

## Origin of Sulfur in Some Magmatic-Hydrothermal Ore Deposits of South China

Shunso Ishihara<sup>1</sup>, Ping' An Wang<sup>2</sup>, Yoshimichi Kajiwara<sup>3</sup>  
and Yasushi Watanabe<sup>3</sup>

Shunso Ishihara, Ping' An Wang, Yoshimichi Kajiwara and Yasushi Watanabe (2003) Origin of sulfur in some magmatic-hydrothermal ore deposits of South China. *Bull. Geol. Surv. Japan*, vol. 54 (3/4), 161-169, 3 figs, 2 tables.

**Abstract:** Mill concentrates of ore sulfides from three magmatic-hydrothermal ore deposits were studied for  $\delta^{34}\text{S}$  at the granite-hosted Xihuashan deposits, and carbonate-hosted Shizhuan and Huashaping deposits. These ore deposits occur in the South China Fold System, which is composed of mid-Paleozoic "miogeosynclinal" sediments dominant in carbonates toward the Devonian age. Averages of the ore sulfides are -0.9 permil for the Xihuashan, +7.0 permil for the Shizhuan and +13.2 permil for the Huashaping deposits. Endogranitic ore sulfur of the Xihuashan and the Shizhuan deposits are considered magmatic, derived from by ca.+2 ‰  $\delta^{34}\text{S}$  granitic magma, but the carbonate-hosted ore sulfurs at the major part of the Shizhuan and Huashaping deposits are much higher than those expected from rock sulfur  $\delta^{34}\text{S}$  values of the Yanshanian granites of the South China Fold System. Thus, addition of  $^{34}\text{S}$ -enriched sulfur into the ore solutions is considered.

Devonian and Carboniferous carbonates of the South China Fold System are very high in the  $\delta^{34}\text{S}$  values of structurally substituted sulfate (SSS) sulfur, averaged as +25.7 and +15.7 permil, respectively, which are higher than the reported values from other areas of these ages. The SSS contents of the Paleozoic carbonates are very low at present, but recent carbonates contain typically 0.1 to 1 ‰ equivalent sulfate. The very low SSS contents in the wall rock carbonates and high  $\delta^{34}\text{S}$  values in the ore sulfides may have been resulted from carbonate SSS extracted during recrystallization and somehow mixed with magmatic ore fluids when the granitic magmas intruded, then precipitated as the ore sulfides.

**Keywords:** South China, Devonian, carbonates, Huangshaping, Shizhuyuan, Xihuashan, SSS (structurally substituted sulfate) content,  $\delta^{34}\text{S}$  value.

### 1. Introduction

In mineralized granitic terranes, both rock and ore sulfurs show a distinct negative/positive  $\delta^{34}\text{S}$ -paired zoning in the Japanese Islands, which is called the Japanese-type  $\delta^{34}\text{S}$ -distribution, but unclear pairing biased to heavy  $\delta^{34}\text{S}$  values in Korea, which is named as Korean-type  $\delta^{34}\text{S}$ -distribution (Ishihara *et al.*, 2000). The  $\delta^{34}\text{S}$  values higher than so-called classic mantle value of +1 permil are considered due to (1) seawater sulfate brought up to granitic magmas by subduction processes (Sasaki and Ishihara, 1979, Ueda and Sakai, 1984), (2) fossilized sulfate of evaporite beds assimilated into the magmas within the continental crust (Thode *et al.*, 1962; Cai, 1980; Chen *et al.*, 1982; Chu *et al.*, 1986; Ishihara *et al.*, 1986; Chen and Chu, 1988; Zhou *et al.*, 1994, 1995; Zhou and Yue, 1996), or (3)

minor amounts of SSS (structurally substituted sulfate) contained in carbonate beds recycled into the granitic magmas, or directly mixing with the ore solution. Possibility of the SSS origin was examined both in regional scale (Ishihara *et al.*, 2002a) and also individual deposits (Ishihara *et al.*, 2002b).

Situated in the same continental margin environment, the ore deposits of South China have different  $\delta^{34}\text{S}$  values from those of South Korea, suggesting own history of the metallogenic background. A summary of sulfur isotopic data ( $\delta^{34}\text{S}$ ) of sulfides from 157 ore deposits, associated with Jurassic and Cretaceous granitic activities in South China, indicates that averaged  $\delta^{34}\text{S}$  values of individual deposits vary widely from -9.3 to +20.6 permil, with several highly positive  $\delta^{34}\text{S}$  values (Wang and Ishihara, 2000).

Reconnaissance sampling was made on the sulfide

<sup>1</sup> Geological Survey of Japan, AIST Central 7, Higashi 1-1-3, Tsukuba, 305-8567, Japan

<sup>2</sup> Faculty of Engineering, University of Tokyo, Hongo, Tokyo, 113-8656, Japan

<sup>3</sup> Institute of Geoscience, University of Tsukuba, Tsukuba 305-8571, Japan

ores and limestones in South China during a short visit under the Institute of Transfer of Industrial Science (ITIT) Project of the Ministry of International Trade and Industry in autumn of 2000. The analytical results indicated important contribution of the host carbonate sulfur to some of the ore geneses. This paper describes result of the sulfur isotopic analyses, and discusses genetic bearing of these results, particularly to the provenance of the ore sulfur.

