9154

TABLE 8b. Variation of interplaner-spaceings.

Locality	(hkl)	α	$2(\theta)$	d(Å)	a(Å)
Eagle Picher	(440)	α	138.27	0.956	5.411
	(440)	α	139.00	0.956	5.413
	(511, 333)	α	118.17	1.042	5.413
					5.412
Budô	(440)	α	138.22	0.956	5.413
	(440)	α	139.00	0.956	5.413
	(511, 333)	α	118.18	1.041	5.413
					5.413
Osarizawa	(440)	α	138.27	0.956	5.411
	(440)	α	139.00	0.956	5.413
	(511, 333)	α	118.17	1.042	5.418
					5.414
Toyoha	(440)	α	138.27	0.956	5.411
	(511, 333)	α	118.18	1.042	5.417
					5.414
Kamioka	(440)	α	138.27	0.956	5.411
	(440)	α	139.04	0.956	5.412
	(511, 333)	α	118.18	1.042	5.417
					5.413
Kamioka	(440)	α	138.16	0.957	5.414
	(440)	α	138.52	0.957	5.416
	(511, 333)	α	118.18	1.042	5.417
					5.416
Daira	(440)	α	138.20	0.957	5.417
	(511, 333)	α	118.18	1.042	5.417
					5.417
Iitoyo	(440)	α	138.18	0.957	5.414
	(440)	α	138.58	0.957	5.414
	(511, 333)	α	118.18	1.042	5.417
					5.415
Funauchi	(440)	α	138.00	0.958	5.419
	(440)	α	138.32	0.958	5.421
	(511, 333)	α	118.12	1.043	5.420
					5.420
Nakatatsu	(440)	α	137.56	0.958	5.421
	(511, 333)	α	118.10	1.043	5.421
					5.421
Chichibu	(440)	α	137.58	0.958	5.420
	(440)	α	138.32	0.958	5.421
	(511, 333)	α	118.06	1.043	5.423
					5.421
Kamioka	(440)	α	137.54	0.958	5.421
	(440)	α	138.28	0.958	5.423
	(511, 333)	α	118.06	1.043	5.423
					5.422
Yonaihata	(440)	α	138.16	0.957	5.418
	(511, 333)	α	118.24	1.042	5.414
					5.416
Taro	(440)	α	138.20	0.957	5.417
	(511, 333)	α	118.18	1.042	5.417
					5.417
Tatemata	(440)	α	138.14	0.958	5.419
	(511, 333)	α	118.14	1.043	5.419
					5.419

(after Mino, 1957)

of iron content (IWASAKI, et al., 1940; MINO, 1957; TAKANE, et al., 1937;

TOKUNAGA, 1958; 1959). About this phenomenon the present writer made observations on samples from the Hosokura Mine, Miyagi Prefecture, the data are shown in Table 8. They are additional to data hitherto

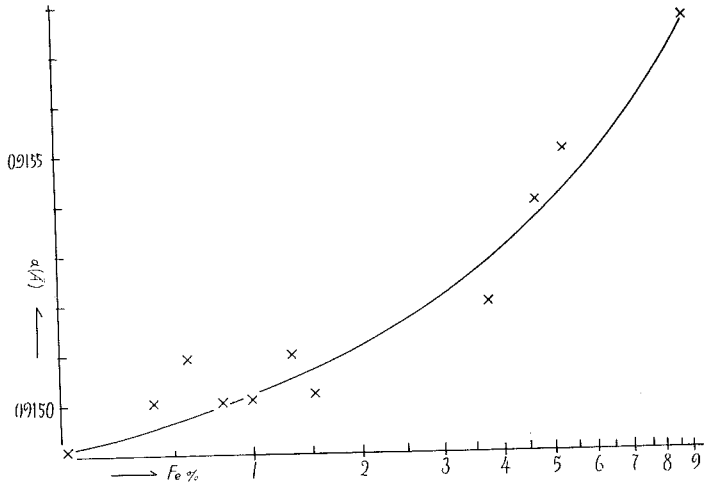


Fig. 4a. Relation between Fe content and inter-planer-spacing.

