Bulletin of the Geoligical Survey of Japan, vol.51(7), p.283-297, 2000

Paired Sulfur Isotopic Belts: Late Cenozoic Ore Deposits of Southwest Japan

Shunso ISHIHARA[1], Akira SASAKI[1], Tetsuo MINAGAWA[2], Michiaki BUNNO[1], Akira SHISHIDO[3] and Ryoji TANAKA[4]

Shunso ISHIHARA, Akira SASAKI, Tetsuo MINAGAWA, Michiaki BUNNO, Akira SHISHIDO and Ryoji TANAKA (2000) Paired Sulfur Isotopic Belts: Late Cenozoic Ore Deposits of Southwest Japan. *Bull. Geol. Surv. Japan*, vol. 51 (7), p.283-p.297, 6 figs, 2 tables, 3 appendix-tables.

Abstract: Sulfides from late Cenozoic ore deposits of Southwest Japan were analyzed for $\delta^{34}S$ value on 68 samples from the Outer Zone and Setouchi volcanic province of the fore-arc region, and 26 samples from the Miocene Green Tuff region of the Hokuriku-Sanin Districts and Plio-Pleistocene volcanic province of Kyushu Island of the back-arc region. The results are summarized together with the published data, and the calculated average values for individual ore deposits are considered in a magmatic view point. Sulfur isotopic ratios vary regionally rather than sulfide species or type and commodities of the ore deposits. The $\delta^{34}S$ values are generally negative in the fore-arc region, and positive in the back-arc region. This regional variation is considered to reflect the ilmenite/magnetite pairing of the genetically related granitic or volcanic activities.

Among the fore-arc negative values observed in the ore deposits of the Outer Zone and in the southernmost zone of the Setouchi volcanic province, the ore deposits occurring closely with ilmenite-series granitoids, such as those in the Obira mining area, Takakumayama, and Yakushima, return the $\delta^{34}S$ values from -10 to -3 permil. The most depleted values of -15 to -11 permil are seen in copper and antimony deposits in the southernmost part of the Outer Zone. The famed euhedral stibnite crystal from the Ichinokawa mine has -8.5 permil. An exceptional value of +3.8 permil was discovered at Tano mine, and the sulfur is considered originated in the hidden magnetite-series body belonging to the Kyushu-Palao ridge intrusive activity.

Sulfur isotopic ratios of the back-arc region vary from +2 to +7 permil in the main Green Tuff region of the Hokuriku and Sanin Districts. But gold-silver and antimony deposits along the Plio-Pleistocene volcanic chain of Kyushu Island show a wide variation between −7 and +6 permil, indicating that these volcanic rocks have been variable in their redox state.

1. Introduction

Late Cenozoic magmatism occurs widely in the region to the west of the Fossa Magna in Japan, which is here defined as Cenozoic Southwest Japan. Ore deposits of magmatic-hypothermal and epithermal types are also widespread in the region (Fig. 1). These ore deposits show a paired asymmetrical zoning on the $\delta^{34}S$ values, negative in the fore-arc zone, but positive in the back-arc zone (Ishihara *et al.*, 1992). Genesis of the interesting feature has been discussed by Sasaki and Ishihara (1980), and Ishihara and Sasaki (1991). Additional studies in recent years strengthened the previous results and interpretation, but also revealed a new facet of the mineralization characters.

The main purpose of this paper is to describe the new $\delta^{34}S$ data of recent years, which are composed of 69 samples from the fore-arc zone including the Outer Zone of Southwest Japan and further north of the Ryoke Belt where the Setouchi volcanic rocks are distributed, and 26 samples from the back-arc zone including the Green Tuff belt of the Hokuriku-Sanin Districts and also Plio-Pleistocene gold-silver deposits along the volcanic front of the Kyushu Island. The reults are compared with the previous data and geneses of the regional variation are discussed under a magmatic concept.

The analyzed samples are single minerals hand

[1] Geological Survey of Japan, 1-1-3, Higashi, Tsukuba, 305-8567.
[2] Ehime University, 2-5 Bunkyo-cho, Matsuyama 790-8577.
[3] 35-11, Komatsudai-Kitamachi, Miyazaki 880-2113
[4] Solid Earth Sci. Res. Center, 827, Yamada, Misasa, Tottori, 682-0193.

Keywords: Southwest Japan, Late Cenozoic, ilmenite series, magnetite series, granitoids, antimony, mercury, gold, ore deposits, $\delta^{34}S$ value

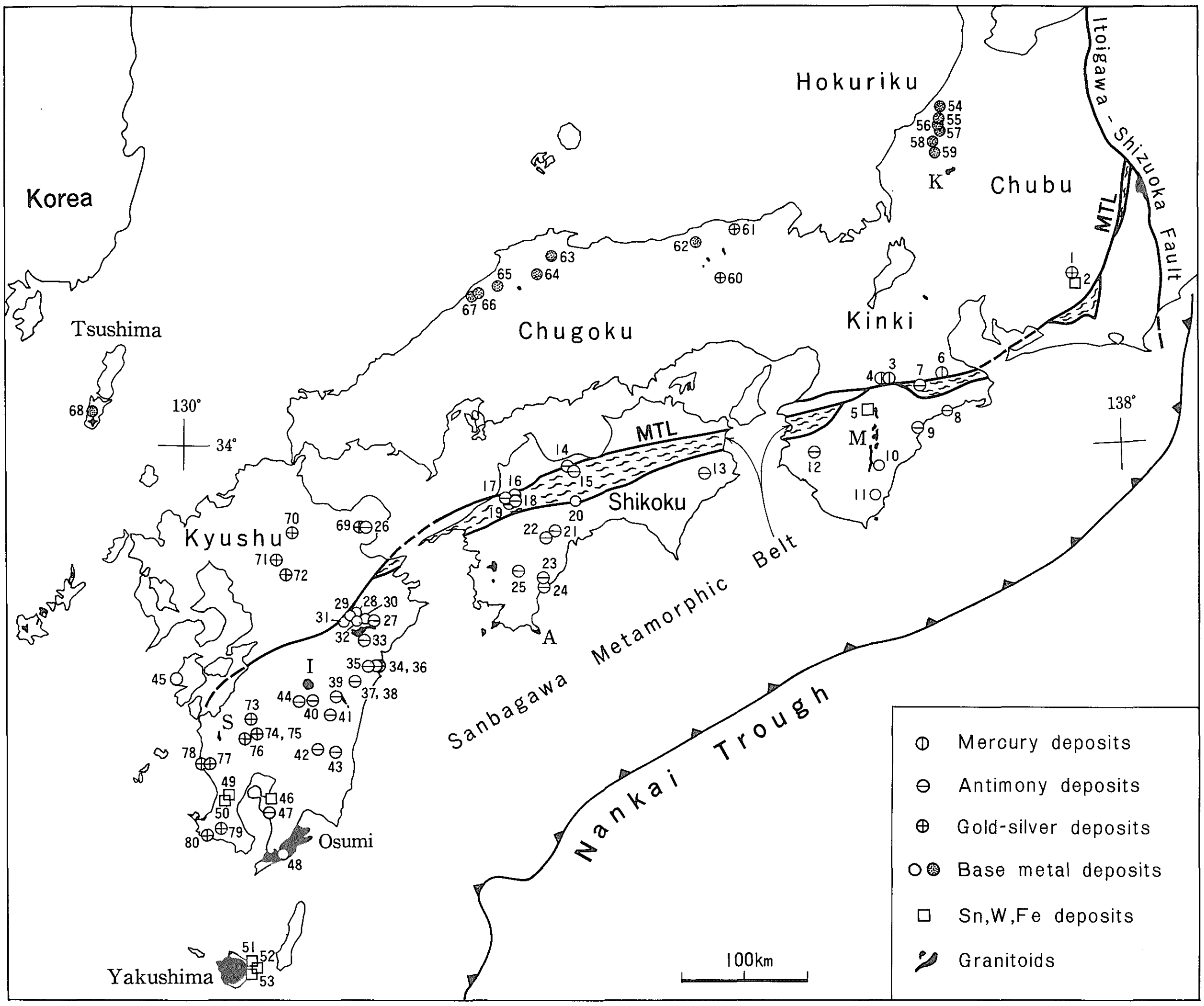


Fig. 1 Locality map of the studied ore deposits. The numbers correspond to those in Tables 1 and 2. Miocene plutonic bodies with A, Cape Ashizuri body; I, Ichifusayama body; K, Kadohara body; M, Omine-san complex; S, Shibisan body; MTL, Median Tectonic Line.

-picked or composites when the sulfides are very fine -grained. The results are usually representative for given ore deposits (e.g., Sasaki and Ishihara, 1980). Analytical methods are described elsewhere (Sasaki *et al.*, 1979; Sasaki and Ishihara, 1979). Analytical data are shown in conventional $\delta^{34}S_{CDT}$ notation. Analytical error is considered ± 0.2 permil (2σ). The analytical results are listed in Tables 1 and 2.

In the following chapters, the studied ore deposits and the analytical results are described from the fore -arc zone to back-arc zone, and northeast to southwest. The studied ore deposits are shown in Figure 1, together with exposures of the Miocene plutonic bodies.

2. Fore-arc Zone

This zone includes ilmenite-series granitic magmatism in the Outer Zone of Southwest Japan and also Setouchi volcanism of possibly ilmenite or intermediate series in the southernmost Inner Zone (Fig. 1). Both are Miocene in age. Major ore deposits of this zone are copper veins in the Kii Peninsula, large stibnite crystal-bearing antimony veins in Shikoku, and tin-polymetallic skarn and vein of the Obira mining area, northeastern Kyushu. However, antimony mineralization is characteristic as far as the number of ore deposits is concerned, and mercury mineralization is concentrated in the Ryoke metamorphic terrane of the Kinki District.

2.1 Chubu District

Miocene sedimentary and volcanic rocks occur in a depressed basin of E-W 20 km and N-S 30 km in the Ryoke metamorphic and grantic basement, which is called Shitara basin. Early rhyolitic and dacitic volcanism was followed by late intrusive and partly eruptive activities of basaltic and andesitic composition, forming Otaki couldron (Takada, 1987). Reconnaissance magnetic studies in field by KT-5 magnetic susceptibility meter indicate that both magnetite-series and ilmenite-series values exist on exposure of these volcanic rocks.

Tsugu Au-Sb deposits: Au-Sb-polymetallic quartz veins of Tsugu mine occur along N-S fractures in the basaltic dike (Fig. 2), associated with silicification and sericitization. These ores are composed of native Au, stibnite, jamsonite, cinnabar, galena, sphalerite, chalcopyrite, pyrite, marcasite, pyrrhotite, arsenopyrite and molybdenite, which show a fan-shaped metal zoning around the intrusive neck of the host basalt (Tatsumi, 1948, 1955).