The analytical methods for sulfide ores are conventional  $\text{SO}_2$  method and measured by MAT 251 EM mass-spectrometer. The analytical uncertainty is  $\pm 0.2$  permil. Sulfate and sulfide sulfur in carbonate rocks were analyzed at the University of Tsukuba by the methods described in detail in Ishihara *et al.* (2002a).

## 2. Geological Background

The studied areas, shown by solid circles in Fig. 1 with local names, belong to a part of South-China fold system (Zone II, Fig. 1), which is a mid-Paleozoic miogeosynclinal intra-continental fold system developed on the Precambrian basements, and folded sedimentary formations composed mainly of late Proterozoic to Silurian terrigenous clastic rocks. Carbonate rocks become dominant in the Devonian Period onwards, especially in the northern Guangxi Autonomous Region including famed limestone cities of Guilin and Yangshuo, and the central Hunan Province.

The Devonian rocks can be subdivided into three parts as follows:

Upper part ( $D_3$ ): Thin-layered siliceous marl, limestone, mudstone, shale, with siltstone and oolitic hematite interbeds. Sandstone occurs only locally and interbedded with limestone.

Middle part ( $D_2$ ): Limestone, bioclastic limestone, dolomite, argillaceous limestone, marl with mudstone interbeds.

Lower part ( $D_1$ ): Mainly clastic rocks with some interbeds of limestone, bioclastic limestone and dolomite.

The Carboniferous rocks are widely distributed in South China. They are stable neritic sediments including carbonates with coal, iron-manganese beds, bauxite, clays and gypsum.

These Paleozoic formations are intruded by Hercynian, Indosinian and Yanshanian granitoids, among which the Jurassic to Cretaceous, Yanshanian ones are most extensively distributed in South China. Many ore deposits of vein, skarn and porphyry types are associated with the Yanshanian granitoids. Skarn-type ore deposits are common wherever they intrude carbonate formations. The Yanshanian granitoids are divided into the early Yanshanian (Jurassic) and the Late Yanshanian (Cretaceous) stages.

## 3. Rock $\delta^{34}\text{S}$ Values - A Review

In order to interpret ore sulfur  $\delta^{34}\text{S}$  data of magmatic-hydrothermal ore deposits, we need to know rock  $\delta^{34}\text{S}$  values. Unfortunately, all the available data so far

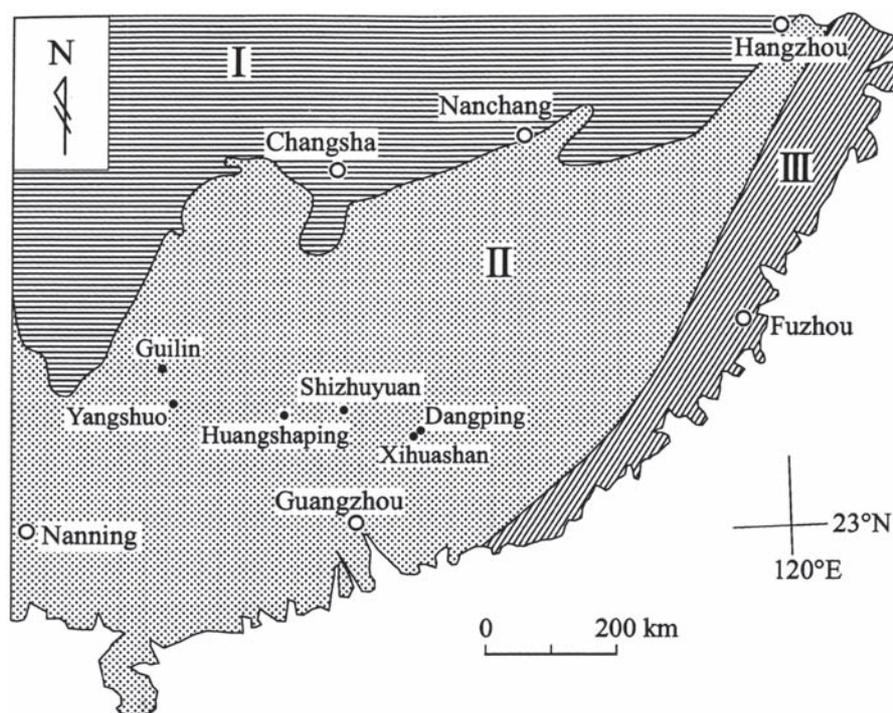


Fig. 1 Index map of the studied areas with the geotectonic divisions in South China. I, Yangtze paraplatform; II, South China fold system; and III, Southeastern maritime fold system.

appeared in literature are measured on pyrite contained in granitoids, which could not be primary magmatic mineral. If the host granitoids are “fresh” or least altered, however, this may demonstrate the closest  $\delta^{34}\text{S}$  value of the original granitic magmas.