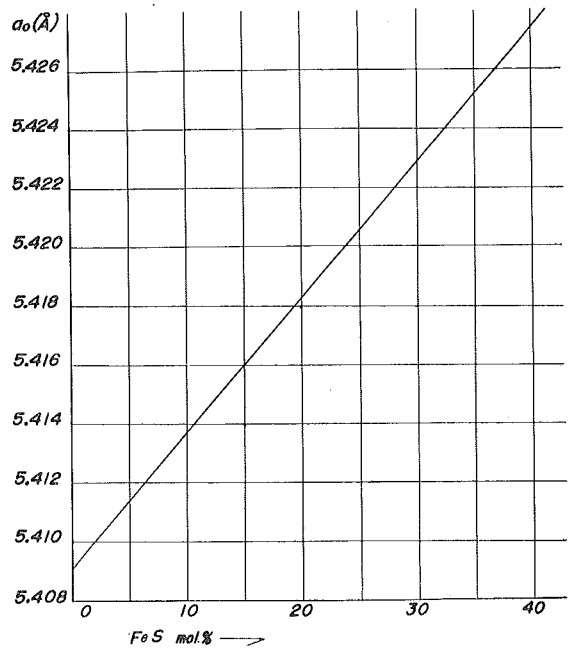


Fig. 4b. Relation between FeS content and lattice constant.

accumulated. Symbol of V in table indicates samples from early stage to latter stage from the same vein. The illustration of variation about concerned with these data is shown in Fig. 4.

It has been said that lattice constant of sphalerite is changed by variation of iron content substitution in the position of the zinc atom in the crystal structure; in other words iron contents may be determined by measurements of lattice constants or inter planer-spacings.

V-2 *Polymorphism and polytype*

Three polymorphs of zinc sulphide have been described already; they are α-zinc sulphide, β-zinc sulphide, and γ-zinc sulphide. Sphalerite is known undnern the name of mineral β-zinc sulphide; wurtzite as α-zinc sulphide. The former is stable in comparatively lower temperature, while the latter is stable in higher temperature, and also metastable in lower one. The γ-zinc sulphide may be an intermediate type between sphalerite and wurtzite, but it is doubtful (FRYKLUND, et al., 1956; FRONDEL, et al., 1950; IMAI, 1941; ITO, 1947; IWASAKI, et al., 1940; JAGODZINSKI, 1949; NISCHIO, 1937; SMITH, 1955; TAKEUCHI, et al., 1950; TSUBOYA, 1933; WATANABE, M., 1941; WATANABE, S., 1937).

Recently several polytypes of wurtzite have been found. These are determined to be iso-typic with the corresponding polymorphs of silicon carbide, already well known. The interfacial angles of crystals of the several polytypes are found to agree to within a few minutes of an arc. The symmetry and relative dimensions of the various structures have been predicted theoretically by BELOV (1939) and ZHDANOV (1945) from a consideration of the possible arrangements of equally sized spheres in closest packing. RAMSDELL (1947) has discussed the problem of the nomenclature of the several types of structure, and has recommended a notation comprising a letter, H or R, depending on whether the unit cell is hexagonal or rhombohedral, and a number which states the total number of hexagonally closet-packed individual layers which are stacked within the length of the unit cell. At present 3c, 2H, 4H, 6H, 8H, 9H, 10H, 15R, and 21R are represented by known polytypes in zinc sulphide. Besides, the polytype is related to the variaton in crystal habit. Therefore it is an important phenomenon in morphological studies. However polytypes of zinc sulphide are not yet discovered in Japan; but this must be an interesting study.

Sphalerite is found almost throughout Japan, but wurtzite is rare and in addition was not determined (WATANABE, M., 1941) except for Okoppe, Aomori Prefecture.

On heating, pure sphalerite inverts to wurtzite at about 1020°C; the

inversion temperature is lowered markedly by the substitution of iron for zinc, and occurs at 880°C in material with 17.06 percent iron. Therefore it is interesting that polymorphs are used as a geothermometer as well as polytypes.

VI. Colour of sphalerite

The colour of sphalerite is white to nearly colourless when pure, but it occurs seldom in nature. The colourless sphalerite from the Hosokura mine, Miyagi Prefecture is the sole occurrence; it was reported many years ago. Commonly its colour is brown, yellow, black and also red and green. It has been considered that the high iron content members approach black in colour.

In this paper is explained the colour variation and the cause of colouring of sphalerite.

VI-1 *Variation in colour*

Variation in colour of Japanese sphalerite is wide, but yellow sphalerite is most frequent in appearance, and black also often appears. The other colours are green, orange and red which may be pale or deep, and dark or light.

Blue, violet and purple sphalerite do not occur in the least.

There are three subordinative properties in colour, viz., brilliance, hue and saturation; they are independent of each of each other. No study of colour has ever been made an experiment nor above mentioned properties has been discussed.