In a reconnaissance study of the sulfide minerals, sphalerite was found to have high FeS contents (FeS 20.9-27.8 mol. %), which are characteristics of the Outer Zone mineralizations (Tsukimura *et al.*, 1987), and tetrahedrite and Pb-Sb-S mineral were discovered (Appendices I-III). Pyrite, sphalerite, galena and stibnite from this mine give $\delta^{34}S$ values from -5.5 to -7.9 permil (Table 1). An average of our studied results is -6.6 permil $\delta^{34}S$, which is close to -7.9 permil of composite samples given by Shimazaki (1985). These negative $\delta^{34}S$ values and existence of pyrrhotite and Fe-rich sphalerite indicate that the Tsugu mineralization is related to hidden subvolcanic rocks of ilmenite series of afelsic composition.

Awashiro sericite deposit: This mine is located 8 km due south of the Tsugu mine and geologically at the southwestern margin of Otoge cauldron in the same Miocene basin. The sericite alterations are related to the Otoge cone sheet and cross-cutting N-S dikes (Okamura, 1999). Several ore bodies occur in dacitic dike and nearby felsic tuff breccia. The K-Ar age of the sericite is 14.0 Ma (Miyashita and Misaki, 1995). Pyrite is often disseminated in the altered dike, but metallic sulfides such as arsenopyrite and stibnite, are

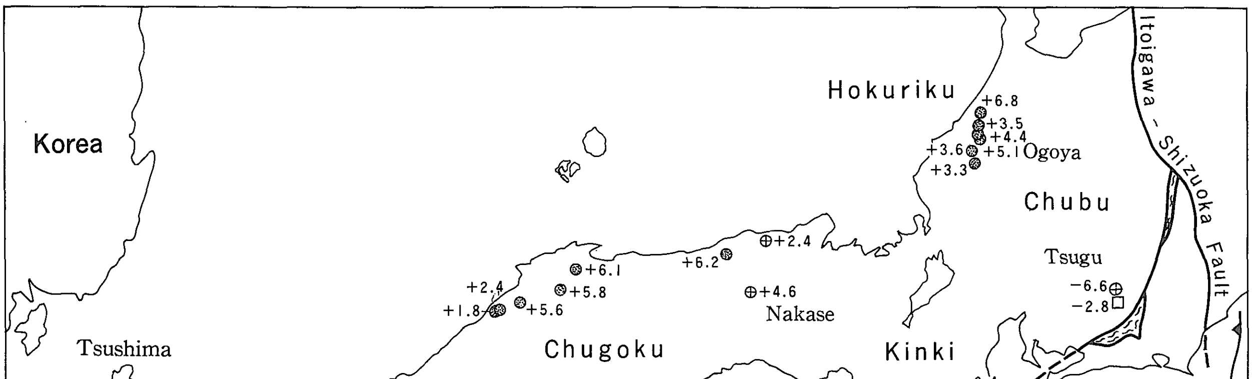
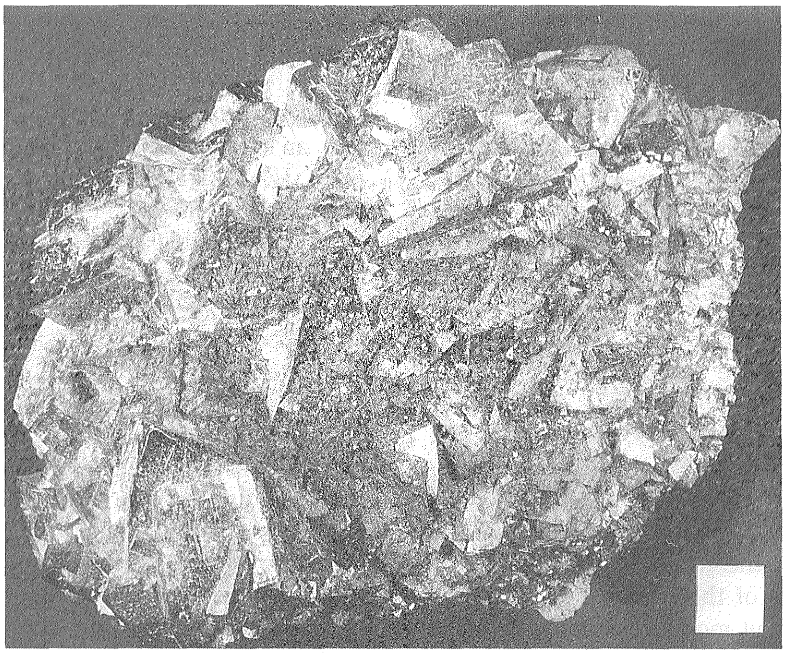


Fig. 2 Regional distribution of averaged $\delta^{34}S$ values of individual ore deposits of Southwest Japan. Open circle, ore deposits related to the Outer Zone granitoids and Setouchi volcanic rocks of Miocene age (ilmenite to intermediate series); solid circle, those related to Miocene-Pleistocene volcanic rocks (mostly magnetite series).

Table 1 $\delta^{34}S$ of Miocene ore deposits from the Outer Zone of Southwest Japan

