

Sulfur isotope ratios of sulfide minerals from the deposit of the Tsuchikura mine, Shiga Prefecture, Japan

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Sulfur isotope ratios of sulfide minerals in the ore specimens from the deposit of the Tsuchikura mine are distributed in a range from -0.8 to $+5.4\%$, mostly from $+0.5$ to 3.0% , close to the previous data (from $+1$ to $+3\%$) by Miyake and Sasaki (1980). The distribution range is also similar to the major Besshi-type deposits of the Sambagawa terrain. Sulfur isotope fractionation between coexisting pyrite and chalcopyrite is not uniform. This may be largely due to spatial rearrangement of the initial orebodies to the present form. Sulfide minerals mostly pyrite from host rocks (siltstones, sandstones, basaltic rocks) exhibit remarkably low $\delta^{34}\text{S}$ values ranging from -49.3 to -2.6% , distinctly different from the $\delta^{34}\text{S}$ values for sulfide minerals of ores. The low $\delta^{34}\text{S}$ values may indicate the bacteriogenic origin of host rock sulfides, although it seems peculiar that basaltic rocks also have extremely low $\delta^{34}\text{S}$ values.

Keywords: Sulfur isotope ratio, Besshi-type deposit, Tsuchikura mine, Pyrite, Chalcopyrite

I. Introduction

There are now a large number of sulfur isotope data available for sulfide minerals of the Besshi-type deposits, as compiled by Sato and Kase (1996). The deposit of the Tsuchikura mine in the Tamba-Mino Belt is of Besshi-type, but different from the typical Besshi-type deposits in the Sambagawa Belt in that it occurs in a non-metamorphosed, chert-dominated sequence and is not tabular in form. We are now in the course of mineralogical and geochemical studies of the Tsuchikura deposit. The present paper is a part of the studies and reports sulfur isotope ratios of ores and host rocks, and also sulfur isotope fractionation between coexisting pyrite and chalcopyrite. Miyake and Sasaki (1980) determined sulfur isotope ratios of sulfide minerals from the Tsuchikura deposit and found that the variation range for 16 samples was very narrow, from $+1$ to $+3\%$. The present results will be comparatively discussed with their results.

II. Brief description of the deposit

The deposit of the Tsuchikura mine, located near Lake Biwa, occurs in an Early Jurassic non-metamorphosed accretionary complex that contains basaltic volcanic rocks, probably of Carboniferous age, and Carboniferous to Triassic chert (Sato and Kase, 1996). The Tsuchikura deposit consists of three deposits: the Eastern, Middle and Western deposits. Each deposit consists of a number of lenticular or fusiform orebodies (Hatanaka, 1965). The size of the orebodies is very variable, ranging from pebble to 20,000 tons (Nakamura and Asano, 1967).

Ores consist mainly of fine-grained pyrite, although in

some specimens the grain size reaches 0.2 mm. The grain is usually euhedral to subhedral in shape and often fractured. Fragmental pyrite ores are very common. Colloform pyrite is frequently observed. Chalcopyrite and sphalerite fill the interstices of pyrite grains. In the Eastern deposit that is Cu-rich compared to the Middle and Western deposits, some ores consist mainly of chalcopyrite with lesser amounts of pyrite. Bornite sometimes occurs in such Cu-rich ores.

III. Sample preparation

Pyrite and chalcopyrite powders were scraped from the ore specimens using a micro-grinder. They were mixed with vanadium pentoxide and silica and heated to prepare sulfur dioxide gas for mass spectrometry. The procedure was essentially the same as that of Yanagisawa and Sakai (1983), except that we used sulfide powders directly instead of barium sulfate. Host rocks that contain around 1 vol. % of sulfide minerals (mainly pyrite) were analyzed for their sulfur isotope ratios. Sulfur dioxide gases from the host rocks were prepared by heating mixtures of finely ground rock samples and vanadium pentoxide. Sulfur isotope ratios were determined at the Central Research Institute of Mitsubishi Material Co. Ltd.