For such studies the trichromatic specification through the photo-electric-spectro photometer is the best method (TOGARI, 1959), but that apparatus is not available in the writer's laboratory. In this paper the quantitative analysis of sphalerite colour was determined by Ostwald's standard colour table (TOGARI, 1954; 1958; 1959). In order to determine the chromaticity in colour the absorption curve through spectroscope is used in several parts of specimens at the same time. That apparatus is shown in Fig. 5, and the data in Fig. 6.

All specimens of sphalerite were marked with the symbol of Ostward's standard colour panels. Then the chromatically coloured on each side of the axis were marked firstly with the number borne by the hue of their full colour in the chromatic circle, and secondly with those two letters on the grey axis which crosses in them, the undermost letter being placed first. This triple symbol consisting of one number and two letters, completely defines the colour in each panel for it expresses the percentages

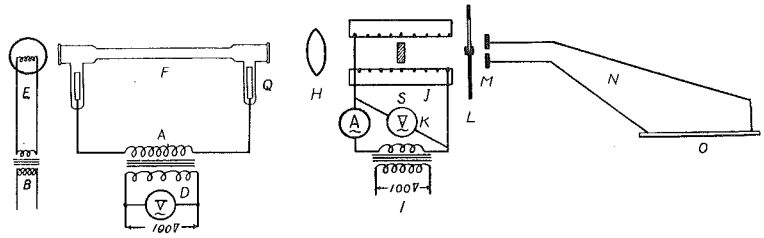


Fig. 5. Photographing apparatus of absorption curve.

A Transformer
B Slidac for Projection lamp
D Voltmetr for hydrogen electric discharge tube
E Projection lamp
F Hydrogen-electric-discharge-tube
Q Quartz-window
H Quartz lens
S Sample
L Logarithm secor
M Slit of spectrograph
N Spectrograph
O Photographic plate

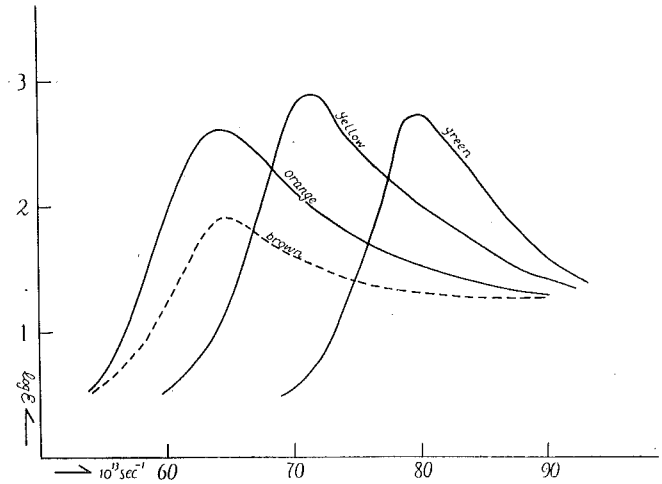


Fig. 6. Absorption curve of sphalerite from Hosokura mine.

of white, black, and full colour which it contains.

The isovalent and composition of colour of all sphalerite specimens are shown in Table 9.

For example in these data, if one member in the symbol of isovalent

TABLE 9. Colour of sphalerites according to the Ostwald colour standards.

Sample. no.	Isovalent colour	Composition of colour		
		% white	% black	full colour
No. S-1a	5 pn	3.5	94.4	2.1
No. S-1b	5 li	8.9	86.0	5.1
No. S-16	6 li	8.9	86.0	5.1
No. S-17	4 ig	14.0	78.0	8.0
No. S-21a	5 li	8.9	86.0	5.1
No. S-21b	6 nl	5.6	91.1	3.3
No. S-21c	4 ig	14.0	78.0	8.0
No. S-24a	3 li	8.9	86.0	5.1
No. S-24b	5 nl	5.6	91.1	3.3
No. H-1	24 pe	3.5	65.0	31.5
No. H-9	2 na	5.6	11.0	83.4
No. H-10	3 lc	8.9	44.0	47.1
No. H-7	3 ng	5.6	78.0	16.4
No. H-3	4 nc	5.6	44.0	50.4
No. H-4	4 pc	3.5	44.0	52.5
No. H-8	4 ne	5.6	65.0	29.4
No. H-2	4 lg	8.9	78.0	13.1
No. H-1	5 gc	22.0	44.0	34.0
No. H-14	6 ie	14.0	65.0	21.0
No. H-12	6 ei	8.9	86.0	5.5
No. H-5	6 ne	5.6	91.1	3.2
No. H-13	6 pl	3.5	91.1	5.4
No. H-6	7 pe	3.5	91.1	5.4
No. V-1	24 pe	3.5	65.0	31.5
No. V-5	3 lc	9.8	44.0	47.1
No. V-3	4 ne	5.6	91.1	3.3
No. V-4	5 pl	3.5	91.1	5.4
No. V-5	5 oj	5.6	86.0	8.4