No. Mine & locality	Metal produced	Ore deposit	Analyzed sample	$\delta^{34}S$ (‰)	Analyst & Reference
Aichii Prefecture					
1-1 Tsugu	Sb, Au	Au-Ag-bearing sulfides-quartz vein	Copmposite	-7.9	Shimazaki (1985)
1-2 ditto, GSJ13222	ditto	ditto	gn crystal	-7.9	A. Sasaki (this study)
1-3 ditto, GSJ10667	ditto	ditto	st	-7.4	ditto
1-4 ditto, RT9501	ditto	ditto (mine dump)	py	-5.5	Mitsubishi (this study)
1-5 ditto, RT9502	ditto	ditto (ditto)	ditto	-6.1	ditto
1-6 ditto, RT9503	ditto	ditto (ditto)	Fe-sp	-6.1	ditto
2-1 Awashiro (99010603)	Sericite	Pyrite-disseminated sericite orebody replacing Miocene volcanics; Idoiri adit, C Mining Section	Euhedral py	-3.3	CAGS (this study)
2-2 ditto (99010607)	ditto	ditto; Hyuga adit, -135 mL	ditto	-3.8	ditto
2-3 ditto (99010606)	ditto	ditto, pyrite concentrates of Wilfray Table	ditto	-1.4	ditto
2-4 ditto(99010611)	ditto	ditto, apy in druse of quartz vein	apy	-0.7	ditto
2-5 ditto (99010610)	ditto	ditto, stibnite in quartz nodule in sericite clay	st	+1.0	ditto
Nara Prefecture					
3 Kamio	Hg	Fracture-filling in Cretaceous granitoids	cn, py	-11.7	Shimazaki (1985)
4-1 Yamato-Suigin	Hg	Hg-clay vein in biotite granite	Composite	-4.6	ditto
4-2 ditto, GSJ12709	ditto	ditto	cn	-2.6	A. Sasaki (this study)
5 Goyomatsu	Fe	Magnetite skarn	Composite	-13.3	Shimazaki (1985)
Mie Prefecture					
6 Nyu, GSJ13002	Hg	Hg network vein in Cretaceous granitoids	cn	-8.4	A. Sasaki (this study)
7 Mori, TM9603	Sb	St-qz vein in pelitic shist of Sanbagawa Belt	st	-10.6	CAGS (this study)
8 Miejima, TM9602	Sb	St-qz vein in shale of Shimanto Supergroup	st	-11.8	ditto
9 Funatsu, TM9601	Sb	St-qz vein in shale of Shimanto Supergroup	st	-14.0	ditto
ditto	ditto	ditto	st	-14.2	A. Sasaki (this study)
10-1 Kishu	Cu	Cp-quartz veins in Miocene sediments	Composite	-14.2	Shimazaki (1985)
10-2 ditto, Flotation head	ditto	ditto	Composite	-13.5,-14.2	Sasaki & Ishihara (1980)
10-3 do. Josen-Honpi S (97093006A)	ditto	Cp-quartz drusy vein in chloritized sandstone	cp (py)	-15.4	A. Sasaki (this study)
10-4 ditto, ditto (97093006C)	ditto	Py disseminated in chloritized tuff	py	-15.9	ditto
10-5 ditto, Yutani (97093008)	ditto	Py filling fractures in chloritized sandstone	py	-14.2	ditto
Wakayama Prefecture					
11-1 Myoho, 3rd vein (97093001)	Cu	Py disseminated in Miocene sandstone, Eastern veins	py	-9.1	ditto
11-2 do. Enmanji, 29th vein (3003A)	ditto	Py in chloritized and silicified sediments	py	-13.3	ditto
11-3 do. Enmanji, 30th vein (3003C)	ditto	Py disseminated along fault in black shale	py	-12.6	ditto
11-4 do. 31st vein (97093004A)	ditto	Py in vuggy amethistic quartz vein	py	-13.1	ditto
11-5 ditto, 37th vein (97093005)	ditto	Cp-py disseminated in black siltstone	cp>>py	-8.9	ditto
12 Funahara (K. Yamamoto)	Sb	St-qz vein in siltstone of Shimanto Supergroup	st	-8.5	ditto
Tokushima Prefecture					
13 Aioi, GSJ10666	Sb	St-clay-quartz vein in Chichibu sediments	st	-3.0	ditto
Ehime Prefecture					
14-1 Ichinokawa	Sb	St-qz veins in Cretaceous sediments and Sanbagawa schist	st	-9.3	Shimazaki (1985)
14-2 ditto, GSJ-16655	ditto	ditto, beautiful euhedral crystal from GSJ Museum	st	-8.5	A. Sasaki (this study)
14-3 ditto, UMUT MII376	ditto	ditto, beautiful euhedral crystal from Univ. Tokyo Museum	st	-8.5	ditto
15 Besshi, TM9613	Sb	St-quartz vein cutting Bessi Kieslager orebody	st	-3.7	CAGS (this study)
16 Koboushi, TM9609	Sb	Sb-quartz vein in altered Ishizuchi volcanics	st	-8.5	ditto
17 Man-nen, TM9610	Sb	ditto	st	-9.6	ditto
18 Tomishige, TM9611	Sb	ditto	st	-8.4	ditto
19-1 Choshidaki, TM9612	Sb	St-quartz vein cutting Kieslager ore body of Sanbagawa Belt	st	-9.5	ditto
19-2 ditto, GSJ32981	ditto	ditto	st	-7.8	A. Sasaki (this study)
Kochi Prefecture					
20 Takaiwa	FeS	Po-(py-cp) lens body in Sanbagawa schist and Gp	po>py,cp	-9.6	Ishihara et al. (1988)
21 Kurakawa, TM9604	Sb	Br-quartz vein in sandstone/shale of Shimanto Supergroup	br	-4.8	CAGS (this study)
22 Kudarukawa, TM9605	Sb	ditto	br	-5.7	ditto
23 Kamioka, TM9606	Sb	St-quartz vein in sandstone/shale of Shimanto Supergroup	st	-12.0	ditto
24 Hiyoshi, TM9607	Sb	ditto	st	-15.1	ditto
25 Fujinokawa, TM9608	Sb	ditto	st	-9.1	ditto
Oita Prefecture					
26 Fuso, GSJ33028	Sb	St-clay vein in Cretaceous granitoids and Pliocene andesite	st	-5.2	A. Sasaki (this study)
27 Yanase, TM9720	Sb	St-quartz vein in Shimanto sediments and Gp	st	-7.4	CAGS (this study)
28 Hoei	Sn, Zn, FeS	Polymetallic skarn related to hidden biotite granite	Individual ores	-8.9	Sasaki & Ishihara (1980)
29 Obira	Sn, Cu, Ag	Polymetallic quartz vein in granitoids	Composite	-6.7	Shimazaki (1985)
30 Kiura	Sn, Pb, Zn, FeS	Polymetallic skarn	ditto	-6.2	ditto
Miyazaki Prefecture					
31 Mitate	Sn, Zn, Pb, Cu, FeS	Polymetallic skarn deposit	Composite	-7.8	ditto
32 Toroku	Sn, Pb, Zn, Ag, FeS	ditto	ditto	-7.8	ditto
33 Shimo-Shishigawa,TM9717	Sb	St-quartz vein in hornfels of Shimanto Supergroup	st	-8.4	CAGS (this study)
34 Yonesho-Hyuga AS9904	Sb	Massive st with quartz in Shimanto Supergroup	st	-0.4	A. Sasaki (this study)
35 Tomitaka, TM9614	Sb	St-br vein cutting Kieslager orebody of Shimanto Sg	st, br	-1.5	ditto
36 Kakusa, GSJ4643	Sb	St-clay vein in slate of Shimanto Supergroup	st	-1.8	ditto
37 Binsho, TM9615	Sb	St vein in sandstone/shale of Shimanto Supergroup	st	-6.3	ditto
38 Tsuboya, TM9716	Sb	St vein in Shimanto Supergroup	st	-3.6	ditto
39-1 Matsuo, GSJ13119	As, Au, Ag	Polymetallic vein in granite and Shimanto hornfels	st	-3.8	ditto
39-2 ditto, GSJ13119	ditto	ditto	st	-4.3	Mitsubishi (this study)
40 Murasho (97101701B)	Sb	St vein in altered granite porphyry dike	st	-1.3	A. Sasaki (this study)
41 Hibino, AS9903	Sb	St (less than 1 cm long)-qz vein in slates	st	+0.2	ditto
42-1 Shika, TM9719	Sb	St-po-qz vein in siltstone of Shimanto Supergroup	st	-4.0	CAGS (this study)
42-2 ditto, AS0001	Sb	ditto (mine dump)	st	-3.8	A. Sasaki(this study)
42-3 ditto, AS0002	Sb	ditto (ditto)	st	-3.5	ditto
43-1 Tano, TM9718	Sb	St-quartz vein in sandstone of Shimanto Supergroup	st	+3.5 +3.9	CAGS (this study) A.Sasaki(this study)
43-2 Tano, AS9901	Sb	St crystals filling silicified breccia in Shimanto sandstone	st	+3.9	ditto
43-3 Tano, AS9902	Sb	St crystal band in drusy quartz vein in Shimanto sandstone	st	+3.8	ditto
Kumamoto Prefecture					
44 Nagatani, GSJ4620	Sb	St-qz vein in slate of Shimanto Supergroup	st	-2.3	ditto
45 Takahama, GSJ12636	Sb	St-clay vein in Cretaceous sandstone	st	-1.0	ditto
Kagoshima Prefecture					
46 Tarumizu	Sn	Cs-cp-qz vein in biotite granite	Composite	-3.9	Sasaki & Ishihara
47 Shinshiro-west, GSJ13120	Sb	St-py-apy-qz vein in sandstone/shale of Shimanto Sg	st	-3.3	A. Sasaki (this study)
48 Manguro (58K107B)	Cu	Cp-po-C lens in biotite granite	po>cp	-6.2	Ishihara et al.(1988)
49-1 Suzuyama	Sn, Cu	Cs-cp-po-quartz vein in Shimanto sediments	Composite	-6.2	Shimazaki (1985)
49-2 ditto	ditto	Cassiterite concentrates from the mine office	po, py	-8.3	A. Sasaki (this study)
50 Kimposan (98050901)	FeS	Pyrrhotite-bearing sedimentay enclave	po	-6.0	CAGS (this study)
51-1 Hayasaki (97101301)	W	Py-quartz vein in sandstone/shale of Shimanto Sg	py	-5.9	ditto
51-2 ditto (97101302)	ditto	Py-quartz vein in silicified sandstone	py	-8.3	ditto
52 Yakushima-Juseki	W	Wf-tm-quartz vein in sandstone/shale of Shimanto Sg	py	-10.0	Sasaki & Ishihara (1980)
53 Nita (97101303)	ditto	Po-quartz vein in sandstone of Shimanto Sg	po	-4.4	A. Sasaki(this study)

Abbreviations : Apy, arsenopyrite; br, bercherite; bt, biotite; cn, cinnabar; cp, chalcopyrite; cs, cassiterite; gn, galena; po, pyrrhotite; py, pyrite; qz, quartz; ser, sericite; sp; sphalerite; st, stibnite; tm, tourmaline; wf, wolframite. Gp, granite porphyry; Sg, Supergroup.
CAGS, Chinese Academy of Geological Science; Mitsubishi: Central Lab., Mitsubishi Material Corp.



Photograph 1 Euhedral arsenopyrite occurring in drusy part of sericitized volcanic rocks at Awashiro mine (No. 2-4, -0.7 ‰ $\delta^{34}S$). Scale box is 1 cm.

found very rarely in drusy parts of the ore bodies.

Pyrite has $\delta^{34}S$ values of -3.8 to -1.4 permil, while euhedral crystals of arsenopyrite occurring on druse (Photograph 1) gives -0.7 permil and radiating crystals of stibnite in drusy quartz vein yield +1.0 permil (Table 1). An average of the disseminated pyrites may be representative for the ore deposits, which is −2.8 permil, nearly 4 permil higher than that of the Tsugu mine.

2.2 Kinki District

In the middle part of Kii Peninsula, there is one of the oldest mining districts in Japan, where people started to use cinnabar for vermillion ever since the beginning of 7th century. Yamato-Suigin mine is representative and the second largest mercury mine in Japan after Itomuka, Hokkaido. The production between 1928-1945 was 103 tons (Hori, 1953) and that of 1955-1966 was 261 tons (JMIA, 1968), but the historical record is unclear.

Both Yamato-Suigin (Yajima *et al.*, 1956) and Kamio (Kishimoto, 1962) deposits occur in Cretaceous biotite quartz diorite of the Ryoke Belt, which was locally intruded by Miocene dacite domes. Cinnabar occurs filling irregular fractures of generally E-W and N-S directions. Kaolinite, sericite, calcite, and less chlorite, quartz and pyrite are common alteration minerals. Ore minerals are mostly cinnabar, and locally pyrite, marcasite, stibnite and native mercury. Four stages of mineralization were recognized in the Yamato-Suigin deposit:
(1) pyrite-calcite-dolomite, (2) calcite-cinnabar, (3) quartz-cinnabar, (4) calcite-quartz-marcasite, and (5) native mercury.

Cinnabar and cinnabar-pyrite mixed samples give $\delta^{34}S$ values from -11.7 to -2.6 permil (Table 1).

In the southern part of Kii Peninsula, there occur two middle-class copper deposits: Kishu mine with the total production of 65,800 tons Cu and Myoho mine of 2,400 tons Cu (JMIA, 1968). These ore deposits are vein type occurring in Miocene sedimentary basin developed within the accretionary complex of Shimanto Supergroup, both of which have been intruded by Miocene granite porphyry and rhyolite. Number of the ore veins occur in wide areas: 21 major veins distributed in an E-W 3.3 km by N-S 5.3 km area at Kishu mine, and 9 major veins in an E-W 5.7 km by N-S 2.7 km area at Myoho mine .

The Kishu vein swarms were formed by the following 4 stages of mineralization (Ono, 1969):
(1) Cu-py stage: composed mainly of chalcopyrite and pyrite with dark green chlorite and quartz.
(2) Pb-Zn stage: galena and sphalerite, and minor chalcopyrite, pyrite and pyrrhotite, associated with calcite, quartz, fluorite and dark-pale green chlorite;
(3) Au-Ag stage: Native Au, argentite, pyrite, galena, sphalerite, chalcopyrite and pyrrhotite, associated with pale green chlorite, quartz, adularia, sericite (14.5 Ma, K-Ar age, Ono, 1984), calcite and fluorite.
(4) Calcite stage.

Nakamura (1998) reported the following negative $\delta^{34}S$ values for the three stages of mineralization: the first stage; -14.9 to -13.6 permil, the second stage; -14.6 to -14.1 permil, and the third stage; -14.2 to -13.8 permil, i. e., no differences were observed among the different stages. Our results on chalcopyrite and pyrite range from -15.9 to -13.5 permil and an average of those listed in Table 1 is -14.6 permil.

The Myoho veins are similar to the Kishu veins, containing mainly chalcopyrite and pyrite, and locally bornite, chalcocite, sphalerite and galena, but no pyrrhotite present. The veins were formed in three stages: (1) Chalcopyrite-bearing pyrite-calcite -quartz-chlorite, (2) Chalcopyrite-pyrite-calcite -quartz-chlorite, and (3) Chalcocite-bornite-chalcopyrite-pyrite (Yora, 1967).

Pyrite and chalcopyrite from this mine are slightly ^{34}S enriched, relative to the $\delta^{34}S$ values of the Kishu mine, ranging from -8.5 to -13.3 permil $\delta^{34}S$, and an average is -11.4 permil.

Many antimony deposits of various sizes are distributed from the Kinki to Kyushu Districts. They are fracture or breccia-filling stibnite (rarely berthierite) -quartz veins. Here in the Kinki District, some are hosted in pelitic schists of the Sanbagawa metamorphic belt (e.g., Mori), but most occur in turbidites of the Shimanto Supergroup (e.g., Miejima, Funatsu and Funahara). Their $\delta^{34}S$ values are low, -14.0 to -8.5 permil, in the Kinki District.