Rock  $\delta^{34}\text{S}$  values of the least altered granitoids near ore deposits from the Yangtze paraplatform (Zone I, Fig. 1), appear to be higher than the other terranes as follows: diorite-granodiorite at Mashan (Au, pyrite), Anhui, is averaged as +5.1 permil (n=8, Zhou, 1984; Xia, 1999), and granodiorite porphyry of Tongshan/Liuxiashan (Cu-W/Au-Pb-Zn), Anhui, has +5.8~+5.9 permil (Yang, 1991). These intrusive rocks may belong to magnetite series.

Extremely high value of +12.5 permil is seen on the pyrite-bearing least altered magnetite-series diorite and granodiorite in the Ningwu Basin, near Nanjing, where Triassic anhydrite discovered by drilling have averaged  $\delta^{34}\text{S}$  values of +30.2 permil. The anhydrite beds were most probably intruded by the Yanshanian magmas and  $^{34}\text{S}$ -enriched sulfur was incorporated into the intrusive rocks, giving rise to the high value (Ishihara *et al.*, 1986).

In the South-China fold zone (Zone II, Fig. 1), the rock  $\delta^{34}\text{S}$  values range mostly from +1 to +9 permil, and averaged as +5.1 permil (n=5), as follows. In the Sn-mineralized region including Tiandong, Wuhengtian, Shuimei, Sanjiaowo, Tashan and Qingkeng mines, Guangdong Province, their rock  $\delta^{34}\text{S}$  values of the related granite-quartz monzonite porphyry are averaged as +8.9 permil (Lei, 1994). The intrusive rocks must be ilmenite series, because of Sn mineralization associated. In the Lianhuashan W-Mo-Sn mineralized area, Guangdong Province, the related quartz diorite and granite porphyry have an average  $\delta^{34}\text{S}$  value of +1.3 permil (n=6, Man *et al.*, 1983). In the famed Sn-Cu-Zn mineralized Dachang, Guangxi Autonomous Region, granite porphyry gives +6.2 permil, but biotite granite of the Sn-free Lamo ore deposit has an average of +1.4 permil (n=4, Chen *et al.*, 1993; Fu *et al.*, 1991). Granodiorite porphyry related to Zhuxi Cu vein, Jiangxi Province, has a rock  $\delta^{34}\text{S}$  value of +2.8 permil (Xiang, 1992).

Granitoids in the Fe-skarn mineralized Makeng and Yangshan deposits, Fujian Province, give  $\delta^{34}\text{S}$  values of +1.0 and +3.3 permil, respectively (Zhao *et al.*, 1983). Granite related to the Zijinshan Cu-Au porphyry-epithermal type deposits (Zhang *et al.*, 1991), Fujian Province, has the average rock  $\delta^{34}\text{S}$  value of -0.3 permil (n=9) (Chen *et al.*, 1994), but granodiorite porphyry from the Cu-Mo mineralized Luoboling mine shows +3.0 permil (Chen *et al.*, 1994). In Zhejiang Province, granite porphyry dike in the Yinkengshan (Zhilingtou) Au-Ag vein area has +6.4 permil (Liang *et al.*, 1985), and felsite dike in the Au-Mo mineralized Jinjiyan deposit gives average of +1.1 permil (Du

*et al.*, 1998).

These previous studies show that the rock  $\delta^{34}\text{S}$  values of South China have generally positive average values, similarly to the Korean Peninsula which has +5.5 permil for the Jurassic and +2.2 permil for the Cretaceous (Ishihara *et al.*, 2000), but a wider range in the variation, reflecting more complex geologic background. There seems to be no systematic variations depending upon the granitoid series like those found in the Japanese Islands, although the magnetite series/ilmenite-series classification is only done by the bulk  $\text{Fe}_2\text{O}_3/\text{FeO}$  ratios (Ishihara and Wang, 1999).

#### 4. Studied Carbonates and Ore Deposits

Both regional and mine-site samples were analyzed for bulk sulfur contents and  $\delta^{34}\text{S}$  values of sulfate and sulfide sulfur of the Paleozoic carbonates (Table 1). Mill concentrates, which should give us an average  $\delta^{34}\text{S}$  composition of given ore deposits (Sasaki and Ishihara, 1980), were studied at three early Yanshanian deposits of Xihuashan, Shizhuyuan and Huangshaping mines.

##### 4.1 Carbonate Rocks

The Paleozoic carbonates were tentatively analyzed for SSS and sulfide sulfur, in order to find  $^{34}\text{S}$ -enriched sulfur source, besides evaporates which are most common in Triassic continental sediments in China. Carbonate beds which give us scenic view in the Guilin-Yangshuo area are upper Devonian age (D<sub>3</sub>). In Guilin city, two samples were collected at the Qixingyan and Luotuoshan parks. They are milky white limestones devoid of metamorphism. A middle Devonian limestone sample weekly recrystallized was collected from approximately 3 km east of central Yangshuo town, at the SE side of the Yangshuo Bridge.

The other four samples were taken from the mine sites. They are recrystallized and veined with white calcite.