colour is 24, this hue is so-called "yellowish leaf-green". Thus if 7, the hue is so-called "red inclines to orange" or "vermilion," two is yellow, five is orange, and so on.

VI-2 *Cause of colouring*

Until now it has been almost universally considered that the variable colouring of sphalerite is due to the iron content (DOELTER, et al., 1929; FRYKLUND, et al., 1956; ITO, et al., 1947; MIYAKE, 1950; YAGI, 1915). But

that is doubtful, because the sphalerites showing change of iron content are marked to the same chromaticity, but the high iron content members approach to dark colour from light colour (not pale colour).

Firstly, the cause of colouring seems to show three types (TOGARI, 1959) as follows:

a) Colouring by transition elements
b) Colouring by F-center
c) Colouring by semi-conductance

As it has been explained in the writer's preceding report, the main elements of sphalerite are not transition ones, and sphalerite must not include F-center. Because the F-center is peculiar property to an insulator, and sphalerite is a typical semi-conductor. Accordingly the colouring of sphalerite due to the peculiar property of semi-conductance (TOGARI, 1954; 1958; 1959).

By reference to above Table 9 and Fig. 7 the cause of colouring is shown as follows.

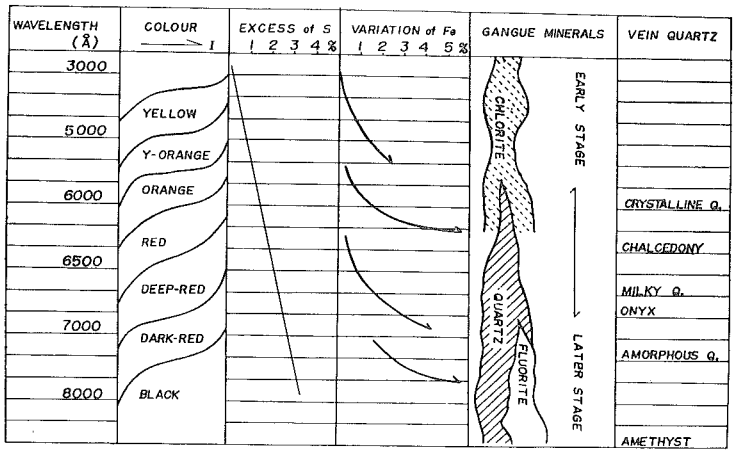


Fig. 7. Relation between chromaticity and brilliance.

The chromaticity in colour is due to semi-conductivity of sphalerite, and the variation of the chromaticity is due to change in amount of excess sulphur in sphalerite. On the other hand the brilliance in colour is due to variety of the iron content substituting the position of zinc atom. The theoretical consideration of this conclusion is omitted in this paper.

VII. Conclusion

The writer has made systematical examinations on sphalerites from the various occurrences and localities in Japan. He also discussed and considered the remarkable relations between chemical components, crystal structure, and physical properties from the mineralogical stand point.

From these examinations, discussions, and considerations, he reaches the following conclusion.

Commonly, sphalerite from Japan shows simple form with few sorts of faces. Then tetrahedron and octahedron faces are dominant, and the number of crystal faces reported in Japan amounts to only eight.

Japanese sphalerite is nearly always containing iron, so that its varition changes the lattice constant, and changes the brilliance in colour. Colouring is caused by the peculiar property of semiconductance and variable chromaticity in colour is due to the excess sulphur on chemical component.

The samples were arranged firstly according to Ostwald's colour standards. Next, the composition of every colour is represented by an equation of the form C+W+B=100%, where C=full colour, W=white, and B=black. In this manner, the relations between chromaticity and brilliance are determined. Hue in colour is corrective with the wave length of its absorption peak. Regarding the relations between brillance and iron content, the former shows dark in naccordance with increase of the latter.

Besides there is a tendency among sphalerites to be more pale in colour than dark in regard to the contents of minor elements. According to the type of ore deposit, or the province, minor elements are characteristic, and then a certain minor element concentrates in an specific colour of sphalerite.