2.3 Shikoku District

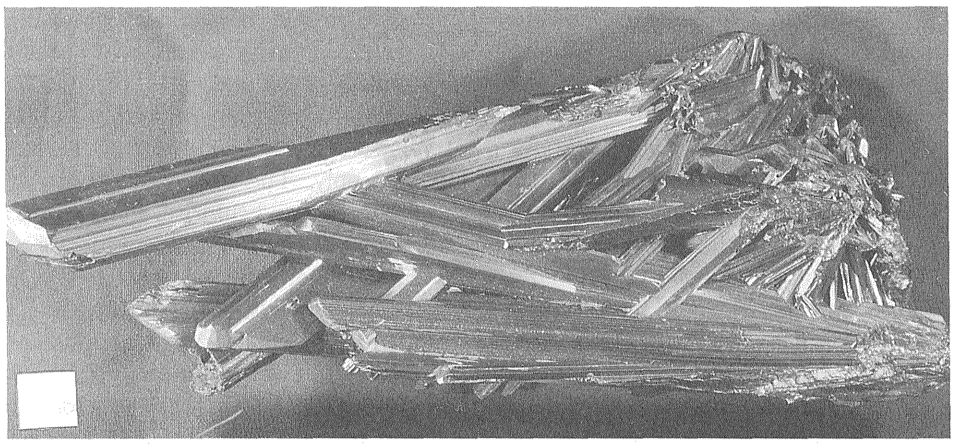
In the Shikoku District, the most famous epigenetic ore deposit is stibnite-quartz veins at Ichinokawa where large euhedral crystals were once mined and now are decorating many museums of the world. The beautiful crystals were obtained from flat veins during an early stage of the mine history, the early Meiji Era (Iwasaki, 1898). The production of this mine was highest in 1882-1897 (Tatsumi, 1955), and the total production is 19,053 tons Sb metal (JMIA, 1968).

The veins at Ichinokawa are located at just south of the Median Tectonic Line and hosted in fractures developed in pelitic and psammitic rocks of the Sanbagawa metamorphic belt and partly Ichinokawa conglomerates of unknown age developed very locally in the metamorphic rocks. The conglomerates were so named but large blocks, a few meters in diameter, and angular fragments of the Sanbagawa metemorphic rocks (Photographs 2A, B) are filled with little amount of clastic materials. Iwasaki (1898) noted that the conglomerates occur in irregularly shaped zones and cavities in the matrix are sometimes filled with euhedral quartz and stibnite crystals. Thus this rock unit could be not conglomerate but tectonic or vent breccia, whose genesis may be connected with development of large druses in the Yoko-hi that hosted euhedral stibnite crystals (Photograph 3).

The veins are hosted mostly in pelitic metamoprhic

Photograph 2A Ichinokawa conglomerates exposed in front of the Sin-ni Adit. Note large block (left) and angular fragments of the Sanbagawa metamorphic rocks. Limonite after decomposition of iron sulfides stained some parts of the matrix.

Photograph 2B Close-up of the fragments of pelitic and psammitic origin. Matrix is filled with powders of the same materials. Diameter of the coin is 23 mm.



Photograph 3 Beautiful euhedral crystals of stibnite from the Yoko-hi of the Ichinokawa mine (No. 14 - 3, -8.5 ‰ $\delta^{34}S$). Scale box is 1 cm.

rocks and partly in the conglomerates, and are composed of "Yoko-hi" (flat vein) and Tate-hi (vertical vein). The flat veins follow thrust faults having strike of E-W or N40°E and dips down to 20°, and the vertical veins strike E-W or N60°E and dip 70-90° N or rarely S and cut the flat veins. The veins are solely composed of stibnite and quartz, but may contain small amount of calcite and jamesonite (Tatsumi, 1955). Pyrite and arsenopyrite may disseminate in the vein envelop.

Similar stibnite-quartz veins occur in various host rocks in Ehime Prefecture. They cut through Besshi

-type massive sulfide orebodies at Besshi and Choshidaki. They also occur in Miocene volcanic rocks of the Ishizuchi cauldron. All of these stibnites, except for the one from Besshi, have a narrow range of the $\delta^{34}S$ values from -9.6 to -7.8 permil, suggesting common source of sulfur. The value of -3.7 permil for the Besshi sample may indicate contamination with the relatively heavy sulfur (+1 to +4 permil) of the Besshi massive sulfide ores (Sato and Kase, 1996).

In Kochi Prefecture, pyrrhotite lens orebody occurs in the Sanbagawa schists intruded by granite porphyry at Takaiwa (Sawamura *et al.*, 1964), which may be subvolcanic facies of the Outer Zone granitoids. The pyrrhotite gives -9.6 permil (Table 1).

Other metallic ore deposits are stibnite or berthierite quartz veins hosted in turbidites of the Shimanto Supergroup. The berthierite had -5.7 to -4.8 permil, while the stibnite yielded -15.1 to -9.1 permil.

2.4 Kyushu District

In the east-central Kyushu District, many important tin-polymetallic skarn and vein deposits (e.g., Hoei, Kiura, Mitate, Toroku skarns, Obira vein) are known to occur around small ilmenite-series granitic stocks related to the Sobo-Katamuki cauldrons and the Okueyama pluton, which has rock sulfur isotopes of -4.8 and -4.2 permil (Sasaki and Ishihara, 1979; Ishihara *et al.*, 1988). Ores from these ore deposits have consistent values between -8.9 and -6.2 permil.

To the south, there occur many small tin and antimony deposits related to the Osuzuyama cauldron and associated dikes (nos. 34 - 41, Table 1). Stibnite at Murasho is hosted in fractures of ilmenite-series granite porphyry, and Matsuo arsenic deposits occur in and around the top of fine-grained biotite granite (JMIA, 1968), but all the others are present in the intruded sedimentary rocks. Stibnite at Matsuo Mine occurs in the veins marginal to the main Au-Ag -bearing arsenopyrite veins (Miyahisa and Hashimoto, 1958). They have $\delta^{34}S$ values between -6.3 and +0.2 permil, heavier than the ores from the Okueyama area. Stibnites at Tano are exceptionally heavy as +3.5 to +3.9 permil, which will be discussed in the fourth chapter.

In Kagoshima Prefecture, copper-bearing cassiterite quartz veins at Tarumizu (-3.9 ‰) are hosted in ilmenite-series biotite granite (Ishihara and Kawachi, 1961). Stibnite-bearing quartz vein at Shinshiro (-3.3 ‰) occurs in the roof pendent of the Takakuma -yama pluton. Thus both are genetically related to the Takakuma-yama granite, which has -3.1 permil $\delta^{34}S$ of the rock sulfur (Ishihara *et al.*, 1988).

Pyrrhotite at Manguro of the ilmenite-series Osumi pluton is taken from enclaves of mostly sedimentary and partly igneous origins (Ishihara, 1982). The $\delta^{34}S$ value (-6.2 ‰) is slightly heavier than those of the host granitoids (-8.3 to -7.0 ‰, Ishihara *et al.*, 1999). Pyrrhotite of Kimposan stock (-6.0 ‰) is also taken from enclaves.

In Yakushima, several small wolframite-quartz veins are associated with fine-grained biotite granites (Hayashi and Maruyama, 1961) around the margin of porphyritic biotite granitic pluton, which has rock $\delta^{34}S$ value of 9.1 permil (Ishihara *et al.*, 1988). Sulfides from the tungsten deposits show an average $\delta^{34}S$ value of -7.1 permil at Hayasaki, and -4.4 permil at Nita.

3. Back-Arc Zone

In the back-arc basin of Southwest Japan, sedimentation and succeeding volcanism occurred in late Cenozoic time. Coeval plutonic rocks are seen only as small stocks (e.g., Kadohara body, Ishihara *et al.*, 1988). These igneous activities are generally of magnetite series and accompanied by vein, skarn and Kuroko-type ore deposits along the Japan Sea coast.

3.1 Hokuriku District

In the Hokuriku District of the northwestern Chubu District (Fig. 1), vein-type deposits are seen in Miocene sedimentary and volcanic rocks at Yusenji, Kanehira, Sawa and Ogoya, among which the Ogoya veins are the largest, with the following records of base metal and sulfur production (JMIA, 1968): Cu 65,853 tons (1932-1966), Zn 20,802 tons (1956-1966), Pb 3,750 tons (1956-1966), S of pyrite 92,773 tons (1956-1966).

At Ogoya, many veins occur in lower Miocene formation composed of tuff breccia and intercalated fine tuffs and musdtones, which are extruded and intruded by lavas and dikes of andesites and rhyolites. Rhyolitic dike and plug are considered genetically related to the mineralizations (JMIA, 1968). The veins strike N-S to N75°W, but sometimes ENE, and dip steeply. The wall rock alteration is characterized with quartz and chlorite, but sericite and some calcite are also present. The ore minerals are mainly pyrite, chalcopyrite, bornite and sphalerite, and small amounts of galena, chalcocite and magnetite. Barite and hematite (Shimada, 1949) occur locally indicating high oxygen fugacity of the ore fluids.

There occur also skarn-type deposits, such as Bandojima and Kutani, replacing crystalline limestones of the Hida metamorphic complex in the Hokuriku District. Miocene intrusive rocks, which have been partly altered and mineralized, are seen in the vicinity. Thus, these skarn deposits are considered genetically related to the Miocene intrusive activities.

All the vein-type deposits have $\delta^{34}S$ values from +1.5 to +7.3 permil, and the skarn type deposits have also similar values between +2.8 and +4.1 permil (Table 2).