The  $\delta^{34}\text{S}$  values for pyrite from Lower Carboniferous host rocks in the Huangshaping area were reported by Wang *et al.* (1988) as (1) -3.1 permil for disseminated pyrite from the thin-layered carbonaceous limestone of the Lower Carboniferous Shidengzi Formation; and (2) -22.6 permil and -11.7 permil for nodular pyrite from the carbonaceous shale of the Lower Carboniferous Ceshui Formation.

##### 4.2 Xihuashan Deposits

Xihuashan vein-type deposits occur in Jurassic biotite granitic stock (19 km<sup>2</sup>), which intruded Cambrian low-grade metamorphic rocks of psammitic and pelitic origins. The working areas are divided into the Xihuashan mining area in the southern part and Dangping mining area in the northeastern part of the stock.

Table 1 Sulfur isotopic data for carbonate rocks from the Guilin area.

Sample No., Locality and Rock Type	Sulfate Sulfur		Sulfide Sulfur		$\delta^{34}\text{S}(\text{‰})$ Sulfate-sulfide
	Content (ppm)	$\delta^{34}\text{S}(\text{‰})$	Content (ppm)	$\delta^{34}\text{S}(\text{‰})$	
Regional samples					
20 Qixingyan, Guilin, Guangxi Milky white limestone, D <sub>3</sub> (Upper Devonian)	1.4	+30.9	33.3	+10.4	20.5
21 Luotuoshan, Guilin ditto, D <sub>3</sub> (ditto)	2.7	+33.0	3.5	+2.5	30.5
22 Yangshuo, Guangxi Milky white marble, D <sub>3</sub> (Middle Devon.)	1.2	+28.9	1.9	+12.9	16.0
41 East of Yantang, Guiyang County, Hunan Milky white gray limestone, C <sub>1</sub> (Lower Carboniferous)	19.9	+25.7	3.5	+7.0	18.7
Mine-site samples					
55 Shizhuyuan mine, 200m from the main adit Gray marble, Middle/Upper Devonian	12.2	+20.6	2050.0	-1.8	22.4
42 Tangxia Village near Huangshaping mine Black limestone, with calcite veinlet, C <sub>1</sub>	55.9	+9.8	561.0	-16.6	26.4
46 Huangshaping mine, 56mL, Guiyang Black limestone, with calcite veinlet, C <sub>1</sub>	4.0	+19.4	1270.0	-8.0	27.4
50 East of Huangshaping mine: black limestone, C <sub>1</sub>	7.8	+17.9	140.6	-3.0	20.9

Analyst: Y. Kajiwara

Magnetic susceptibility of the granite was measured in one meter interval at several places of the underground tunnels by a portable device of KT5 meter. It ranges from 0.02 to 0.91 x 10<sup>-3</sup> SI in the Xihuashan mine area and 0.02 to 0.12 x 10<sup>-3</sup> SI in the Dangping mine area, indicating the granite is free of magnetite belonging to ilmenite series.

The ore deposits consist of wolframite-(K-feldspar)-quartz veins trending E-W direction with steep dips. The associated alteration is K-feldspartization and greisenization. The ore minerals are wolframite and

small amounts of cassiterite, bismuthinite, molybdenite, chalcopyrite and pyrite. Sulfide concentrates of molybdenite, pyrite and chalcopyrite were analyzed (Table 2).

### 4.3 Shizhuyuan Deposits

Shizhuyuan W(-Sn-Bi-Mo-Be) skarn deposits occur in the Devonian carbonate rocks intruded by a small stock of granitic compositions, which is called Qianlishan stock.

Magnetic susceptibility of the Qianlishan granite was measured at five places in a few km apart as follows: A; 0.09~0.40 x10<sup>-3</sup> for granite and 3.3~4.7 x10<sup>-3</sup> for

Table 2 Average  $\delta^{34}\text{S}$  values of ore sulfides from Xihuashan, Shizhuyuan, and Huangshaping ore deposits in southern China.

Locality	Rock description	$\delta^{34}\text{S}(\text{‰})$
Xihuashan		
15-70	Molybdenite flake concentrates	+0.3
15-71	Pyrite concentrates	-2.1
15-76	Chalcopyrite concentrates	-0.9
	Average	-0.9
Shizhuyuan		
13-60	Molybdenite concentrates	+7.3
13-61	Bismuthinite concentrates	+5.2
13-62	Pyrite concentrates	+8.4
	Average	+7.0
Huangshaping		
12-47	Galena concentrates	+12.9
12-48	Sphalerite concentrates	+14.2
12-49	Pyrite concentrates	+12.6
	Average	+13.2

Analyst: R.M. Bai, Chinese Academy of Geological Sciences, Beijing.