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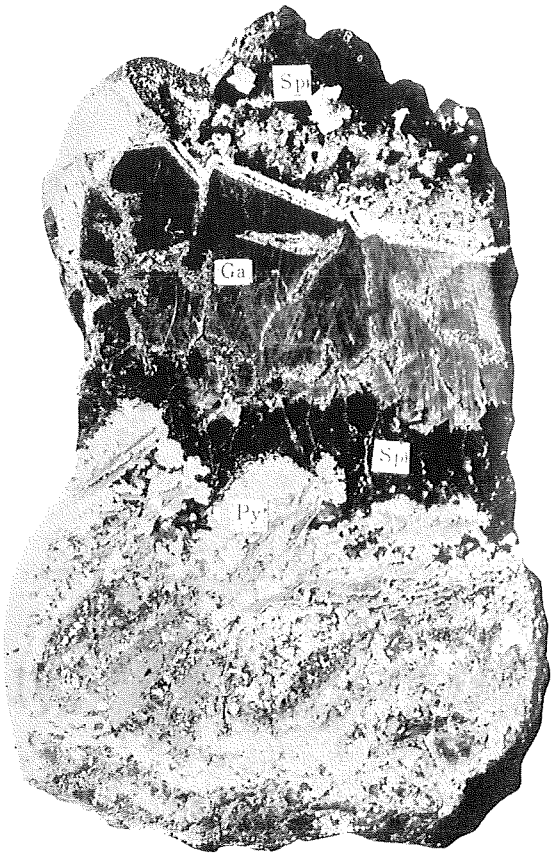
References

1) AKAOKA, J. (1920): Correlation between chalcopyrite, sphalerite, and barite from the Hitachi mine. J. Georg., 27, 434.
2) DOELTER, C. und LEITMEIER, H. (1929): Handbuch der Mineralchemic.
3) FRODEL, C. and PALACHE, C. (1950): Three new polymorphs of zinc sulfide. Am. Mineral., 35, 29-42.
4) FRYKLUND, V. C. and FLETCHER, J. J. D. (1956): Geochemistry of sphalerite from the Star mine, Coeur D' alena district, Idaho. Econ. Geol., 51, 223-247.
5) FRONDEL, C. and PALACHE, C. (1950): Three polymorphs of zinc sulfide. Am. Mineral., 35, 29-42.
6) GEBHARDT, T. (1933): Uever zinkblende. N. Jb. Miner., 67, Abt. A, 1-52.
7) GEOLOGICAL SURVEY OF JAPAN (1959): Minor elements in sulphide minerals. Geol. News, 63, 21-23.
8) GOLDSCHMIDT, V. (1923): Atlas der Krystallformen.
9) HAMACHI, T. (1955): On the zinc ore in Odomori and Ikezuki mine, Miyagi Prefecture. Bull. Geol. Survey Jap., 6, no. 2, 31-36.
10) HENRIQUOS, A. (1957): Cell dimension of sphalerite. Arkiv Miner. Geol., Bd. 2, Häfte 3, Nr. 13, 275-278.
11) HORI, S. (1940): Geology and ore deposits of the Osarizawa mine, and its environs. J. Geol. Soc. Jap., 47, 409-421.
12) ———, and HORIUTI, H. (1942): Geology and ore deposits of the Nakatatu mine, and environs. J. Geol. Soc. Jap., 49, 297-318.
13) HORIKOSHI, Y. and KATANO, T. (1940): Geology and ore deposits of the Mineno-sawa mine, Shizuoka Prefecture. J. Geol. Soc. Jap., 47, 91-102 (1940).
14) ———, and KUBOTA, K. (1940): Geology and ore deposits of the environs of the Izusi mine, Ehime Prefecture. J. Geol. Soc. Jap., 47, 103-111.
15) ICHIKAWA, S. (1908): Garnet from Nerimata, Echizen Province. J. Geol. Soc. Jap., 15, 90-91.
16) ——— (1910): Some minerals from Iwomi. J. Geol. Soc. Jap., 17, 326-327.
17) ——— (1919): Some notes on Japanese Minerals. Am. J. Sci., 4th Ser., 48, 124-131.
18) IGI, T. (1896): Minerals of Japan in Imperial Museum. J. Geol. Soc. Jap., 3, 283-286.
19) IMAI, H. (1941): On wurtzite from the Hosokura mine, Miyagi Prefecture. J. Geol. Soc. Jap., 48, 506-515.
20) ISHIBASHI, M. (1954): Minor elements in pyrite and sphalerite. Bull. Geol. Comm. Hokkaido, 26, 21-23.
21) ITO, T. (1935): Beiträge zur Mineralogie von Japan. Neue Folge, 1.
22) ——— (1937): Japanese minerals in pictures. Vol. 1, 51-55.
23) ———, and SAKURAI, K. (1947): Wada's minerals of Japan. 3rd Ed., 61-68.
24) IWASAKI, I. et al. (1940): X-ray study on Japanese minerals. J. Chem. Jap., 61, 719.
25) JAGODZINSKI, H. (1949): Eindimentionale Fehlordnung in Kristallen und ihr Einfluss auf die Röntgeninntnerferenzen. Acta Cryst., 2, 201-207, 208-214, 298-304.
26) JIMBO, K. (1898): Optical anomalies of Japanese minerals. J. Geol. Soc. Jap.,