Table 2 $\delta^{34}S$ of metallic ores from the Inner Zone of Southwest Japan

No. Mine & locality	Metal produced	Ore deposit	Analyzed sample	$\delta^{34}S$ (‰)	Analyst & Reference
Ishikawa Prefecture					
54-1 Yusenji (98100107)	Cu	Sp-gn disseminted in Miocene altered andesite	sp, gn	+6.2	CAGS (this study)
54-2 ditto (98100108)	ditto	Py disseminated in silicified felsic tuff	py	+7.3	ditto
55-1 Kanehira (98100104)	Cu	Cp-py-quartz vein in Miocene felsic tuff and rhyolite	py>>cp	+4.5	ditto
55-2 ditto (98100105)	ditt	Galena crystal in silicified felsic tuff	gn	+1.5	ditto
55-3 ditto (98100106)	ditto	Pyrite disseminated in silicified felsic tuff	py	+4.5	ditto
56-1 Sawa (98100113)	Zn, Cu	Pyrite disseminated in Miocene altered felsic tuff	py	+4.2	ditto
56-2 ditto (98100114)	ditto	Galena-pyrite disseminated in argillized tuff	py>gn	+4.5	ditto
57-1 Ogoya	Cu, Zn, Pb, FeS	Base metal vein in Miocene felsic tuff.	Composite	+4.9	A. Sasaki (this study)
57-2 ditto (98100109)	ditto	ditto	Pure cp	+3.9	CAGS (this study)
57-3 ditto (98100110)	ditto	Euhedral pyrite disseminated in altered felsic tuff	py	+6.7	ditto
57-4 NSB6	ditto	Base metal vein in Miocene felsic tuffs	Sp, py, cp, gn	+4.9	Shikazono (1987)
58 Kutani	Zn, Pb	Base metal skarn in Hida metamorphic rocks	Composite	+3.6	Shimazaki (1985)
Fukui Prefecture					
59-1 Bandojima	Pb, Zn, Cu	Base metal skarn in Hida metamorphic rocks	Composite	+4.1	Shimazaki (1985)
59-2 ditto (98093001)	ditto	Gn-sp disseminated in Miocene (?) altered andesite	gn>sp	+2.9	CAGS (this study)
59-3 ditto (98093002)	ditto	Galena-calcite rock	gn>>sp	+3.5	ditto
59-4 ditto (98093003)	ditto	Gn>>sp disseminated in carbonate rock	gn	+2.8	ditto
Hyogo Prefecture					
60-1 Nakase, GSJ10545	Au, Sb	St-sp-py-apy-qz vein in metamorphic rocks	st	+2.4	A. Sasaki (this study)
60-2 Nakase, M2 stage	Au, Sb	ditto	sp	+4.3	Miyoshi et al.(1988)
60-2 ditto, ditto	ditto	ditto	py	+4.9	ditto
61 Takeno	Au, Ag	Au-Ag-qz vein in Miocene valcanic and sediments	Cp, sp, gn	+2.4	Shikazono (1987)
Tottori Prefecture					
62 Iwami	Cu	Cp-quartz network in Miocene sediments and volcanics	Euhedral py	+6.2	Mitsubishi (this study)
Shimane Prefecture					
63 Homanzan GSJ4282	Cu	Cp-quartz vein in Miocene felsic volcanics	py	+6.1	A. Sasaki (this study)
64-1 Higashiyama (65HY773)	None	Pyrite disseminated in Miocene andesite sheet	py	+6.0	Mitsubishi (this study)
64-2 ditto (65HY755)	ditto	Pyrite-clay in Miocene andesite sheet	py	+5.5	ditto
65-1 Eiki	Cu, Zn	Cp-sp-(gn)-quartz vein in Miocene rhyolite	cp>>py	+5.8	A. Sasaki (this study)
65-2 ditto	ditto	ditto	Pure sp	+5.4	ditto
66 Yoshinaga	Cu	Cp-quartz vein in rhyolite and andesite	cp>py	−2.4	ditto
67 Omori	Ag, Cu, Zn, Pb, Ag	Base metal veins in Miocene volcanics and sediment.	Cp, py	+1.8	Shikazono (1987)
Nagasaki Prefecture					
68-1 Taishu	Pb, Zn, Ag, FeS, Cu	Base metal vein in Tertiary sediments	Avg po (n=13)	+3.8	Kiyosu (1977)
68-2 ditto	ditto	ditto	Avg. gn (n=22)	+3.6	ditto
68-3 ditto	ditto	ditto	Avg. sp (n=30)	+5.1	ditto
68-4 ditto (98051104)	ditto	ditto	Sp concentrates	+5.0	CAGS (this study)
68-5 ditto (98051106)	ditto	ditto	Gn concentrates	+3.1	ditto
Oita Prefecture					
69 Bajo	Au	Au-quartz vein in Cretaceous granitoid and Pliocene andesite	py	−3.6	ditto
70 Asahi	Au	Au-quartz vein in Pliocene andesite	py, cp, sp, gn, pyr, pol, pr	+1.0	Shikazono (1987)
71 Hoshino	Au	Au-quartz vein in Pliocene andesite	py, mc, arg, st	−7.4	ditto
72 Taio	Au	Au-Ag-quartz vein in Pliocene andesite volcanics	sp, arg, cp	+0.2	ditto
Kagoshima Prefecture					
73 Okuchi	Au	Au-quartz vein in Pliocene andesites	py, sp, st	+3.4	Shikazono (1987)
74 Hishikari	Au	Au-quartz vein in Shimanto sediments	py	+0.3	Ishihara et al. (1986)
75 Yamada	Au		py, sp, cp. gn	+5.0	Shikazono (1987)
76 Yamagano	Au	Au-quartz vein in Pliocene altered andesites	Py	+5.6	ditto
77 Kushikino	Au	Au-quartz vein in Pliocene altered andesite	Num, arg, py, cp, sp	+1.6	ditto
78 Arakawa	Au	ditto	Py, num	−0.5	ditto
79 Akeshi	Au	High-sulfidation-type Au disseminated body	Native S	−2	ditto
80 Kasuga	Au	ditto	Enargite	−0.8	ditto

Abbreviations: Those other than listed in Table 1: Arg-argentite, el-electrum, mc-marcasite, num-naumannite, pol-polybasite, pyr-pyrargyrite.

3.2 Kinki District

At Nakase mine of the northwestern Kinki District, there occur an interesting Au-Ag-Sb vein-type deposit, which are hosted in the Sangun metamorphic rocks and the associated serpentinite and volcanic vent breccia filled with Miocene andesites. The ore deposits have not been dated, but are considered to have a Miocene age. More than twelve veins, mostly E-W striking with steep dips to north, have average ore grades up to 50 g/t Au (*e.g.*, Manju Vein), 365 g/t Ag (*e.g.*, Ishimabu Vein) and 9.5 % Sb (*e.g.*, Kita 2nd Vein, JMIA, 1968). Major ore minerals are pyrite, arsenopyrite, sphalerite, chalcopyrite, berthierite, Ag-tetrahedrite, jamesonite, native Au, stibnite and cinnabar (JMIA, 1968). The sulfides give an average $\delta^{34}S$ value of +4.6 permil.

3.3 Sanin District

In the eastern Sanin District, pyrite of copper veins of the Iwami and Homanzan mines give $\delta^{34}S$ values around +6.0 permil, which is very similar to pyrite (+5.8 ‰) disseminated in propylitized andesite sheets at Higashiyama Mo mine (Ishihara, 1971) and sulfides (+5.6 ‰) at the Eiki base metal veins. But base metal sulfides at Yoshinaga and Omori are slightly depleted in ^{34}S (+1.8 to +2.4 ‰). Barite occurs commonly in the upper part of Omori deposits (Kuhara, 1926; JMIA, 1968).

3.4 Kyushu District

Gold-silver deposits are dominant particularly in Kyushu Island. They are either of vein or disseminated types, and occur along the Quaternary-Pliocene volcanic fronts. The gold-silver veins in northern Kyushu vary from -7.4 to +1.0 permil in their $\delta^{34}S$ values, indicating existence of ilmenite-series volcanic rocks in this district, but those of the Hokusatsu district (northern Kagoshima Pref.) show mostly positive values ranging from -0.5 to +5.6 permil, suggesting their genetic link with magnetite-series volcanism.

Hishikari ores have an average of +0.5 permil (Ishihara *et al.*, 1986), which is much lower than +5.0 permil of nearby Yamada ore deposit. A detailed study is necessary on these ore deposits. The Nansatsu-type disseminated gold deposits give their $\delta^{34}S$ values of -2.0 and -0.8 permil (Table 2).

In Tsushima Island of northwestern Kyushu District, where Miocene magnetite-series granitoids have been partly reduced by sedimentary carbon from the wall rocks, lead-zinc-pyrrhotite veins occur in the roof sedimentary rocks. The sulfides gave $\delta^{34}S$ values between +3.1 and +5.1 permil (see Ishihara and Imai, 2000 for further details).

4. Paired Sulfur Isotopic Belts

Figure 2 illustrates the regional distribution of averaged $\delta^{34}S$ values for individual ore deposits examined here. It is clear that the $\delta^{34}S$ values are low in the fore-arc side but high in the back-arc side, especially from the Chubu District to the Chugoku-Shikoku Districts. This pairing was explained by that of rock sulfur isotopic ratios of ilmenite/magnetite-series granitoids (Sasaki and Ishihara, 1979). This interpretation is valid as far as the genetically related granitoids are exposed or positively expected in given areas.

Ilmenite-series granitoids do not crop out beyond the Median Tectonic Line, but gold-silver, antimony and mercury ore deposits occur in the southernmost part of the Inner Zone, just north of the Median Tectonic Line, in the Chubu-Kinki Districts. One candidate for the igneous activity genetically related to the mineralizations is Miocene volcanic rocks of the Setouchi Province including the Shitara Basin. These volcanic rocks were extruded on non-magnetic ilmenite-series Ryoke granitic and metamorphic rocks; thus their magnetic characters may easily be seen on aeromagnetic maps.

The IGRF (International Geomagnetic Reference Field) residual magnetic maps of NEDO (1985) indicate that only weak magnetic anomalies recognized on Miocene volcanic rocks of Shodoshima Island and Ritsurin Park of Takamatsu city, Kagawa Prefecture, and Kashiwabara City area of Kinki District, very weak ones on those of Goshikidai and Teshima, but no anomalies on those of Yashima-Aji area, which may be due to very small amounts of volcanic rocks existed. Reconnaissance study of magnetic susceptibility on volcanic rocks of Kagawa Prefecture indicates that these rocks are low to intermediate in magnetic susceptibility, especially on those assimilating crustal materials (Ishihara, 1979). Thus, sulfide ores having negative $\delta^{34}S$ values in the fore-arc zone are all considered originated in ilmenite-series and partly intermediate-series igneous activities.

Within the Outer Zone of Southwest Japan, exceptional positive $\delta^{34}S$ values were observed at the Tano ore deposit, southwest of Miyazaki City (Fig. 3). The original analysis was cross-checked by different analyst and the analyzed samples were duplicated. Then, positive $\delta^{34}S$ values between +3.5 and +3.9 permil were confirmed. Stibnite from nearby Shika ore deposit was also carefully examined, but this ore deposit gives negative values between -4.0 and -3.5 permil. Thus, two sources of the ore fluids are expected in this area.