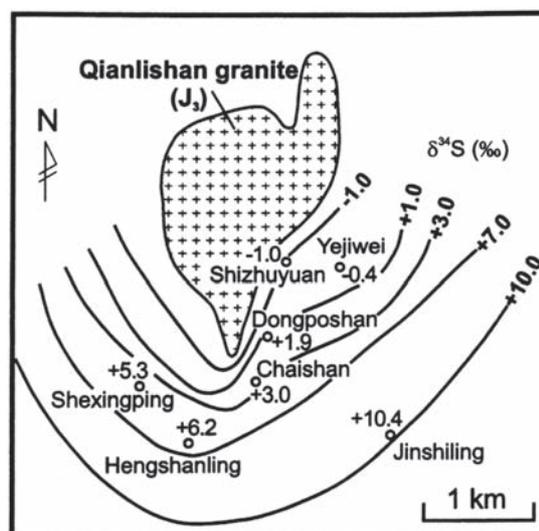


Fig. 2 Sulfur isotopic zoning observed in the Shizhuyuan-Dongpo ore field. Simplified from Tong *et al.* (1995).

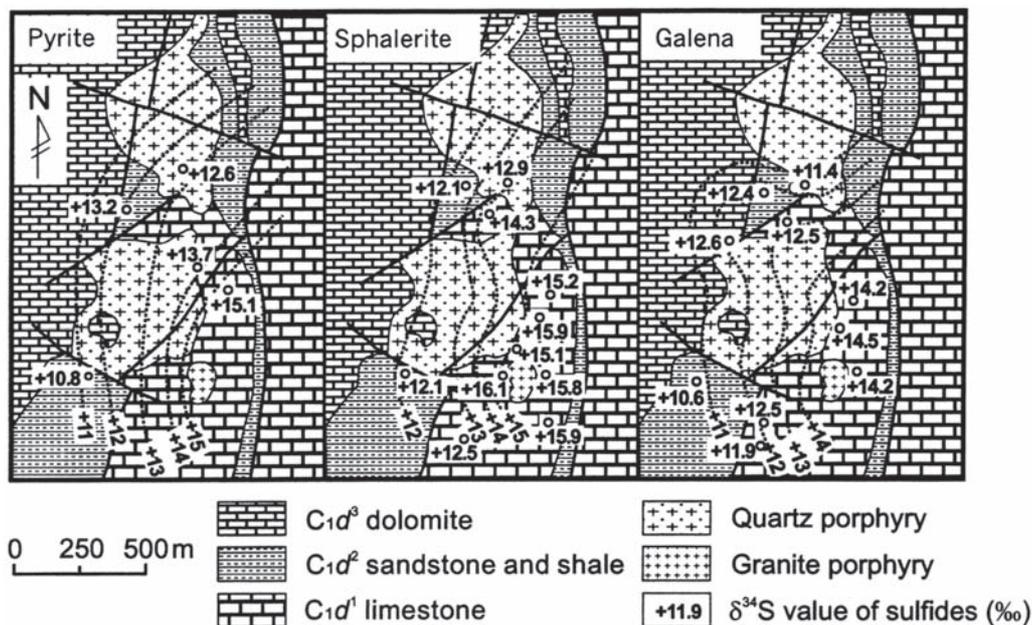


Fig. 3 Sulfur isotopic zoning observed in the Huangshaping orefield (Tong *et al.*, 1995). C<sub>1d</sub><sup>1</sup>, C<sub>1d</sub><sup>2</sup>, C<sub>1d</sub><sup>3</sup>: Lower, middle and upper parts, respectively, of the Datang Member of lower Carboniferous Formation.

granite porphyry dike (30 m wide), B; Taipingli 0.11~0.29  $\times 10^{-3}$ , C; 0.10~0.27  $\times 10^{-3}$ , D; (near the entrance of the main adit); 0.05~0.53  $\times 10^{-3}$  with two high values of 7.0  $\times 10^{-3}$  and 21.7  $\times 10^{-3}$  SI, which may be due to local presence of magnetite. The Qianlishan granite belongs essentially to ilmenite series.

The ore deposits occur mostly in the carbonate rocks as thick lens having horizontal dimensions of 1,100 m by 700 m in the average and the thickness of 150- 300 m. The ores can be divided into (1) marble-Sn ore, (2) skarn-W-Bi ore, (3) stockwork greisen-quartz vein - skarn W-Sn-Mo-Bi ore and (4) greisen W-Mo-Bi ore. Common ore minerals are wolframite, scheelite, molybdenite, bismuthinite, cassiterite and various sulfides, and major gangue minerals are fluorite, garnet, diopside, vesuvianite, amphiboles, micas, feldspars and quartz (ECMDC, 1992).

Three sulfide concentrates of molybdenite, bismuthinite and pyrite were analyzed (Table 2).

#### 4.4 Huangshaping Deposits

Huangshaping Pb-Zn deposits are skarn and magmatic hydrothermal type occurring in Carboniferous sedimentary rocks around small Jurassic plugs of felsic porphyries. Their intrusive sequence is as follows: dacite, quartz porphyry, granite and granite porphyry, and these rocks are regarded as crust-remelting type (Zhong, 1996).

The ore deposits contain mainly galena and sphalerite, with some amounts of Cu, Ag, Mo, W, Sn and Bi minerals. The Pb-Zn ore bodies occur mostly around the hidden granite porphyry stock in the southeastern

sector of the ore field. The Cu mineralization is mainly related to granophyre.