The results are given in $\delta^{34}\text{S}$ value defined:

$$\delta^{34}\text{S} (\%) = (R_x - R_{\text{CDT}}) / R_{\text{CDT}} \times 1,000,$$

where R_x and R_{CDT} are $^{34}\text{S}/^{32}\text{S}$ ratios of a sample and the standard (Canyon Diablo Troilite), respectively.

Table 1. Sulfur isotope ratios of sulfide minerals from ores

Sample No.	Mineral	$\delta^{34}\text{S}$ (permil)	$\Delta^{34}\text{S}_{\text{py-cp}}^*$	Location	Abundance
1) From the Eastern deposit					
TS-283	py	+2.7		Upper 6th L	py>cp>sp
TS-296	py	- 0.8	- 1.7	Upper 5th L	cp>py>>sp
	cp	+0.9			
TS-114	cp	+1.9		Upper 4th L	cp>py
TS-109	py	+1.7		Upper 4th L	py>cp
TS-91	py	+3.6		Upper 3rd L	py>>cp
TS-117	py	+0.2	- 0.9	Upper 3rd L	py=cp>>sp
	cp	+1.1			
TS-263	py	+3.0	- 2.4	Upper 3rd L	py=cp>>sp
	cp	+5.4			
TS-246	cp	+1.1		Upper 3rd L	cp>sp
TS-232	py	+1.1	+0.2	Upper 2nd L	py>cp>>sp
	cp	+0.9			
TS-118	py	+2.1	+0.4	Upper 1st L	py=cp=sp
	cp	+1.7			
TS-1	py	+2.5		Adit L	py>>cp=sp
TS-52	py	+1.5	- 0.5	Adit L	py>cp>>sp
	cp	+2.0			
TS-60	py	+1.6	- 0.5	Lower 1st L	py>cp
	cp	+2.1			
TS-260	py	+2.0	+1.1	Lower 1st L	py>cp>>sp
	cp	+0.9			
TS-79	py	- 0.4	- 1.8	Lower 1st L	py=cp>>sp
	cp	+1.4			
TS-249	cp	+0.7		Lower 4th L	cp>sp
TS-251	cp	- 0.7		Lower 4th L	cp>>py=sp
TS-295	cp	+1.6		Lower 4th L	cp>>py=sp
2) From the Middle deposit					
TS-272	py	+1.5		Upper 3rd L	py>>sp>cp
TS-278	py	+1.6		Upper 2nd L	py=cp
TS-265	py	+2.8		Adit L	py>>cp>>sp
TS-266	py	+2.2		Adit L	py>>sp>cp
3) From the Western deposit					
TS-68	py	+2.5		Upper 8th L	py>>cp
TS-172	py	+0.8		Upper 2nd L	py>cp
TS-173	py	+2.7		Upper 2nd L	py>>cp
TS-174	py	+2.3		Upper 2nd L	py>>cp>sp
TS-178	cp	+1.3		Upper 1st L	py>cp
TS-185	py	+2.5		Upper 1st L	py>>cp>sp
TS-198	py	+2.1	+0.2	Upper 1st L	py=cp>>sp
	cp	+1.9			
TS-144	py	+2.3		Adit L	py
TS-14	py	+1.1	+0.4	Adit L	py>cp
	cp	+0.7			

Abbreviations are py: pyrite, cp: chalcopyrite, and sp: sphalerite.

$$*\Delta^{34}\text{S}_{\text{py-cp}} = \delta^{34}\text{S}_{\text{py}} - \delta^{34}\text{S}_{\text{cp}}$$

IV. Results and discussion

1. Sulfur isotope ratios of sulfide minerals from ore specimens

Sulfur isotope ratios of pyrite and chalcopyrite from ores are given in Table 1, and shown in Fig. 1, together with the previous results by Miyake and Sasaki (1980). The $\delta^{34}\text{S}$ values of pyrite and chalcopyrite from the Tsuchikura deposit in the present study range from -0.8 to $+5.4\text{‰}$, mostly in a range from $+0.5$ to $+3.0\text{‰}$, similar to the range (from $+1$ to $+3\text{‰}$) obtained by Miyake and Sasaki (1980). Sato and Kase (1996) classified the Besshi-type deposits in Japan into two groups according to the sulfur isotope distribution: Group A of deposits that have narrow ranges of sulfur isotope ratios (0 to $+5\text{‰}$) and Group B of deposits that have wide ranges of sulfur isotope ratios with averages of $+5$ to $+10\text{‰}$. The major deposits in the Sambagawa terrain were classified into Group A. Based on the data of Miyake and Sasaki (1980), the Tsuchikura deposit was also classified into Group A. The present results confirm their conclusion.

As shown in Fig. 1, the distribution range of the Eastern deposit seems to be somewhat wider than the Western and Middle deposits. However, considering the difference in number of determinations for the deposits, it is not apparent whether or not the difference in isotope distribution reflects the possible difference in genetic conditions.

No systematic sulfur isotope distribution can be found

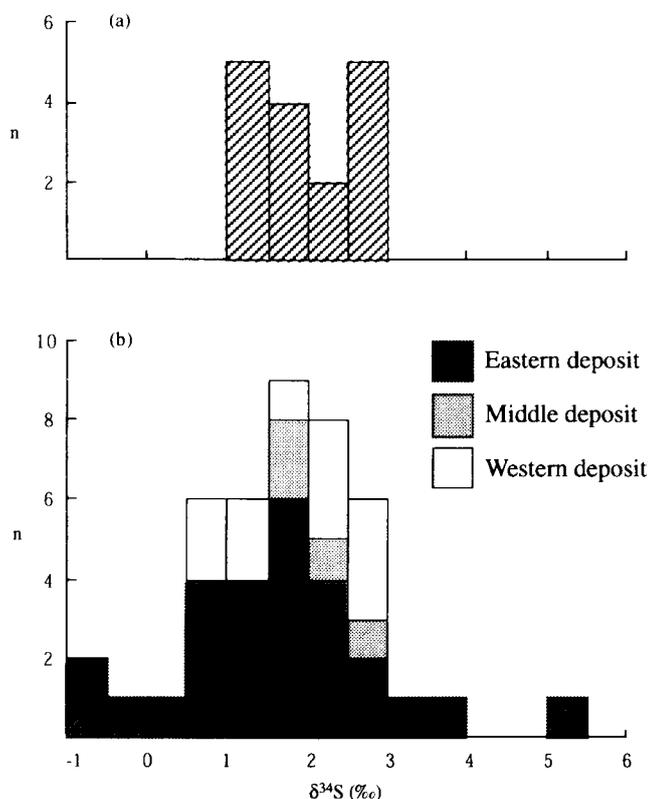


Fig. 1 Histograms showing the distribution of sulfur isotopes in the Tsuchikura deposit. (a) Miyake and Sasaki (1980), (b) present study.

with reference to the vertical and horizontal locations of the samples. Further, no apparent relationship between the $\delta^{34}\text{S}$ values and modes of occurrence of sulfide minerals can be recognized.

The distribution range in the Tsuchikura deposit is similar to the ranges of sulfide samples from the EPR at 21°N (from $+0.7$ to $+4.5\text{‰}$) (Hekinian *et al.*, 1980; Arnold and Sheppard, 1981; Zierenberg *et al.*, 1984) and the Juan de Fuca Ridge (from $+1.4$ to $+5.7\text{‰}$) (Shanks *et al.*, 1984; Shanks and Seyfried, 1987). This may indicate that also in the Tsuchikura deposit, seawater sulfate contributed to the sulfide minerals, although at the present state of knowledge the extent of the contribution can not be quantitatively estimated.

2. Sulfur isotope fractionation between pyrite and chalcopyrite

Sulfur isotope fractionation between pyrite and chalcopyrite was determined for 11 ore specimens. The fractionation is not uniform. Of 11 pairs, 5 pairs show the normal fractionation (that means the $\delta^{34}\text{S}$ value of pyrite is higher than that of chalcopyrite), whereas 6 pairs show the reverse fractionation (Table 1).