The negative values are derived from ilmenite-series subvolcanic activity, but the positive values at Tano could be related to the possible hidden, magnetite-series intrusive rock, which indicated in an aeromagnetic map of Watanabe *et al.* (1977). The Tano ore deposit is located at just south of a magnetic anomaly (Fig. 3), which was interpreted to have the following dimensions and intensities: 20-25 km in length, 10-15 km in width, 4.5-6.0 km in depth, magnetic susceptibility, $k=1{,}000\times10^{-6}$ emu/cc, and density, $\rho=3.0\text{-}3.1$ (Watanabe and Hattori, 1980).

For these data and also a northeasterly elongation of the magnetic anomaly, they assume the presence of some mafic igneous body hidden in the basement. For the sulfur isotopic data, we prefer to assume a young magnetite-series granitic body intruding into the basement rocks, which may be correlated to the magnetite-series granitoids exposed along the Kyushu-Palao Ridge in the Philippine Plate. The ore fluids responsible for the Tano deposit may have derived from this hidden magnetite-series pluton.

Mixed occurrence of negative and positive values on gold-silver vein deposits in Kyushu Island can be interpreted in the same manner. Gold-silver veins with positive $\delta^{34}S$ values in the Hokusatsu area including Okuchi (+3.4 ‰), Hishikari (+0.3 ‰), Yamada (+5.0 ‰) and Yamagano (+5.6 ‰) are genetically related to Pleistocene magnetite-series volcanic rocks, which are shown by their magnetic susceptibility trends (Ishihara *et al.*, 1990) and also by aeromagnetic maps (NEDO, 1985). Pliocene gold-quartz veins at Kushikino and Arakawa may have had similar geologic background. In northern Kyushu, however, $\delta^{34}S$ values vary widely from -7.4 at Hoshino to +1.0 permil at Asahi. Some antimony deposits (*e.g.*, Nagahama) occur unrelated to the Plio-Pleistocene volcanic rocks along the volcanic front. Thus, a wide variation in terms of redox state is expected for the volcanic rocks of this district, because of local crustal contamination happened sporadically in the small-scale volcanisms of the whole region since Miocene time.

Within the Outer Zone, the $\delta^{34}S$ values vary areally. Base metal deposits of the Kinki District show -11 to -15 permil, but those of east-central Kyushu District range between -6 and -9 permil. Antimony deposits are most widely distributed in the Outer Zone. They have $\delta^{34}S$ values between -9 and -14 permil in the Kinki District. In the Shikoku District, they are generally around -9 permil near the Median Tectonic Line, but have two groups of the values of -3 and -6 permil, and -9 and -15 permil in the southern part hosted in the Shimanto Supergroup. In the Kyushu District, they vary generally from 0 to -8 permil. Throughout all the commodities, NW-SE variations on the ore $\delta^{34}S$ values across the Outer Zone are not as clear as those of rock sulfur $\delta^{34}S$ values (Sasaki and Ishihara, 1979; Ishihara *et al.*, 1988) and $\delta^{18}O$ values of the Outer Zone granitoids (Ishihara and

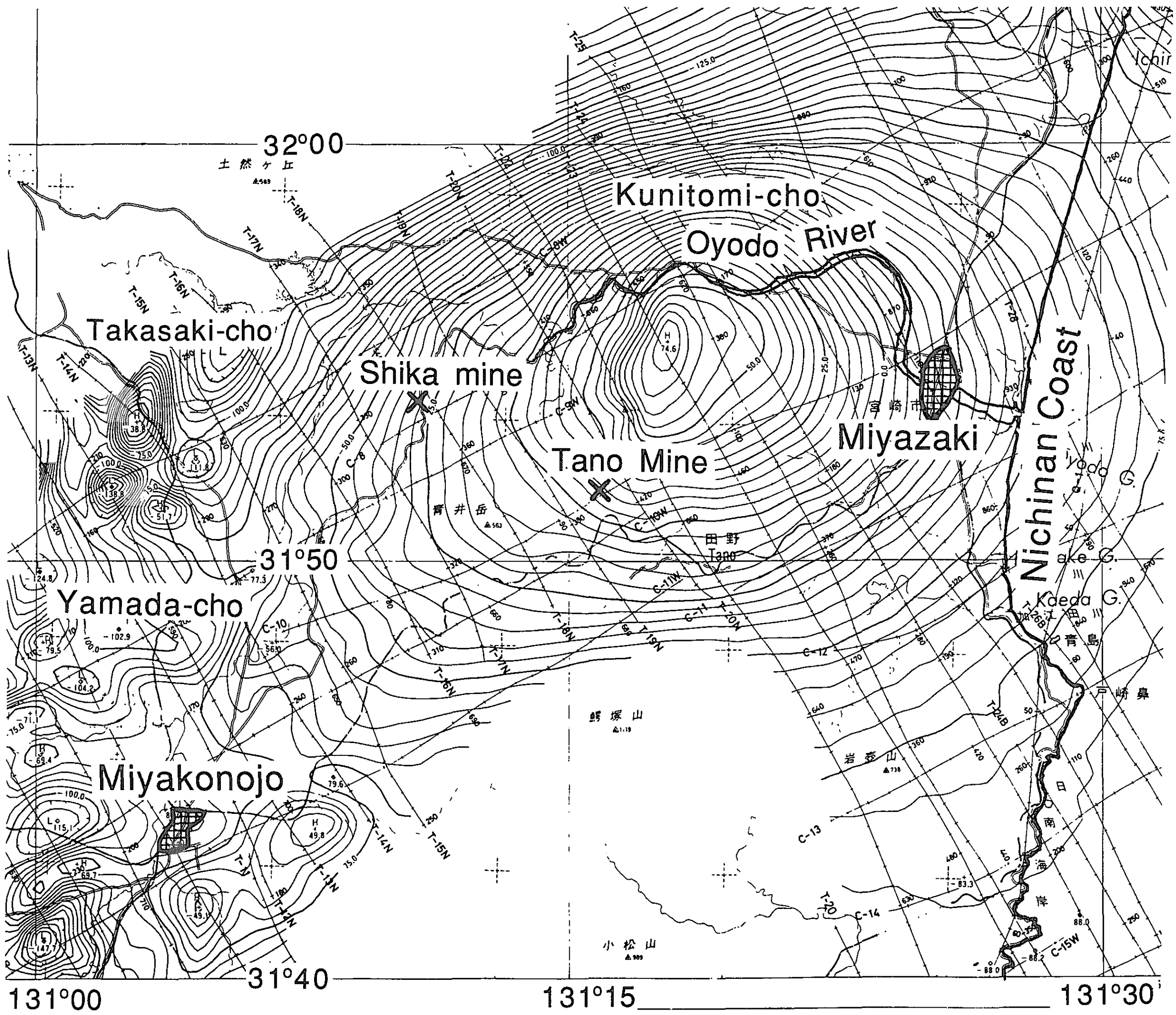


Fig. 3 Magnetic anomalies and location of the Tano deposit, Miyazaki Prefecture. A large deep anomaly in the Tano-Kunitomi area, which may be due to hidden Tertiary intrusive body, and small shallow anomalies in the Yamada-Takasaki area, which are caused by Plio-Pleistocene volcanic rocks, are observed. The magnetic data taken from Watanabe et al. (1977).

Matsuhisa, 1998).

5. Conclusions

Sulfur isotopic study of sulfides from late Cenozoic ore deposits of Southwest Japan indicate that their $\delta^{34}S$ values vary regionally rather than sulfide species or type and commodities of the ore deposits. The $\delta^{34}S$ values are low and negative in the fore-arc region including Miocene granitic terrane of the Outer Zone and Setouchi volcanic province, and high and positive in the back-arc region of Miocene Green Tuff region and Plio-Pleistocene volcanic province in Kyushu Island. This regional variation is considered essentially to reflect that of ilmenite-series and magnetite-series granitic and volcanic activities.

References

Hayashi, S. and Maruyama, S. (1961) Uraniferous ore deposits in Yaku-shima, Kagoshima Prefecture. *Rept. Geol. Surv. Japan*, no. 190, 356-362.

Hori, S. (1953) Mercury deposits of Japan. *Rept. Geol. Surv. Japan*. no. 154, 126 p.

Ishihara, S. (1971) Major molybenum deposits and related granitic rocksin Japan. *Rept. Geol. Surv. Japan*, no. 239, 178 p.

Ishihara, S. (1979) Kappameter KT-3 and its applications for some volcanic rocks in Japan. *Bull. Geol. Surv. Japan*, **30**, 513-519.

Ishihara, S. (1982) Sulfide-rich inclusions in the Osumi granitoids, Kagoshima Prefecture, Japan. *Bull. Geol. Surv. Japan*, **33**, 285-291.

Ishihara, S. and Imai, A. (2000) Geneses of high chlorine and silver-lead-zinc mineralized granitoids in Tsushima, Japan. *Resource Geol.*, (in press).

Ishihara, S. and Kawachi, Y. (1961) On the Takakuma-yama granitic stock and related uraniferous ore deposit of Nagao-ko at Tarumizu mine, Kagoshima Prefecture. *Rept. Geol. Surv. Japan*, no.190, 333-349.

Ishihara, S. and Matsuhisa, Y. (1999) Oxygen isotopic constraints on the geneses of the Miocene Outer Zone granitoids in Japan. *Lithos*, **46**, 523-534.

Ishihara, S. and Sasaki, A. (1991) Ore deposits related to granitic magmatism in Japan: A magmatic view point. *Episodes*, **3**, 286-292.

Ishihara, S., Sasaki, A. and Terashima, S. (1988) Sulfur in granitoids and its role for mineralization. *Proc. 7th (1986) Quad. IAGOD Sym.*, 573-581., E. Schweizerbart'sche Verlagsbuchhandlung.

Ishihara, S., Shibata, K. and Uchiumi, S. (1988) Discovery of Miocene granitoids in eastern Fukui Prefecture, central *Japan. Jour. Miner Petrol. Econ. Geol.*, **83**, 332-337.

Ishihara, S., Sasaki, A. and Sato, K. (1992) *Metallogenic map of Japan: Plutonism and mineralization* (2): Cretaceous-Tertiary. Geol. Surv. Japan.

Ishihara, S., Shibata, K. and Terashima, S. (1990) Alkalinity and initial $^{87}Sr/^{86}Sr$ ratios of igneous rocks related to late Cenozoic gold mineralization of the Ryukyu Arc, Japan. *CCOP Tech. Bull.*, **21**, 1-16.

Ishihara, S., Yamamoto, M. and Sasaki, A. (1999) Sulfur and carbon contents and $\delta^{34}S$ ratio of Miocene ilmenite-series granitoids: Osumi and Shibi-san plutons, SW Japan. *Bull. Geol. Surv. Japan*, **50**, 671-682.