A spatial zonation is observed from granite porphyry outward; the ore mineral assemblage becomes less complex, and the ore-forming temperature gets lower outward. The ore genetic type varies outwards from skarn type Fe (Sn) to skarn-hypothermal type W-Mo, then to hypo-mesothermal type Pb-Zn (Fe) or Cu-Pb-Zn. A temporal sequence from earlier to later of Fe, Fe (Sn), W (Mo), (Cu) Pb-Zn is identified (Deng, 1997). Hydrothermal alteration associated with Pb-Zn ores, other than skarnization, includes chloritization, sericitization, silicification and fluoritization.

Three sulfide concentrates of galena, sphalerite and pyrite were analyzed (Table 2).

## 5. Results and Discussion

### 5.1 Sulfur in Carbonates

The Devonian carbonates are very low in SSS content (average 1.8 ppm S, Table 1) and high in the  $\delta^{34}\text{S}$  values (average +30.9 ‰). Strauss (1999) gave a general value of +24.1 permil for sulfate sulfur in the Upper Devonian, so that our data are the highest among the Devonian carbonates. Sulfide sulfur is averaged as +8.6 permil (n=3, Table 1), which is again higher than the general Upper Devonian value of -2.8 permil given by Strauss (1999).

Lower Carboniferous carbonate at east of Yantang gives SSS content of 19.9 ppm S and  $\delta^{34}\text{S}$  values of +25.7 permil, which is again higher than the general value of +15.7 permil given by Strauss (1999) for the

Carboniferous carbonates.

The carbonate rocks collected from the mine sites have dark color containing possibly organic carbon and a large variation on sulfur contents and their  $\delta^{34}\text{S}$  values. Sulfide sulfur contents are high as 141-2050 ppm S, and the  $\delta^{34}\text{S}$  values are negative, being -1.6 to -16.6 permil. These sulfide sulfur could well be originally biogenic sulfur concentrated in local euxenic environment at the bottom of sea.

The SSS contents vary from 4 to 56 ppm S and  $\delta^{34}\text{S}$  values range from +9.8 to +20.6 permil, whose average of +16.9 permil is close to that of Strauss (1999).

## 5.2 Origin of Ore Sulfur

$\delta^{34}\text{S}$  data of sulfides from the Xihuashan mine vary from -2.1 to +0.3 permil and the average is -0.9 permil (Table 2), which is very close to the previous summary value of -0.4 permil for the Xihuashan-Dangping ore deposits (see Wang and Ishihara, 2000). The ore deposits belong to pegmatitic quartz vein type hosting in granite and therefore the  $\delta^{34}\text{S}$  values may be close to those of the host granites themselves, implying the granitic magma had ca. +2 permil value, in assuming sulfur in the ore fluid may have been fractionated a few permil (Sasaki *et al.*, 1984).

The exo-granitic polymetallic W deposits of the Shizhuyuan mine are higher, ranging from +5.2 to +8.4 permil and averaged as +7.0 permil (Table 2). Tong *et al.* (1995) described a beautiful zoning of the  $\delta^{34}\text{S}$  values of the constituent sulfides around the Qianlishan granitic body, ranging from -1.0 permil near the body but over +10 permil along the outer fringe (Fig. 2). The innermost value is similar to that of the endogranitic Xihuashan deposits. Thus, the Qianlishan felsic magmas may have had also ca. +2 permil  $\delta^{34}\text{S}$ .

If given ore solutions were cooled down after separation from the host granitic magmas, they might have oxidized by meeting meteoric water, and thus forming oxidized sulfur species in the ore solution which takes  $^{34}\text{S}$  out to leave  $^{32}\text{S}$ -enriched sulfides in the ore deposits far from the granite. A reverse zonal pattern of Fig. 2 strongly suggests that mixing of  $^{34}\text{S}$ -enriched sulfur from the carbonates by interaction between the magmatic ore fluid and the sedimentary wall rocks made  $\delta^{34}\text{S}$ -enriched nature of the ore solution in the fringe ore zone of the Shizhuyuan deposits.

The studied sulfides from Huashaping Pb-Zn deposits hosted in Carboniferous carbonates show high values between +12.6 and +14.2 permil (Table 2). Similar high values with slight east-west zoning has been reported in this mine (Fig. 3) by Tong *et al.* (1995). These high  $\delta^{34}\text{S}$  values are also considered originated in the carbonates due to the interaction of the ore fluids with the sedimentary wall rocks.

Sulfate sulfur contents of the Paleozoic carbonates are low as 1-20 ppm. However, modern marine car-

bonate shells and tests from a variety of taxa reveal typical values from 0.1 to 1 % equivalent sulfate (Pingitore *et al.*, 1995). Calcic travertine can contain up to 2.5 %  $\text{SO}_3$  (Takano *et al.*, 1980). It is assumed therefore that the carbonates had higher sulfate contents originally, but expelled later and now depleted. Resetting of the SSS sulfur in the carbonates could be happened through diagenesis but largely recrystallization due to granitic intrusion. Mechanism of SSS sulfur migration from the carbonates to ore deposits is an interesting and important subject to solve in future.