Yamamoto *et al.* (1983, 1984) observed the normal and uniform fractionation between pyrite and chalcopyrite in the Besshi deposit and the Hitachi deposit. They attributed the uniform fractionation to initial deposition of pyrite and chalcopyrite in or near isotope equilibrium rather than to isotope equilibration during metamorphism. On the contrary, in their sulfur isotope study of Besshi-type deposits of various metamorphic grades, Watanabe *et al.* (1997) found that sulfur isotope fractionation between pyrite and chalcopyrite is more uniform in highly metamorphosed deposits than in weakly metamorphosed deposits and concluded that uniform fractionation is produced by the isotopic re-equilibration or homogenization during metamorphism.

In the present case of the Tsuchikura deposit in non-metamorphosed rocks, the isotope disequilibrium between pyrite and chalcopyrite may be due either to original deposition in isotope disequilibrium, or to later modifications. The sulfide samples from the Galapagos Rift show the isotope equilibrium between pyrite and chalcopyrite (Skirrow and Coleman, 1982). The EPR 21°N sulfides also show close attainment of isotope equilibrium (Arnold and Sheppard, 1981). The original orebodies of the Tsuchikura deposit most probably has been considerably restructured to form the present deposit consisting of a number of lenticular orebodies. Therefore, taking into account the isotope data for the present submarine deposits above cited, we prefer the view that the disequilibrium between pyrite and chalcopyrite in the Tsuchikura deposit is not the initial one, but largely due to changes in spatial arrangement of ores during restructuring.

Table 2. Sulfur isotope ratios of host rocks

Sample No.	$\delta^{34}\text{S}$ (permil)	Location	Rock type	Content of sulfide (vol. %)
TS-158	-2.6	Western, upper 8th L	Siltstone	1%
TS-134	-49.3	Eastern, upper 3rd L	Siltstone	1%
TS-191	-6.4	Western, upper 1st L	Sandstone	1%
TS-258	-20.4	Western, upper 1st L	Sandstone	1%
TS-115	-3.0	Eastern, upper 1st L	Sandstone	1%
TS-313	-5.9	Eastern, adit L	Sandstone	2%
TS-103	-45.3	Eastern, lower 4th L	Basaltic rock	5%
TS-95	-25.3	Eastern, lower 4th L	Basaltic rock	1%

3. Sulfur isotope ratios of sulfide minerals from rock specimens

Sulfide minerals (mainly pyrite with subordinate chalcopyrite) dispersed in siltstones, sandstones and basaltic rocks distributed near the orebodies were analyzed for their sulfur isotope ratios and the results are given in Table 2. Cherts that contain significant amounts of sulfide minerals are regarded as low-grade ores and their data are included in Table 1. We attempted to analyze chert samples in which sulfide minerals are not easily visible in the naked eye, but after all analyzed no chert samples because selected specimens were all too low content of sulfide minerals to apply the present preparation method. The obtained $\delta^{34}\text{S}$ values are all negative and in a range from -49.3 to -2.6‰, and completely different from ore samples. In siltstones and sandstones pyrite grains are usually less than 10 μm in size, and often occur as framboidal aggregates (in TS-158, TS-134 and TS-258). Subhedral and anhedral pyrite grains of 50 to 100 μm in size may also occur in the same specimen. In basaltic rocks pyrite occurs as subhedral and anhedral grains with sizes of 20 to 600 μm . In TS-103, pyrrhotite also occurs. No distinct relationship can be found between the $\delta^{34}\text{S}$ values and the modes of occurrence.