5, 315-320.
27) ——— (1908): Mineral Collection of Mr. Tomura. J. Geol. Soc. Jap., 15, 96.
28) KADOKURA, M. (1915): A zinc blende twin from Kusakura, Echigo Province. Beiträge zur Mineralogie von Japan, 5, 262-263.
29) KARASHIMA, Y. (1932): Studies onn the sulphatizing roasting of zinc ores. J. Mining Inst. Jap., 48, 243-258.
30) KATAYAMA, N. (1933): Crystal of sphalerite from the Arakawa mine. J. Geol. Soc. Jap., **15**, 609.
31) ——— (1933): Crystal of sphalerite from the Mamioka mine. J. Geol. Soc. Jap., **15**, 610.
32) KINOSHITA, K. (1930): On the "Kuroko" (black ore) deposits. Jap. J. Geol. Geogr., 8, 281-352.
33) ———, and MUTA, K. (1950): Minor elements in the minerals from the epithermal deposits. J. Geol. Soc. Jap., **56**, 423-432.
34) KO, S. (1895): Miscellany of Japanese minerals. J. Geol. Soc. Jap., **3**, 86-96.
35) ——— (1897): Sphalerite from the Ikuno mine. J. Geol. Soc. Jap., **4**, 352.
36) KOPP, O. C. and KERR, P. F. (1957): Differential thermal analysis of sphalerite. Program 1957 Annual Meetings **58**.
37) KULLERUD, G. (1953): The Ees-ZnS system. A geological thermometer. Norsk Geologisk. **32**, 61-144 (1953).
38) MATSUKUMA, T. and MIYAHISA, M. (1957, 1958): Exsolution intergrowths of the marmatite and the Cu-Fe-S system minerals from Kyushu. (1), (2). J. Jap. Ass. Miner. Petr. Econ. Geol., **41**, 89, 97, 173-180.
39) MILNE, J. (1879): List of Japanese minerals, with note on species which are to be new. Miner. Mag., 3, 96-100.
40) MINO, H. (1957): Fundamental studies on sphalerite in relation to mineral dressing. (1), (2) J. Mining Inst. Jap., **73**, 93-102; 221-229.
41) MIYAKE, T. (1950): Detailed statistical microscopic analyses of mill products of the Hosokura flotation concentrator, Miyagi Prefecture. J. Mining Inst. Jap., **66**, 324-334.
42) MUKAIYAMA, M. (1950): On some gold-silver ores from the Sado mine, Sado Island, Niigata Prefecture, Japan. J. Geol. Soc. Jap., **56**, 181-187.
43) MURAKOSHI, T. and HASHIMOTO, K. (1956): Geology and Mineral resources of Japan.
44) MUTA, K. (1960): Minor elements in sphalerite from xenothermal deposits. J. Jap. Ass. Miner. Petr. Econ. Geol., **44**, 34-43.
45) NAKANO, O. (1937): The determination of dissolving temperature of skeletal crystals of zincblende in chalcopyrite from Kamioka. J. Jap. Ass. Miner. Petr. Econ. Geol., **18**, 137-150.
46) NISHIO, S. (1927): Variation of the refractive indices sphalerite and their iron contents. J. Mining Inst. Jap., **43**, 850-853.
47) ——— et al. (1955): Temperatures of minerals formation in some deposits in Japan, as measured by the decrepitation method. (1), (2) Mining Geol., 3, 25-26; 5, 14-15.
48) PAUL, B. Barton, Jr. and KULLERUD, G. (1957): Preliminary report on the system FeS-ZnS-S and implications regarding the use of the sphalerite geothermometer. Program 1957 Annual Meetings, 29.

49) SAITO, T. (1953): On minor elements in ore minerals of the Yakumo mine, Hokkaido, Japan. J. Geol Soc. Jap., **59**, 129-137.
50) SAKURAI, K. and SORITA, E. (1948): Studies on the Minerals of Japan (6). Miner. Geol., **12**, 21-25.
51) SAKURAI, K. and FUJIYAMA, I. (1955): Minerals of Chichibu district (Part 1). Bull. Chichibu Museum Nat. Hist., **5**, 39, 66.
52) SATO, M. (1959): Rapid analysis of sphalerite by use of iron exchange resin and volumetric method. J. Miner. Soc. Jap., **4**, 293-298.
53) SHINOMOTO, J. (1893): Minerals from the Uchinokuchi mine in Bungo Province. J. Geol. Soc. Jap., **1**, 399-400.
54) ——— (1900): Sphalerite from the Schimotugu mine in Mikawa Province. J. Geol. Soc. Jap., **7**, 31.
55) Smith, F. G. (1955): Structure of zinc sulphide minerals. Am. Miner., **40**, 658-675.
56) STOIBER, R. E. (1940): Minor elements in sphalerite. Econ. Geol., **35**, 50.
57) SUGAKI, A., TASHIRO, C. and HAYASHI, T. (1956): Skeletal crystals of sphalerite in chalcopyrite. J. Ass. Miner. Petr. Econ. Geol., **40**, 12-21.
58) SUGAKI, A. and TASHIRO, C. (1956): Unmixing textures of the ores from the Daira mine, Akita Prefecture. J. Ass. Miner. Petr. Econ. Geol., **40**, 223-230.
59) ———, and ——— (1957): Thermal studies on the skeletal crystals of sphalerite in chalcopyrite. Sci. Rep. Tohoku Univ., 3rd Ser., **5**, 293-304.
60) SUNAGAWA, I. (1954): Explanatory text of the geological map of Japan, Ashio, appendix mineralogy.
61) TAKANE, K. and YAGI, K. (1937): The comparison of the lattice constants in the zincblende crystals from Ashio and Budô. J. Jap. Ass. Miner. Petr. Econ. Geol., **18**, 158-161.
62) TAKENAKA, S. (1954): Thermal studies on the chalcopyrite-sphalerite intergrowths from pyrrhotite deposits in Japan. J. Jap. Ass. Miner. Petr. Econ. Geol., **38**, 127-132.
63) TAKEUCHI, T. and NANBU, M. (1950): Geologie and ore deposits of the Ainai mines Akita Prefecture (2). J. Jap. Ass. Miner. Petr. Econ. Geol., **34**, 21-28.
64) TAKIMOTO, K., MINATO, T. and HIRONO, S. (1958): On the distribution of selenium in some sulphide minerals showing the relations of intimate paragenesis. J. Jap. Ass. Miner. Petr. Econ. Geol., **42**, 161-170.
65) TAKUBO, J. et al. (1953): On the dielectric constants of minerals. Miner. J., **1**, 3-24.
66) TEAS, L. R. et al. (1919): The relation of sphalerite to other sulphide in ores. Trans. A. I. M. E., **49**, 62-82.
67) TOGARI, K. (1954): Colour of zincblende from the Hosokura mine, Miyagi Prefecture (1). J. Miner. Ass. Jap., **1**, 391-402.
68) ——— (1958): Sphalerite from the Shimokawa mine, Hokkaido. J. Miner. Ass. Jap., **3**, 702-709.
69) ——— (1959): Colour of sphalerite from the Hosokura mine, Miyagi Prefecture (2). J. Miner. Ass. Jap., **4**, 24-33.
70) ——— (1959): Colour of minerals. J. Miner. Ass. Jap., **4**, 313-326.
71) TOKUNAGA, M. (1958): On the sphalerite from the Nakatatsu mine. Jubilee Publication in the Commemoration of Prof. H. FUJIMOTO 60th Birthday, 454-458.