## 6. Conclusions

Mill concentrates of ore sulfides from three ore deposits of the South China Fold System were found to have the average values of -0.9 permil at Xihuashan, +7.0 permil at Shizhuyuan and +13.2 permil at Huangshaping, among which the latter two deposits are hosted in Paleozoic carbonates. Rock sulfur of the related granitoids of the former two deposits seems to have slightly positive  $\delta^{34}\text{S}$  values (ca. +2 ‰). Thus, another source to make the ore solution heavier is necessary for the Shizhuyuan and Huangshaping deposits. It is proposed therefore that  $^{34}\text{S}$ -enriched SSS of the host carbonates have been involved in the ore solution of the carbonate-hosted ore deposits.

## References

- Cai, B. J. (1980) The relationship of gypsum salt beds with endogenic copper and iron ores in the middle-lower Yangtze valley. *Geochimica*, **2**, 193-199 (in Chinese with English abstract).
- Chen, J. S. and Chu, X. L. (1988) Sulfur isotope composition of Triassic marine sulfates of South China. *Chem. Geol. (Isotope Geosci. Sec.)*, **72**, 155-161.
- Chen, J. S., Zhao, R., Huo, W. G., Yao, Y. Y., Pan, S. L., Shao, M. R. and Hai, C. Z. (1982) Sulfur isotope of Luohe iron deposit an Anhui Province. In *Research on Geology* (IGAS, Institute of Geology, Chinese Academy of Science, ed.). Cultural Relics Pub. House, Beijing, 279-286 (in Chinese with English abstract).
- Chen, Y. C., Huang, M. Z., Xu, J., Hu, Y. Z., Tang S. H., Li, Y. Q. and Meng, L. K. (1993) *Tin deposits of Dachang*. Geol. Publ. House, Beijing, 368 p. (in Chinese with English abstract).
- Chen, H. S., Zhou, S., Wei, L. and Yang, J. (1994) *Geochronology and isotope geochemistry of metallogenesis*. Beijing: Geol. Publ. House, 242 p. (in Chinese).
- Chu, X. L., Chen, J. S. and Wang, S. X. (1986) Study on fractionation mechanism of sulfur isotope and ore formation in Luohe iron deposit, Anhui. *Scientia Geologica Sinica*, **3**, 277-289 (in Chinese with English abstract).