Ishihara, S., Sakamaki, Y., Teraoka, Y. and Terashima, S. (1986) Role of the basement in the genesis of the Hishikari gold-quartz vein deposit, southern Kyushu, Japan. *Mining Geol.*, **36**, 495-509.

Iwasaki, J. (1898) Ichinokawa antimony mine and its stibnite. *Jour. Geol. Soc. Japan*, **5**, 577-589.

JMIA (Japan Mining Industry Association, 1968) *Ore deposit list of Japan*. Japan Mining Assoc., Tokyo, 941 p.

Kishimoto, F. (1962) On the mercury deposit of the Kamio mine, Nara Prefecture. *Bull. Geol. Surv. Japan*, **13**, 239-258.

Kiyosu, Y. (1977) Sulfur isotope ratios of ores and chemical environment of ore deposition in the Taishu Pb-Zn sulfide deposits, Japan. *Geochem. J.*, **11**, 91-99.

Kuhara, M. (1926) Geology and ore deposits of the Omori mine (2). *Jour. Geol. Soc. Japan*, **33**, 211-232.

Miyahisa, M. and Hashimoto, I. (1958) Matsuo mine. In *Report of Un-used Iron Resources Survey—1957*. No. 4, 493-497, Ministry Intern. Trade & Industry.

Miyashita, A. and Misaki, A. (1995) Geology of the sericite ore deposit of the Furekusa mine, Aichi Prefecture-Structural control on the epithermal ore deposit in caldera (abs.). *Abstr. Vol. Annual Mtg. Soc. Resource Geol. Japan*, p.13.

Miyoshi, T. Nakamura, T. and Kusakabe, M. (1988) Sulfur isotopic study of vein deposits in the Kinki district, Inner Zone of Southwest Japan. *Mining Geol.*, **38**, 323-333.

Nakamura, T. (1998) Gold-silver mineralization superimposed on polymetallic vein deposits in the Kinki district, southwest Japan. *Proc. 9th Quad. IAGOD Sym.*, E. Schweizerbart'sche Verlagsbuchhandlung,, 143-149.

NEDO (1985) *Atlas of nationwide geothermal exploration survey; IV.* IGRF residual magnetic, Curie isotherm depth and Isogal contour maps, 475 p.

Okamura, Y. (1999) Sericite deposit of Awashiro mine, Aichi Prefecture-- Characteristic and utility of the sericite. *Geology News*, no. 540, 49-53.

Ono, K. (1969) Structural features and their relation to metal quantities in ore deposits of the Kishu mine. *Mining Geol.*, **19**, 299-311.

Ono, K. (1984) Development of prospecting at the Kishu mine; Exploration History of Ore Deposits in Japan. *30th Anniv. Vol., Soc. Mining Geol. Japan.*, **2**, 113-144.

Sasaki, A. and Ishihara, S. (1979) Sulfur isotopic composition of the magnetite-series and ilmenite-series granitoids in Japan. *Contrib. Petrol. Mineral.*, **68**, 107-115.

Sasaki, A. and Ishihara, S. (1980) Sulfur isotope characteristics of granitoids and related mineral deposits in Japan. *Proc. 5th IAGOD Quad. Sym.* Scheweizerbart'sche Verlagbuchhandlung, 325-335.

Sasaki, A., Arikawa, Y., and Folinsbee, R. E. (1979) Kiba reagent method of sulfur extraction applied to isotopic work. *Bull. Geol. Surv. Japan*, **30**, 241-245.

Sato, K. and Kase, K. (1996) Pre-accretionary mineralization of Japan. *The Island Arc*, **5**, 216-228.

Sawamura, T., Suzuki, T., Aono, C. and Tsumuta, K. (1964) Geology and pyrrhotite deposit of Takaiwa mine, Kochi Prefecture. *Res. Rept. Kochi Univ., Nat. Sci.*, **1**, 7, 1-13.

Shikazono, N. (1987) Isotopic composition and origin of sulfide sulfur of Neogene Au-Ag and base metal vein-type deposits in Japan. *Jour.*

Fac. Sci., Univ. Tokyo, Sec. II, **21**, 239-255.
Shimada, M. (1949) On goelogy and ore deposits of the Ogoya mine (abs.). *Jour. Geol. Soc. Japan*, **55**, 142-143.
Shimazaki, H. (1985) Regional variation of isotopic composition of hydrothermal ore sulfur in Japan. *Jour. Fac. Sci., Univ. Tokyo*, Sec. II, **21**, 81-100.
Takada, A. (1987) Development of the Shitara igneous complex, central Japan and the structure of its cauldrons. *Jour. Geol. Soc. Japan*, **93**, 167-184.
Tatsumi, T. (1948) Some observations on the Tsugu gold-antimony mine, Aichi Prefecture. *Misc. Rept. Res. Inst. Nat. Resour*. **11**, 15-19.
Tatsumi, T. (1955) Antimony ores. In *Ore Deposits of Japan. Vol. I-a*, 155-184, Geol. Surv. Japan.
Tsukimura, K., Sato, K. and Ishihara, S. (1987) Regional and temporal variation in FeS content of sphalerite from Japan and its relation to granitoid series. *Bull. Geol. Surv. Japan*, **38**, 227-246.
Watanabe, S. and Hattori, H. (1980) Magnetic properties and densities of rocks near Miyazaki city for evaluation of regional magnetic and gravitational anomalies in southeastern Kyushu. *Bull. Geol. Surv. Japan*, **31**, 105-136.
Watanabe, S., Saito, T. and Nakatsuka, T. (1977) *Total intensity aeromagnetic map off the coast of Nobeoka-Miyazaki area* (Nobeoka -Satamisaki 1), Scale 1:200,000, Geol. Surv. Japan.
Yajima, S., Tsukada, F. and Ishii, E. (1956) On some aspects of the quick silver deposits in the Yamato metallogenic province. *Jour. Mining Inst. Japan*, **72**, 177-1812.
Yora, M. (1967) Geology and ore deposits of the Myoho mine. *Mining Geol.*, **17**, 107-112.

Received April 4, 2000
Accepted May 29, 2000

硫黄同位体比の対配列：西南日本の新生代後期鉱床

石原舜三・佐々木　昭・皆川鉄雄・豊　遙秋・宍戸　章・田中亮吏

要　旨

西南日本に分布する新生代後期の鉱床に産出する硫化物の硫黄同位体比($\delta^{34}S_{CDT}$)を，瀬戸内火山岩類を含む西南日本外帯産69個，九州の第四紀火山前線に伴う鉱床を含む西南日本内帯産26個について新たに測定し，既発表データと共に鉱床別の平均値を求めその広域的変化を考察した．

硫黄同位体比は鉱物種・鉱床種よりも地域性に著しく規制される．$\delta^{34}S$ は一般に前弧側で低く負の値を，背弧側で高く正の値を示し，広域的な対をなして分布する．前弧側の負の値は四万十帯の鉱床のみならず，中央構造線から北方の領家帯に分布する鉱床においても設楽盆地・奈良県大和地方・九州中北部で認められる．この広域的な性格は成因的に関係する花崗岩類および火山岩類の起源物質の差を反映したものと解釈される．

西南日本外帯の鉱床においては，成因的に関係する花崗岩類に近い尾平地域・高隈山・屋久島などで $\delta^{34}S$ = -10 ～ -3 パーミルの比較的一定の値を示し，火成岩体から離れる鉱床では変化幅が大きい傾向がある．特に低い値 ($\delta^{34}S$ = -15 ～ -11‰) は紀伊半島南部や高知県南部の銅・アンチモン鉱床に見られる．宮崎県田野鉱床は西南日本外帯において例外的に正の値を示すが，これは九州―パラオ海嶺に貫入する磁鉄鉱系花崗岩類と同様な岩体が潜在することを暗示する．

背弧側の鉱床は北陸―山陰地方のグリーンタフ帯で $\delta^{34}S$ = +2 ～ +7 パーミルの纏まった値を示すが，西南日本の内外帯を切って分布する九州地方の鮮新世－更新世火山前線に伴う金・アンチモン鉱床は -7 ～ +6 パーミルと大きな変化幅を示し，九州地方の火山岩類が酸化還元状態に関して多様性を持つことを暗示する．

Appendix 1-3 Chemical compositions of selected sulfides from the Tsugu deposit, which were determined by a JEOL JXA-733 electron microprobe at Hokkaido University. Analyses were carried out with 20-25kV and 15-20nA. Counting times for major and minor elements are 20 seconds and 50 seconds, respectively. Supplementary standards are synthetic sulfide and natural mineral standard. Matrix corrections were performed by ZAF methods. Analyst, R. Tanaka.

Appendix-table 1 Chemical composition of sphalerite from the Tsugu mine

Sample	Mineral		wt.%							atm.%						mol.%			
No.	assemblage	No.	Zn	Fe	Mn	Cd	Cu	S	Total	Zn	Fe	Mn	Cd	Cu	S	ZnS	FeS	MnS	CdS
TSG-2	Apy-Gn-Cp-	1	49.24	14.35	2.47	0.01	0.05	33.11	99.22	36.06	12.30	2.15	0.00	0.03	49.45	71.43	24.30	4.26	0.01
	(Po)	2	47.04	15.41	3.58	0.00	0.02	32.81	98.85	34.52	13.24	3.12	0.00	0.02	49.09	67.87	25.99	6.14	0.00
		4	45.59	16.22	4.02	0.11	0.04	32.93	98.91	33.37	13.90	3.50	0.05	0.03	49.15	65.71	27.31	6.89	0.09
		5	45.07	16.61	4.17	0.07	0.16	32.67	98.76	33.06	14.27	3.64	0.03	0.12	48.87	64.98	27.80	7.16	0.06
		6	45.41	16.15	4.18	0.00	0.04	32.47	98.26	33.50	13.95	3.67	0.00	0.03	48.84	65.57	27.24	7.19	0.00
		7	45.12	16.26	4.24	0.06	0.06	32.48	98.22	33.30	14.05	3.72	0.03	0.05	48.86	65.23	27.43	7.29	0.05
	Apy-Gn-Py	9	50.68	12.43	2.34	0.00	0.25	32.41	98.11	37.72	10.83	2.07	0.00	0.19	49.18	74.79	21.10	4.11	0.00
	Cp	12	46.50	15.36	3.89	0.08	0.02	33.05	98.89	34.05	13.17	3.39	0.03	0.01	49.34	67.25	25.98	6.70	0.07
		13	46.85	14.92	3.79	0.08	0.09	32.56	98.27	34.62	12.90	3.33	0.03	0.07	49.06	68.12	25.26	6.55	0.06
		14	48.16	14.11	3.26	0.03	0.61	33.37	99.53	35.09	12.04	2.83	0.01	0.46	49.58	70.87	23.40	5.71	0.02
		15	46.91	14.83	3.65	0.11	0.54	32.84	98.87	34.45	12.75	3.19	0.05	0.40	49.17	68.86	24.67	6.37	0.10
		16	49.95	13.13	2.21	0.00	0.65	32.74	98.68	36.89	11.35	1.94	0.00	0.49	49.32	74.24	21.85	3.91	0.00
		17	50.38	12.87	2.46	0.00	0.08	32.81	98.61	37.22	11.13	2.16	0.00	0.06	49.42	73.77	21.95	4.28	0.00
	Py-Gn-Cp	22	48.92	15.07	1.95	0.14	0.12	32.54	98.74	36.12	13.03	1.71	0.06	0.09	48.98	71.07	25.45	3.37	0.12
		23	50.23	13.59	1.71	0.05	0.22	32.31	98.11	37.40	11.85	1.51	0.02	0.17	49.04	73.89	23.08	2.99	0.04
		27	51.88	12.45	1.36	0.11	0.25	32.94	98.98	38.27	10.76	1.19	0.05	0.19	49.54	76.42	21.10	2.39	0.09
TSG-3	Py-Apy-Th-	28	52.02	12.33	1.34	0.04	0.28	32.68	98.68	38.54	10.69	1.19	0.02	0.21	49.36	76.74	20.87	2.36	0.03
	Cp	29	50.13	13.42	1.87	0.00	0.27	32.86	98.55	37.03	11.61	1.64	0.00	0.21	49.51	73.95	22.77	3.28	0.00
		30	50.71	13.73	1.45	0.11	0.05	32.61	98.65	37.53	11.90	1.27	0.05	0.04	49.21	74.01	23.39	2.51	0.09
		34	49.69	15.02	1.11	0.17	0.05	32.07	98.11	37.05	13.11	0.99	0.07	0.04	48.75	72.39	25.53	1.93	0.14
		35	49.79	15.11	1.04	0.15	0.00	32.22	98.30	37.02	13.15	0.92	0.06	0.00	48.84	72.37	25.71	1.80	0.12
		36	50.17	14.93	0.89	0.22	0.00	32.64	98.85	37.05	12.91	0.78	0.09	0.00	49.16	72.88	25.39	1.54	0.19
	Py-Apy-Cp	38	50.12	14.20	1.00	0.13	0.58	32.64	98.67	37.08	12.30	0.88	0.06	0.44	49.23	74.34	23.78	1.77	0.11
		39	50.34	14.31	1.24	0.13	0.02	32.35	98.38	37.39	12.44	1.09	0.05	0.02	49.00	73.36	24.38	2.15	0.11
		40	49.55	14.50	1.44	0.07	0.02	32.52	98.09	36.81	12.62	1.27	0.03	0.01	49.26	72.58	24.85	2.50	0.06
		41	49.56	14.59	1.66	0.06	0.02	32.31	98.21	36.83	12.70	1.47	0.03	0.01	48.95	72.20	24.86	2.88	0.05
		44	50.84	13.69	1.32	0.07	0.11	32.68	98.71	37.60	11.85	1.16	0.03	0.08	49.27	74.36	23.27	2.30	0.06
		45	50.01	14.33	1.47	0.10	0.02	32.43	98.36	37.12	12.45	1.30	0.04	0.01	49.07	72.92	24.44	2.55	0.09
		48	50.47	14.58	1.26	0.12	0.04	32.62	99.09	37.20	12.59	1.10	0.05	0.03	49.03	73.07	24.67	2.16	0.10
		49	50.45	14.60	1.14	0.10	0.02	32.72	99.01	37.18	12.60	1.00	0.04	0.01	49.17	73.19	24.77	1.96	0.08
		50	50.22	14.87	1.15	0.10	0.03	32.87	99.23	36.90	12.79	1.00	0.04	0.02	49.24	72.75	25.18	1.98	0.08
		52	50.83	14.44	1.08	0.04	0.01	32.58	98.99	37.52	12.48	0.95	0.02	0.01	49.03	73.63	24.47	1.86	0.03
	Py-Apy-Cp	53	50.18	14.13	1.23	0.04	0.51	32.28	98.37	37.29	12.30	1.09	0.02	0.39	48.92	74.13	23.67	2.16	0.03
		54	49.88	14.45	1.08	0.09	0.06	32.46	98.01	37.12	12.59	0.96	0.04	0.05	49.25	73.28	24.76	1.89	0.08
		55	51.86	13.39	1.17	0.06	0.02	32.45	98.94	38.37	11.60	1.03	0.03	0.01	48.96	75.22	22.72	2.01	0.05
		56	50.65	14.66	1.12	0.21	0.08	32.70	99.41	37.24	12.62	0.98	0.09	0.06	49.02	73.21	24.69	1.93	0.17
		57	50.83	14.63	1.11	0.20	0.02	33.10	99.89	37.13	12.51	0.97	0.09	0.01	49.30	73.26	24.67	1.91	0.17
		58	50.52	14.42	1.15	0.02	0.02	32.80	98.93	37.23	12.44	1.01	0.01	0.01	49.29	73.47	24.53	1.99	0.02
		59	50.66	14.29	1.47	0.04	0.01	32.18	98.66	37.58	12.42	1.30	0.02	0.01	48.68	73.24	24.18	2.54	0.03
		60	50.46	14.53	1.29	0.11	0.00	32.52	98.91	37.27	12.56	1.13	0.05	0.00	48.98	73.07	24.62	2.22	0.09
		61	50.43	14.55	1.26	0.03	0.03	32.97	99.28	37.01	12.50	1.10	0.01	0.02	49.34	73.13	24.66	2.18	0.03
		62	50.27	14.58	1.14	0.09	0.02	32.51	98.61	37.22	12.64	1.00	0.04	0.02	49.09	73.14	24.81	1.97	0.08

Abbreviations; Apy: arsenopyrite, Cp: chalcopyrite, Gn: galena, Po: pyrrhotite, PS: Pb-Sb-S mineral, Py: pyrite, Th: tetrahedrite

Appendix-table 2 Chemical composition of tetrahedrite from the Tsugu mine

Sample No.	Mineral assemblage	No.	wt.% Cu	Ag	Zn	Fe	Sb	As	S	Total	mol.% Cu	Ag	Zn	Fe	Sb	As	S
TSG-3	Py-Apy-Cp-Sp	1	35.04	3.88	3.27	3.94	28.63	0.47	23.90	99.14	32.5346	2.12248	2.95092	4.16605	13.8696	0.37255	43.9838
		2	34.78	4.19	4.77	4.18	28.26	0.49	24.40	101.07	31.5794	2.24164	4.20982	4.31526	13.3886	0.37506	43.8902
		3	35.68	4.07	3.48	3.81	28.90	0.42	23.93	100.28	32.8439	2.20657	3.11235	3.98544	13.8807	0.32794	43.6432
		4	35.60	3.89	3.22	3.79	28.98	0.28	23.58	99.33	33.1429	2.13047	2.91193	4.01639	14.08	0.21956	43.4987
		5	35.77	4.32	3.39	3.87	28.98	0.37	24.66	101.36	32.421	2.30687	2.98728	3.99263	13.7041	0.28603	44.3021
		6	35.64	4.27	3.17	3.85	29.22	0.56	23.92	100.64	32.7714	2.31485	2.83665	4.02331	14.0203	0.4376	43.5958
		7	36.37	4.04	3.34	3.85	28.87	0.55	24.58	101.60	32.8816	2.15116	2.93108	3.96462	13.618	0.42407	44.0295
		8	35.78	4.27	3.41	3.67	28.79	0.80	24.25	100.96	32.6639	2.29399	3.02133	3.81688	13.7123	0.61956	43.872
		9	35.68	3.47	3.54	4.09	28.32	1.58	24.45	101.11	32.3284	1.84919	3.11563	4.21386	13.3884	1.21208	43.8925
	Py-Cp	10	38.92	0.34	2.80	4.27	29.30	-	24.39	100.01	35.2804	0.17994	2.46611	4.40067	13.8603	-	43.8126
		11	38.66	0.42	2.81	4.35	30.04	-	24.53	100.82	34.8671	0.22417	2.46657	4.46629	14.1367	-	43.8391
		12	37.96	0.49	2.59	4.72	30.22	-	24.78	100.75	34.1963	0.25787	2.26498	4.83529	14.2036	-	44.2420
	Apy-Gn-Sp	13	34.84	5.08	3.52	3.80	29.03	0.35	24.21	100.83	31.9614	2.74624	3.13608	3.96409	13.8967	0.27473	44.0208
		14	30.96	4.28	2.71	3.80	29.90	2.04	23.83	97.53	29.4885	2.40315	2.51034	4.12043	14.8596	1.64407	44.9739
		15	35.15	4.88	3.32	3.89	27.56	1.32	24.16	100.28	32.2304	2.63791	2.95535	4.06329	13.1867	1.02601	43.9003

Appendix-table 3 Chemical composition of Pb-Sb-Fe-Mn-S minerals from the Tsugu mine

Sample No.	Mineral assemblage	No.	wt.% Pb	Sb	Fe	Mn	S	Total	atom.% Pb	Sb	Fe	Mn	S	mol% PbS	Sb2S3	FeS	MnS
TSG-2	Py-Gn	1	42.55	38.07	0.00	0.00	20.89	101.51	17.56	26.73	0.00	0.00	55.71	56.79	43.21	0.00	0.00
		2	40.25	37.91	0.00	0.00	21.04	99.20	16.72	26.80	0.00	0.00	56.48	55.52	44.48	0.00	0.00
		5	40.11	38.01	0.07	0.00	20.80	98.99	16.75	27.01	0.11	0.00	56.13	55.17	44.47	0.36	0.00
		6	41.62	36.56	0.15	0.00	20.70	99.03	17.48	26.12	0.23	0.00	56.17	56.80	42.44	0.76	0.00
TSG-3	Apy-Gn-Th	9	40.99	35.63	1.81	0.58	21.45	100.46	16.46	24.33	2.70	0.88	55.64	51.11	37.79	8.37	2.73
	Gn-Th	13	42.81	35.09	1.43	0.72	21.37	101.42	17.22	24.01	2.13	1.09	55.54	53.06	37.00	6.58	3.37
		14	42.75	34.21	1.35	0.51	20.33	99.15	17.87	24.33	2.09	0.80	54.91	54.27	36.94	6.36	2.44
		15	40.97	34.91	1.55	0.49	21.01	98.93	16.81	24.37	2.36	0.76	55.70	52.35	37.94	7.35	2.36