Such low $\delta^{34}\text{S}$ values reaching -50‰ have often been observed in the sediments on the seafloors of various localities (Sakai and Matsuhisa, 1996) and may not be so surprising. The low $\delta^{34}\text{S}$ values found in the siltstones and sandstones may indicate the sulfides were derived from the bacterial reduction of sulfate. If the $\delta^{34}\text{S}$ value of sulfate is assumed to be about 20‰, the present minimum value means fractionation must be almost 70‰. Such a large fractionation may not have been attained by only one single step of bacterial reduction of sulfate, although Sakai and Matsuhisa (1996) suggested such a large fractionation is possible in a favorable condition. It is quite strange that sulfide minerals from basaltic rocks have also very low values, comparable to the $\delta^{34}\text{S}$ values of siltstones and sandstones. Ridge basalts usually have sulfur isotope ratios around 1‰ or so. The sulfides in the present samples may have been migrated from

the nearby sediments. More detailed discussion will be done in near future, when sulfur isotope data are obtained for rock specimens of low sulfur contents.

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References

- Arnold, M. and Sheppard, S. M. F. (1981), East Pacific Rise at latitude 21°N: isotopic composition and origin of the hydrothermal sulphur. *Earth Planet. Sci. Lett.*, **56**, 148-156.
- Hatanaka, T. (1965), Ore deposits and structural control of the Tsuchikura mine, Shiga Prefecture. *J. Geol. Soc. Japan*, **71**, 458-468 (in Japanese with English abstract).
- Hekinian, R., Fevrier, M., Bischoff, J. L., Picot, P. and Shanks, W. C. (1980), Sulfide deposits from the East Pacific Rise near 21°N. *Science*, **207**, 1433-1444.
- Miyake, T. and Sasaki, A. (1980), *Sulfur isotope study of metallic mineral deposits in Japan*. Sci. Rept. Minist. Educ. (in Japanese).
- Nakamura, T. and Asano, S. (1967), Stratigraphy and genesis of the deposit of the Tsuchikura mine. *Mining Geol.*, **16**, 51-52 (in Japanese).
- Sakai, H. and Matsuhisa, Y. (1996), *Stable Isotope Geochemistry*. Univ. of Tokyo Press (in Japanese).
- Sato, K. and Kase, K. (1996), Pre-accretionary mineralization of Japan. *The Island Arc*, **5**, 216-228.
- Shanks, W. C., III and Seyfried, W. E., Jr. (1987), Stable isotope studies of vent fluids and chimney minerals, southern Juan de Fuca Ridge: sodium metasomatism and seawater sulfate reduction. *J. Geophys. Res.*, **92**, 11,387-11,399.

- Shanks, W. C., III, Koski, R. A. and Woodruff, L. G. (1984), Mineralogy and stable isotope systematics of sulfide deposits from the Juan de Fuca Ridge. *EOS*, **65**, 1113.
- Skirrow, R. and Coleman, M. L. (1982), Origin of sulphur and geothermometry of hydrothermal sulphides from the Galapagos Rift, 86°W. *Nature*, **299**, 142-144.
- Watanabe, M., Osaki, T., Hoshino, K. and Kusakabe, M. (1997), Sulfur isotope fractionation between coexisting pyrite and chalcopyrite from variously metamorphosed Besshi-type deposits, Japan. *N. Jb. Miner. Mh.*, **1997**(2), 61-83.
- Yamamoto, M., Kase, K. and Ueda, A. (1983), Fractionation of sulfur isotopes and selenium between coexisting pyrite and chalcopyrite from the Hitachi deposits, Ibaraki Prefecture, Japan. *Geochem. J.*, **17**, 29-39.
- Yamamoto, M., Kase, K. and Tsutsumi, M. (1984), Fractionation of sulfur isotopes and selenium between coexisting sulfide minerals from the Besshi deposit, central Shikoku, Japan. *Mineral. Deposita*, **19**, 237-242.
- Yanagisawa, F. and Sakai, H. (1983), Thermal decomposition of barium sulfate-vanadium pentoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements. *Anal. Chem.*, **55**, 985-987.
- Zierenberg, R. A., Shanks, W. C., III and Bischoff, J. L. (1984), Massive sulfide deposits at 21°N, East Pacific Rise: chemical composition, stable isotopes, and phase equilibria. *Geol. Soc. Am. Bull.*, **95**, 922-929.