- Deng, S. F. (1997) Zoning regularity of mineral assemblages in the Huangshaping lead zinc deposit. *Mineral Resources and Geology*, **11**, 314-318 (in Chinese with English abstract).
- Du, Y. S., Jiang, Y. H. and Ye, G. S. (1998) Study on features and metallogenic mechanism of Jinjiyan gold deposit, west Zhejiang Province. *Earth Science*, **23**, 262-266 (in Chinese with English abstract).
- ECMDC (Editorial Committee of Mineral Deposits in China) (1992) Mineral Deposits of China. Vol. 2, 271-279.
- Fu, M., Changkakoti, A., Krouse, H. H., Gray, J. and Kwak, T. A. P. (1991) An oxygen, hydrogen, sulfur, and carbon isotope study of carbonate-replacement (skarn) tin deposits of the Dachang tin field, China. *Econ. Geol.*, **86**, 1683-1703.
- Ishihara, S. and Wang, P. A. (1999) The ilmenite-series and magnetite-series classification of the Yanshanian granitoids of South China. *China. Bull. Geol. Surv. Japan*, **50**, 661-670.
- Ishihara, S., Li, W. D., Sasaki, A., Shibata, K., Matsuhisa, Y. and Terashima, S. (1986) Characteristics of Cretaceous magmatism and related mineralization of the Ningwu Basin, Lower Yangtze area, eastern China. *Bull. Geol. Surv. Japan*, **37**, 207-231.
- Ishihara, S., Sasaki, A. and Terashima, S. (1988) Sulfur in granitoids and its role for mineralization. *Proc. 7th Quad. IAGOD Sym.*, 573- 581. E. Schweizerbart'sche Verlagsbuchhandlung.
- Ishihara, S., Jin, M. S. and Sasaki, A. (2000) Source diversity of ore sulfur from Mesozoic-Cenozoic mineral deposits in the Korean Peninsula region. *Resource Geol.*, **50**, 203-212.
- Ishihara, S., Jin, M. S. and Kajiwara, Y. (2002a) Sulfur content and isotopic ratio of Cambro-Ordovician carbonate rocks from South Korea: A possible source for Mesozoic magmatic-hydrothermal ore sulfur. *Resource Geol.*, **52**, 41-48.
- Ishihara, S., Kajiwara, Y. and Jin, M-S (2002b) Possible carbonate origin of ore sulfur from Geumseong Mo deposits, South Korea. *Resource Geol.*, **52**, 279-282.
- Lei, X. Y. (1994) Stable isotope geochemical studies of tin-polymetallic deposits in eastern Guangdong. *Mineral Deposits*, **13**, 322-330 (in Chinese with English abstract).
- Liang, Z. H., Zhu, Q. Z., Han, M. H., Xia, A. N., Yu, W. J. and Zhang, Y. Z. (1985) Metallogenic conditions of the Zhilingtou gold-silver deposit in Zhejiang Province. *Geological Review*, **31**, 330-339 (in Chinese with English abstract).
- Man, F. S., Bai, Y. Z., Ni, S. B. and Li, T. (1983) Preliminary isotope studies of the Lianhuashan tungsten ore deposit. *Mineral deposits*, **2**, no. 4, 35-42 (in Chinese with English abstract).
- Pingitore, N. E., Jr., Meitzner, G. and Love, K. M. (1995) Identification of sulfate in natural carbonates by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta*, **59**, 2477-2483.
- Sasaki, A. and Ishihara, S. (1979) Sulfur isotope 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. Fifth Quad. IAGOD Sym. E.* Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 325-335.
- Sasaki, A., Ulricksen, C. E., Sato, K. and Ishihara, S. (1984) Sulfur isotope reconnaissance of porphyry copper and manto-type deposits in Chile and the Philippines. *Bull. Geol. Surv. Japan*, **35**, 615-622.
- Strauss, H. (1999) Geological evolution from isotope proxy signals - Sulfur. *Chem. Geol.* **161**, 89-101.
- Takano, B., Asano, Y. and Watanuki, K. (1980) Characterization of sulfate ion in travertine. *Contrib. Mineral. Petrol.*, **72**, 197-203.
- Thode, H. G., Dunford, H. B., Shima, M. (1962) Sulphur isotope abundance in rocks of the Sudbury district and their geological significance. *Econ. Geol.* **57**, 565-578.
- Tong, Q. M., Wu, R. H., Peng, J. L., Wang, S. M. and others (1995) Metallogeny of W, Sn, Pb, Zn, Au and Ag deposits in the Chenxian-Guiyang region, South Hunan, China. *MGMR Geol. Mem.*, Ser. 4, no. 50, 98 p. Geol. Publ. House, Beijing (in Chinese with English abstract).
- Ueda, A. and Sakai, H. (1984) Sulfur isotope study of Quaternary volcanic rocks from the Japanese Islands Arc. *Geochim. Cosmochim. Acta*, **48**, 1837-1848.
- Wang, P.-A. and Ishihara, S. (2000) Sulfur isotopic variation of Yanshanian magmatic-hydrothermal deposits in southern China. *Resource Geol.*, **50**, 257-268.
- Wang, Y. M., Zhu, J. A. and Yu Q. H. (1988) *Geology of lead-zinc deposits in Hunan Province*. Beijing: Geological Publishing House, 419 p. (in Chinese).
- Xia, Y. F. (1999) A tentative study on the origin of ore-forming materials of Tian Mashan sulfur-gold deposit. *Mineral Resources and Geology*, **13**, no. 1, 34-38 (in Chinese with English abstract).
- Xiang, X.K. (1992) The Cenozoic tectonic evolution and minerogenesis of the Taqian-Fuchun metallogenic belt in northeastern Jiangxi. *Geology and Prospecting*, **28**, no. 1, 20-27 (in Chinese with English abstract).
- Yang, X.S. (1991) Ore-controlling structure and source material of the Liqiao area, in southern Anhui Province. *Geology and Prospecting*, **27**, no. 2, 1-7 (in Chinese with English abstract).
- Zhang, D. Q., Li, D. X., Zhao, Y. M., Chen, J. H., Li, Z. L. and Zhang, K. Y. (1991) The Zijinshan deposit: the first example of quartz-alunite type epithermal deposits in the continent of China. *Geological Review*, **37**, 481-491 (in Chinese with English abstract).
- Zhao, Y. M., Tan, H. J., Xu, Z. N., Yuan, R. G., Bi, C. S.,

- Zheng, R. L., Li, D. X. and Sun, J. H. (1983) The calcic-skarn iron ore deposits of Makeng type in south-western Fujian. *Bull. Inst. Mineral Deposits, Chinese Academy of Geological Sciences*, **1**, 1-141 (in Chinese with English abstract).
- Zhong, Z. C. (1996) Magma rocks and their ore controlling characteristics in the Huangshaping mining area. *Mineral Resources and Geology*, **10**, 400-405 (in Chinese with English abstract).
- Zhou, T. F. and Yue, S. C. (1996) Isotope geochemistry of copper mineralization in Yueshan, Anhui. *Mineral Deposits*, **15**, no. 4, 341-350 (in Chinese with English abstract).
- Zhou, T. F., Yue, S. and Lan, T. (1994) Sources and transformation mechanism for sulfur component of the Anqing copper deposit, Anhui Province. *Volcanology and Mineral Resources*, **15**, 1-10 (in Chinese with English abstract).
- Zhou, T. F., Yue, S. and Lan, T. (1995) Sulfur isotope geochemistry of the Anqing copper deposit. *Earth Science, Jour. China Univ. Geosciences*, **20**, 705-711 (in Chinese with English abstract).
- Zhou, