Sulfur isotope ratios of the Akatani, Iide and Waga-Sennin skarn deposits, and their bearing on mineralizations in the "Green Tuff" region, Japan

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Sulfur isotope ratios of sulfide minerals from the Akatani, Iide and Waga-Sennin skarn deposits formed in the "Green Tuff" region, fall in a rather broad range from +2.8 to +8.9‰. Estimated formation conditions of ores, that is, high oxygen fugacities and relatively low temperatures and pH, certify the predominance of sulfate sulfur over sulfide sulfur in the ore-forming solutions. Irreversible, fast precipitation of sulfide minerals from such sulfate-dominant solutions is thought to have resulted in insignificant isotopic fractionation between aqueous sulfate and sulfide minerals. The obtained range of isotopic values is almost identical with those for sulfide minerals from other type, vein and kuroko, deposits in the "Green Tuff" region. This regularity of sulfur isotope values for many different type deposits in the region suggests the possibility that ore sulfur was supplied from a common provenance, such as Miocene felsic igneous rocks, without any significant isotopic fractionations in the transportation and precipitation processes.

INTRODUCTION

The sulfur isotope study is indispensable for understanding the origin of sulfur and physico-chemical features prevailing in the ore-forming process. Since a pioneer work by TATSUMI (1965), however, the accumulation of data seems to have been slow, especially on the sulfur isotopic features of individual hydrothermal vein and skarn deposits in Japan. The only available data to date include TATSUMI (1965) on the Osarizawa and Ani Cu vein deposits, Yakumo Mn-Zn-Pb vein deposits, Taishu Zn-Pb vein deposits and Chichibu Cu-Zn-Pb-Fe skarn deposits, KİYOSU and NAKAI (1971) on the Kamioka Zn-Pb skarn deposits, KİYOSU (1974) on the Toyoha Zn-Pb vein deposits, YAMAMOTO (1974a) on the Akenobe Cu-Zn-Pb-Sn-W vein deposits, YAMAMOTO (1976) on the Mihara Cu-Fe skarn deposits, KİYOSU (1977) on the Taishu Zn-Pb vein deposits, SHIMAZAKI and YAMAMOTO (1979) on the Yoshioka Cu skarn deposits, Tsumo Cu-Zn-Pb-W skarn deposits, Kawayama Cu-Zn skarn deposits, Kuga, Fujigatani, Kiwada and Kagata W(-Cu) skarn deposits and Hoei Zn-

Cu-Sn skarn deposits, and ISHIHARA *et al.* (1981) on the Akenobe vein deposits.

In order to collect information as much as possible on the ore-forming process of hydrothermal deposits, the present writers have planned to determine sulfur isotope ratios of representative deposits in Japan (SHIMAZAKI and YAMAMOTO, 1979). The result given in the present paper is a part of those obtained through this project. In the previous paper (SHIMAZAKI and YAMAMOTO, 1979), studied deposits were selected because some features in the deposits suggest relatively reducing environments established at the time of mineral deposition. The reducing environments certify the predominance of reduced sulfur species in the ore-forming solutions, and mostly negative $\delta^{34}\text{S}$ values (+0.7 to -12.2‰) obtained for sulfides are thought to be close to those for total sulfur in the solutions responsible for the deposits.

In the present work, the deposits formed in oxidizing environments are selected in order to check the effect of oxidation states of ore-forming solutions on the fractionation of sulfur isotopes. The Akatani Fe-Cu, Iide Zn-Pb-Cu-Fe,

and Waga-Sennin Fe-Cu skarn deposits are characterized by the precipitation of large amounts of hematite, and are peculiar among many skarn deposits in Japan. The locality of the deposits studied in this paper is given in Fig. 1. All the deposits are distributed in the Miocene submarine volcanic region known as the "Green Tuff" region.

OUTLINE OF ORE DEPOSITS

The Akatani Fe-Cu mine The mine is located about 40km east-southeast of Niigata City, Niigata Prefecture. Many papers were published on the deposits of this area (e.g. IMAI, 1952, 1960; MORITA, 1960; Japan Mining Industry Association, 1965; IMAI and YAMAZAKI, 1967; SUZUKI, 1970). According to these papers, the area consists of late Paleozoic shale, sandstone, chert, limestone and basic tuff, intruded by late Cretaceous granodiorite to leucogranite. In and on this basement rocks, various kinds of intrusive and extrusive rocks occurred in Neogene time. Among them, plagioclase rhyolite of middle Miocene age is widely distributed in the mining area, and is called "Akatani rhyolite". The rock generally occurs as extrusives at the surface covering the basement rocks, while the presence of dikes of the rock is also confirmed at depth.