72) ——— (1959): Zonal arrangement in the skarn of the Nakayama deposit in the Nakatatsu zinc mine, with special reference to the occurrence and nature of sphalerite. Mining Geol., **9**, 211-223.
73) TSUBOYA, K. (1933): Geology and ore deposits of the Hosokura lead-zinc mine, Miyagi Prefecture, Japan. Jap. J. Geol. Geogr., **10**, 167-169.
74) UMEMOTO, S. (1955): Properties of sphalerite in some hydrothermal veins. Bull. Geol. Survey Jap., **6**, no. 1, 23-30.
75) WADA, M. and MAJIMA, H. (1956): Spectal reflectance characteristics of several sulphide and oxide minerals. J. Mining Inst. Jap., **72**, 565-576.
76) WADA, T. (1904): Minerals of Japan.
77) WAKABAYASHI, Y. (1903): Minerals from the ebvirons of the Arakawa mine. J. Geol. Soc. Jap., **10**, 382-399.
78) WARREN, H. W. and THOMPSON, R. M. (1945): Sphalerite from western Canada. Econ. Geol., **40**, 309-336.
79) WATANABE, M. and LANDWEHR, W. B. (1923): On some interesting relations between chalcopyrite and sphalerite in the ores from the Hitachi mine, Japan. J. Geol. Soc. Jap., **30**, 1-4.
80) ——— (1930): Crystal forms of sphalerite from Kamioka mine. J. Jap. Ass. Miner. Petr. Econ. Geol., **3**, 20-21.
81) WATANABE, M. (1941): Prismatic zinc sulphide mineral from the Ohmori mine. J. Jap. Ass. Miner. Petr. Econ. Geol., **25**, 213-229.
82) WATANABE, S. and KOIWAI, M. (1937): Morphological observation of zincblended from the Ashio mine. J. Jap. Ass. Miner. Petr. Econ. Geol., **17**, 38-40.
83) ——— (1937): Polysynthetic twin of zincblende from the Ashio mine. J. Jap. Ass. Miner. Petr. Econ. Geol., **17**, 103-106.
84) YAGI, T. (1915): Report on minerals from Shinano Province. J. Geol. Soc. Jap., 22, 132-133.
85) YAMADA, K. (1896): Abstract descriptions of minerals from Aikawa mine. J. Geol. Soc. Jap., **22**, 132-133.
86) ZAPPE (1879): Der Bergbau Japans und seine Haupterzeugnisse. Z. Bergmaenn-Huetten U.—Salinenwesen im preuss. St., 204-220.
87) ——— (1915): On some minerals from the Aikoku mine, Shinano Province. J. Geol. Soc. Jap., **22**, 180-181.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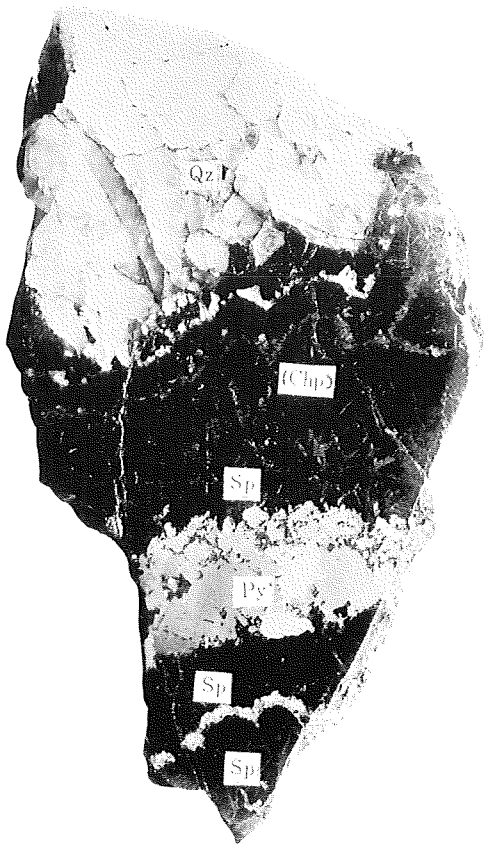
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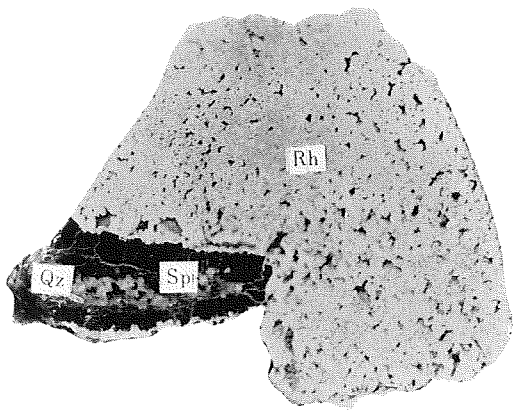
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