There are three large deposits in the mine, named Bawarizawa, Sudachizawa and Mizunashizawa, arranged from the northwest to the southeast, and the first one is the largest. These main deposits are formed in limestone along the contact with Akatani rhyolite or with other members of the Paleozoic formation. They are usually contained in skarns consisting of clinopyroxene, grandite garnet, wollastonite, ilvaite and epidote. These minerals, however, are almost completely altered to hydrous minerals such as tremolite, chlorite, talc, kaolinite and montmorillonite in the vicinity of high-grade ore bodies. Besides this alteration, extensive dolomitization of limestone is also recognized in the proximity of the deposits, and could be cited as one of the characteristic features of the

deposits.

The ore of the mine consists of hematite, and minor pyrite, chalcopyrite, sphalerite and galena. Parts of hematite are often changed to magnetite, preserving its tabular crystal form. The studied specimens are collected widely from the main deposits. Although no detailed information is available on the occurrence, some old specimens at the University Museum, University of Tokyo, are also taken for analyses, because they are thought to have been collected from the upper parts of the deposits at earlier stages of the mine operation. One pyrite (No. 20 in Table 1) is taken from an intensely altered andesite, which contains large pyrite cubes of up to 2cm, collected at an outcrop located between the Akatani and Iide mines.

The Iide Zn-Pb-Cu-Fe mine The mine is located about 2km east of the Akatani mine. Although the mine was closed about 15 years

Fig. 1. Locality map of the studied deposits. Dotted parts show the "Green Tuff" region. Localities discussed in the paper are also shown except for the Iwami mine, which is located out of the map.

Table 1. Sulfur isotopic composition of sulfide minerals from the Akatani, Iide and Waga-Sennin mines

No.	Sample No.	Locality	Rock	Mineral	$\delta^{34}\text{S}(\text{‰})$	Assoc. ore mins.
Akatani mine, Niigata Prefecture, +2.8 - +8.9 (20)						
1	HS72070303	Bawarizawa 480 mL	Fe-Cu ore	cp	+8.8	hm, py
2	HS72070306	ditto	Altered skarn	cp	4.5	hm(mt), py
3	TY420805	Bawarizawa No. 16 O.B.	Powdery Fe ore	py	6.5	hm
4	HS72070403	Mizunashizawa 280 mL	Clinopyroxene skarn	py	6.3	cp
5				sp	6.5	
6				gn	5.5	
7	HS72070404	ditto	ditto	sp	6.5	gn, py, hm(mt)
8	HS72070409	ditto	Fe-Cu ore	py	6.9	hm
9				cp	5.4	
10	HS72070414	Mizunashizawa 310 mL	Altered skarn	py	2.8	sp, cp, gn
11	TY422706	Sudachizawa 368 mL	Brecciated rhyolite	py	6.1	hm
12	UMUTPM01794	Sudachizawa	Fe ore	py	7.1	hm, cp, sp
13	UTUMPM40746	No. 6 O.B.	Brecciated limestone	py	5.6	hm, cp
14	JN1303	Details unknown	Zn-Pb ore	sp	8.4	hm, cp
15				gn	4.8	
16	JN1304	ditto	Fe ore	py	7.0	hm
17				cp	8.9	
18	UMUTMN01586	ditto	ditto	py	6.9	hm, cp
19	UMUTMN01711	ditto	ditto	py	5.8	hm(mt), cp
20	HS72070401	Surface near the mine	Altered andesite	py	7.1	cp, sp
Iide mine, Niigata Prefecture, +3.3 - +8.8 (16)						
21	I-916	Details unknown	Zn-Pb ore	py	+5.9	cp
22				sp	5.8	
23				gn	4.4	
24	I-918	ditto	ditto	py	5.9	cp
25				sp	8.3	
26				gn	7.0	
27	I-922	ditto	ditto	sp	7.9	py, hm(mt), gn, cp
28	I-923	ditto	ditto	py	5.3	hm, gn, cp
29				sp	5.0	
30	I-927A	ditto	ditto	py	7.3	gn, cp
31				sp	8.8	
32	I-947	ditto	ditto	py	6.1	gn, hm(mt), cp
33				sp	7.8	
34	I-956	ditto	ditto	sp	3.3	gn, hm, cp
35	UTMDP2149	ditto	ditto	sp	6.5	hm, py, cp
36				gn	5.5	
Waga-Sennin mine, Iwate Prefecture, +2.8 - +8.6 (5)						
37	TT42081707	Shimotobira	Cu ore	cp	6.8	py
38	HS74110902	Shimotobira 7L	Altered skarn	py	5.8	hm(mt), cp
39	HS72100405	Kanahada dump	Powdery Fe ore	py	2.8	hm
40	UMUTMN01584	Details unknown	Powdery py ore	py	8.6	cp
41	UMUTMN01585	ditto	Fe ore	py	2.9	hm

Abbreviations: cp chalcopyrite, gn galena, hm hematite, hm(mt) hematite partly replaced by magnetite, py pyrite, sp sphalerite, L level, O.B. ore body.

ago, several papers provide the outline of the deposits (ITO and TOMITA, 1951; IMAI, 1952; Japan Mining Industry Association, 1965). According to these papers, the geology of both the Akatani and Iide deposits is almost identical. Two main deposits, named Honko and Sudachi, are formed in limestone along the contact with Cretaceous granodiorite or plagioclase rhyolite. Skarn minerals such as clinopyroxene, grandite

garnet, ilvaite, epidote, actinolite and wolastonite are often associated with ores. As in the case of the Akatani deposits, these minerals have been subjected to intense alteration to tremolite, chlorite and talc. Dolomitization of limestone is also observed, although not so strong as in the Akatani deposits.

The kind of ore minerals precipitated in the deposits is the same as in the Akatani deposits,

but the ratio of the amount is remarkably different. In the Iide mine, sphalerite and galena are predominant, and pyrite, chalcopyrite and hematite are subordinate in amounts. High-grade Zn-Pb ores are often associated with quartz and calcite, and make similar appearance to "Shiroji ore" in the Kamioka Zn-Pb skarn deposits. Hematite is often replaced partly by magnetite. The past production record of magnetite ore from the mine, shows local concentration of magnetite in the deposits. A small amount of copper was once produced from a chlorite- and pyrite-rich massive to vein-form deposit, named Komata adjacent to the west of the main deposits. No samples from this deposit were available in the present study. All but one specimen taken for the sulfur isotope analysis were collected by N. IMAI at various localities of the main deposits.

The Waga-Sennin Fe-Cu mine The mine is located about 50km south-southwest of Morioka City, Iwate Prefecture. The mine was closed in 1976. Since a classical work by ICHIMURA (1919), several papers have been published on the deposits of the mine (e.g. IMAI, 1960, 1977; UENO, 1975; IMAI *et al.*, 1976). According to these papers, similarity of geological and mineralogical features is apparent between the deposits of this area and of the Akatani-Iide region. The basement rocks consist of metamorphic rocks and late Cretaceous granodiorite to leucogranite intruding the former. The metamorphic complex is composed of biotite schist, biotite gneiss, biotite hornfels and crystalline limestone. Original rocks are thought to be of Permian. Covering and intruding the basement rocks, Neogene sedimentary and igneous rocks are widely distributed. Among them, it is noteworthy that plagioclase rhyolite of middle Miocene occurs as dike swarms and stocks in the mining area.

There are several main deposits in the mine. They are formed in limestone with altered skarns along the contact with Cretaceous granitic rocks. Skarn minerals include clinopyroxene, grandite garnet and epidote. As in the Akatani

and Iide deposits, they are intensely altered to tremolite, chlorite, talc and montmorillonite in the vicinity of ore bodies. Dolomitization of limestone also occurs extensively. Igneous and metamorphic rocks near the deposits are partly subjected to silicification, sericitization and chloritization. A main ore mineral is hematite, being partly or thoroughly replaced by magnetite. Minor pyrite and chalcopyrite are associated, and the latter shows local concentration along fissures and faults. Rare occurrences of sphalerite, galena and even pyrrhotite are reported. Unfortunately only a small number of specimens were available for the present study. Some of them were collected from the main deposits, named Shimotohira and Kanahada.

Genesis of the ore deposits Owing to close spatial relations of ore deposits to Cretaceous granitic rocks, these deposits under consideration were once believed to have been formed with genetical relations to the granitic rocks (e.g. ICHIMURA, 1919). Later detailed studies, however, afforded abundant geological evidence of ore depositions genetically connected with the volcanic activity of plagioclase rhyolites of middle Miocene. For example, large ore bodies in the Bawarizawa deposit, the Akatani mine, are formed along the basal plane of a plagioclase rhyolite lava flow and along a volcanic vent of this magma (MORITA, 1960; SUZUKI, 1970). In the Waga-Sennin mine, IMAI (1977) found that parts of plagioclase rhyolite dikes are subjected to hydrothermal alteration and chalcopyrite-hematite dissemination. Based on remanent magnetic data of ores and igneous rocks, UENO (1975) concluded that the Waga-Sennin hematite deposits were genetically related to the plagioclase rhyolite. In all areas, plagioclase rhyolites adjacent to the deposits were more or less subjected to hydrothermal alterations. These lines of evidence undoubtedly indicate the middle Miocene formation of the studied deposits in considerably shallow environments.

According to NAGASAWA (1951), the Mikawa Au-Ag-Cu-Zn-Pb vein deposits are situated about 5km southwest of the Akatani mine, and are

formed with the genetical relation to the activity of Akatani rhyolite. Ores consist of chalcopryrite, sphalerite, galena, pyrite, hematite, argentite and native gold, with quartz, chlorite, dolomite to ankerite, siderite, kaolinite, adularia and barite as gangue minerals. Sericitization, silicification and chloritization of wall rocks are remarkable. The occurrence of, and mineral assemblages in, the deposits, strongly suggest that the ore-forming solution responsible for the deposits is almost identical with those for the Akatani and Iide deposits. That is, the Mikawa deposits seem to be a vein-form equivalent to the studied deposits. Similar vein deposits are widely distributed in the "Green Tuff" region. Two of the representatives of such Au-Ag-Cu-Zn-Pb veins are the Osarizawa and Ani deposits, Akita Prefecture. As stated previously, sulfur isotope data are available on these deposits (TATSUMI, 1965). As to minerals in the Fe-O-S system, hematite-pyrite assemblage is common, and sericitization, silicification and chloritization of wall rocks are also extensive in these deposits (Japan Mining Industry Association, 1968). These features might allow us to suppose that these vein deposits, as well as the Mikawa deposits, were formed under conditions similar to those for the studied deposits, as discussed in later sections.

EXPERIMENTAL

Sulfide minerals were separated from hand specimens by hand picking. Purity of the minerals is more than 95 vol. percent in most cases. Some sphalerites from the Iide mine have many small dots of chalcopryrite, and the amount of impurity reaches 10 vol. percent in some cases. All sulfide minerals were finally converted to Ag_2S by the procedure described by THODE *et al.* (1961). Ag_2S obtained was combusted to SO_2 at $1,200^\circ\text{C}$ in a stream of tank air for the mass spectrometry. The mass spectrometer used for the isotope analysis has been described by SAKAI *et al.* (1970). The results of the isotope analysis are given in the $\delta^{34}\text{S}$ value as defined by:

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

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

RESULTS AND DISCUSSION

$\delta^{34}\text{S}$ values of sulfide minerals Sulfur isotope data obtained are summarized in Table 1, and graphically shown in Fig. 2. All values are distributed in a range from about +3 to +9‰, irrespective of deposits. In each mine, any systematic change of the values is not observed for different occurrences, such as levels, ore bodies, mineral assemblages and so on. The range, +3 to +9‰, is rather broad, compared with other skarn deposits in Japan. That is, the narrow isotopic composition range of sulfide sulfur has been emphasized by previous workers as one of the characteristic features of the skarn deposits. The contrast is graphically demonstrated in Fig. 3. As discussed later, however, positive and relatively wide-range values coincide with those for the vein and kuroko deposits in the "Green Tuff" region. In this respect, it is clear that the studied deposits have a characteristic common to the deposits formed in the "Green Tuff" region.

From some samples, two or three minerals apparently coexisting grain by grain were sepa-

Fig. 2. Distribution of $\delta^{34}\text{S}$ values of sulfide minerals from the studied deposits.

rated for the analysis. These pairs are shown in Table 1 with the same sample numbers. Temperatures estimated for these coexisting sulfide minerals using experimental temperature scales given by KAJIWARA and KROUSE (1971), vary from 200°C to unreasonably high values. In addition, some pairs exhibit isotopic fractionation reverse to the equilibrium trend expected from the experiments. The same relationship was experienced in the course of the previous study on some Japanese skarn deposits (SHIMAZAKI and YAMAMOTO, 1979). In the present study, the reverse fractionation is observed especially on the pairs with pyrite. There is, however, no evidence for the precipitation of pyrite at a stage different from that of Cu-Zn-Pb mineralizations. Pyrite and chalcopyrite are known as the minerals difficult to attain isotopic equilibrium with other sulfide minerals under certain conditions (OHMOTO and RYE, 1979). It is reasonable, therefore, to suppose that only incomplete isotopic equilibrium was attained among sulfide minerals at the time of precipitation of the studied deposits.

Physicochemical conditions of ore deposition

As summarized in previous pages, the mineral assemblages observed in the studied deposits are identical with each other. This fact would allow us to assume a common ore-forming solution responsible for all the deposits under consideration. The sulfur isotope data obtained seem to support this assumption. Although the ratio of the amounts of metals precipitated is quite different in these deposits, there seems no evidence of remarkable differences with respect to major characteristics of the solutions.

ENJOI (1972) reported the data on fluid inclusions found in quartz from the Akatani mine; filling temperature of 250 to 315°C, and salinity of 1.6 to 4.5 wt % NaCl equivalent. Intense alterations of skarn minerals to clayey material also strongly suggest considerably low temperatures for the precipitation of sulfide and oxide minerals in the deposits. On the basis of these lines of evidences, temperature of the

Fig. 3. Distribution of $\delta^{34}\text{S}$ values of sulfide minerals from the skarn deposits in Japan. Numbers in parentheses represent the number of samples analyzed. References are: first three (this study), Kamioka (KIYOSU and NAKAI, 1971), Mihara (YAMAMOTO, 1976), and other deposits (SHIMAZAKI and YAMAMOTO, 1979).

solution will be assumed as 250°C, and ionic strength as unity. These assumptions allow us to draw the stability fields of hematite, magnetite and pyrite as shown in Fig. 4 after OHMOTO (1972). The mineral assemblages observed in the three studied mines, undoubtedly indicate that the ore precipitation occurred under the conditions represented in the figure by the area close to the point where these three minerals can coexist.

As to pH of the solution, extensive occurrence of kaolinite in the Akatani deposits and sericitization of wall rocks in the Waga-Sennin deposits, might suggest the value close to the stability boundary between kaolinite and sericite. MONTOYA and HEMLEY (1975) give:

$$\log([K^+]/[H^+]) = 2.8$$

along the stability boundary at 250°C. Here brackets mean thermochemical activities. If $[K^+]$ in the solution could be assumed to be less than 0.1, pH value should be higher than 3.8. This assumption could be acceptable considering that the ionic strength of the solution is close to unity. Carbonate minerals are stable in the deposits. The dissociation of calcite gives strict constraint to pH of the solution. HELGESON's (1969) compilation gives:

$$\log([Ca^{++}][H_2O]P_{CO_2}/[CaCO_3][H^+]^2) = 8.8$$

at 250°C. That means, if pH value of the solution becomes lower than about 4, $[Ca^{++}]$ and/or P_{CO_2} would reach unreasonably high values. These considerations lead to the conclusion that pH value of the solution was not much lower than 4. The conclusion also means that the total sulfur content of the solution is nearly 0.1 moles/kg H_2O as shown in Fig. 4. The hatched area in the figure represents the estimated condition for the ore depositions.

Sulfur isotopic value of the ore-forming solution In Fig. 4, calculated $\delta^{34}S$ values of pyrites are also shown after OHMOTO (1972), on the assumption of complete isotopic equilibrium between pyrites and the solution in which $\delta^{34}S$ value of total sulfur is zero per mil. The figure shows that the $\delta^{34}S$ value of total sulfur in the solution is about 26‰ heavier than that of pyrite under the supposed condition. According to this figure, the averaged $\delta^{34}S$

value, say +6‰, of pyrites obtained in this study, means that the $\delta^{34}S$ value of total sulfur in the solution is as heavy as +32‰, if isotopic equilibrium was attained during the ore precipitation.

As stated in previous pages, however, only incomplete isotopic equilibrium is observed among sulfide minerals in the studied deposits. This fact strongly suggests that the above estimation on the $\delta^{34}S$ value of total sulfur on the assumption of complete isotopic equilibrium, is not applicable in the present study. In recent works (e.g., OHMOTO and LASAGA, 1982; SHELTON and RYE, 1982), it is confirmed that isotopic equilibrium between aqueous H_2S and sulfide minerals is attained faster than isotopic equilibrium between aqueous sulfate and aqueous sulfide. In the studied deposits, even the aqueous H_2S - sulfide minerals isotopic equilibria were not attained. Therefore, isotopic equilibria among sulfur species in the solution could not be expected to have attained. This means that the rate of sulfide precipitation is much greater than the rate of the isotopic exchange reaction between aqueous sulfide and sulfate ions. The difficulty of obtaining this exchange equilibrium in natural ore-forming processes is pointed out in some previous works (e.g. SAKAI, 1968).

According to OHMOTO and LASAGA (1982), almost half a year would be required for the attainment of isotopic exchange equilibrium under the condition of $T = 250^\circ C$, $pH = 4$ and total sulfur of 0.1 mole/kg H_2O . In the solution under consideration, as estimated above, sulfate sulfur predominated over sulfide sulfur. Slight reduction of sulfate ions, the solution being still in the f_{O_2} field above hematite-magnetite stability boundary, or increase in the activity of simple cations of metals due to the breakdown of complex ions, or both occurred at the sites of ore deposition, and resulted in faster precipitation of sulfide minerals compared with the isotopic exchange reaction. These considerations lead to the conclusion that the important factor controlling the isotopic composition of sulfide minerals is rather the kinetic effect of sulfate reduction than the exchange

Fig. 4. The stability fields of Fe-O-S minerals shown by thick broken and dotted lines at total sulfur contents of 0.1 and 0.01 moles/kg H_2O , respectively (after OHMOTO, 1972). The hatched area indicates the estimated condition for the formation of the studied deposits. $\delta^{34}S$ contours for pyrite precipitated under complete isotopic equilibrium is also shown from the solution of zero per mil $\delta^{34}S$ for total sulfur, $T = 250^\circ C$ and $I = 1.0$.

reaction between sulfate and sulfide species in the solution.

Only little is known about the kinetic isotopic effect of non-biogenic reduction of sulfate ions (OHMOTO and RYE, 1979). KIIYOSU (1980) reported the effect of 7 to 9‰ in the reduction of H_2SO_4 and NaHSO_4 solutions by dextrose at $\text{pH} = 1$ and temperatures from 250 to 340°C. As shown in his experiments, however, the reduction rate depends on pH and sulfate species as well as temperature. In fact, only slight reduction and no isotopic fractionation was observed in his experiments in the case of Na_2SO_4 solution. In some natural hydrothermal systems, very small fractionations, say less than two per mil, between sulfate and sulfide species are reported from Broadland and Ngawha (OHMOTO and LASAGA, 1982, Fig. 7). The rate of non-bacterial reduction of sulfates depends also on the types of reducing compounds as pointed out by OHMOTO and LASAGA (1982). The kinetic isotopic effect increases with a decrease in the rate of reduction (OHMOTO and RYE, 1979). In the natural process under consideration, it is difficult to estimate all such factors controlling the kinetic effect, especially the reducing compounds which have caused the sulfide precipitation.

On the basis of above consideration, it only could be stated that the kinetic fractionation of nearly zero to ten per mil might have occurred during the sulfate reduction in the studied deposits. It seems, however, most reasonable to the present writers to conclude tentatively that the kinetic effects of the sulfate reduction were not so large that the sulfur isotopic values of sulfates in the ore-forming solution was reserved approximately as the values of sulfide minerals in these deposits. The reason of this tentative conclusion will be stated in the following section.

COMPARISON WITH OTHER DEPOSITS IN THE "GREEN TUFF" REGION AND POSSIBLE SOURCE OF ORE SULFUR

It is worthy to note that the obtained iso-

Fig. 5. Distribution of $\delta^{34}\text{S}$ values of sulfide minerals from the deposits in the "Green Tuff" region. Abbreviations are: s skarn, v vein and k kuroko deposits. Numbers in parentheses represent the number of samples analyzed. References are: first three deposits (this study), Toyoha (KIIYOSU, 1974), Osarizawa and Ani (TATSUMI, 1965), Shakanai No. 1 (KAJIWARA, 1971), Doyashiki to Kosaka (KAJIWARA and DATE, 1971) and Iwami (YAMAMOTO, 1974b). All kuroko deposits except for Iwami are located in the Hokuroku district shown in Fig. 1.

topic values coincide with those for the ores from vein and kuroko deposits in the "Green Tuff" region. The sulfur isotope data available to date for the ores from the region are summarized in Fig. 5. Studied minerals in these works are the same as those in the present study, namely pyrite, chalcopyrite, sphalerite and galena, except for TATSUMI's (1965) work, which includes tetrahedrite and bornite, too. Based on these data, it could be stated with certain confidence that the $\delta^{34}\text{S}$ values of sulfide minerals fall mostly in the range of +2 to +9‰ for Miocene ore deposits formed in the "Green Tuff" region.

As stated previously, some major vein deposits in the "Green Tuff" region, such as the Osarizawa and Ani deposits, are thought to have been formed under conditions similar to those

for the studied deposits, that is, high oxygen fugacity indicated by the precipitation of hematite, relatively low pH indicated by sericite, and relatively low formation temperatures around 250°C estimated from fluid inclusion data, as summarized in Japan Mining Industry Association (1968). According to TATSUMI (1965), sulfur isotope values are +2.8 to +8.1‰ and +1.4 to +6.3‰ for the Osarizawa and Ani deposits, respectively, as shown in Fig. 5. On the Toyoha vein deposits, KIIYOSU (1974) reported +2.0 to +7.0‰ of $\delta^{34}\text{S}$ values for sulfide minerals as shown in Fig. 5, and stated that sulfide minerals were precipitated from aqueous sulfide species partly disequibrated with the redox environments. Because the mineral assemblages in the Fe-O-S system observed in the deposits clearly show variable oxygen fugacity prevailed during the mineralization (e.g. SHIKAZONO, 1975). As to the Shakanai No. 1 kuroko deposits, KAJIWARA (1971, Fig. 8) explained the $\delta^{34}\text{S}$ value of sulfide minerals, +0.3 to +8.2‰, supposing that sulfides precipitated from Miocene sea water sulfate of +20‰, under conditions near the stability boundary of sulfide and sulfate species in the solution. If this is the case, considerably constant oxygen fugacity had to be achieved throughout the time of ore formations in many different kuroko deposits.

Recently SASAKI and ISHIHARA (1980) established a positive correlation between isotope ratios of sulfur from granitoids and from related hydrothermal deposits. ISHIHARA and SASAKI (1978) extended this idea to the deposits in the "Green Tuff" region including kuroko, and tried to explain the isotopic regularity supposing granitic magma as the source of sulfur. If this is the case, no large isotopic fractionation could have occurred during complex transportation and precipitation processes, although they made no comments on it. Especially in the case of the deposits associated with the magnetite-bearing felsic igneous rocks, such as those in the "Green Tuff" region, little isotopic exchange and kinetic effects should be supposed, because the large amounts of sulfur is thought to be derived from the magmas in the form of

sulfates (BURNHAM and OHMOTO, 1980).

In short, there have been various models proposed on the $\delta^{34}\text{S}$ values for the deposits in the "Green Tuff" region. If the sulfide ores in the "Green Tuff" region were really formed through the processes proposed by various authors, the common range of $\delta^{34}\text{S}$ values among skarn, vein and kuroko deposits, say +2 to +9‰ as found in Fig. 5, is concluded to be nothing more than coincidence. To the present writers, however, the range given above does not seem to be a result of coincidence. Because, it is possible to give simpler and more plausible explanation for the obtained common range, supposing extensive and homogeneous reservoirs of sulfur with several per mil positive $\delta^{34}\text{S}$ values, and also supposing little kinetic effects of sulfate reduction at the sites of sulfide precipitation as stated in the previous section. Otherwise the isotopic values for sulfide minerals would be very variable, owing to different oxidation states of the ore-forming fluids prevailed in the "Green Tuff" region. As extensive sulfur reservoirs, Miocene felsic igneous rocks seem to be the most plausible, as suggested by ISHIHARA and SASAKI (1978).

The rather broad isotopic range for the deposits in the "Green Tuff" region might be due to the small kinetic effects of sulfate reduction. On the contrary, the narrow isotopic range for skarn deposits shown in Fig. 3, could be explained by the precipitation of minerals from sulfide sulfur-rich solutions. Most of the deposits given in Fig. 3 except those studied in the present paper, are thought to have been formed under relatively reducing conditions. It is apparent that necessary are the accumulation of more isotopic data on individual deposits with estimation of oxidation state of the ore-forming solutions, and further examinations of the data from the viewpoint of exchange and kinetic fractionations among sulfur species in the ore-forming solutions.

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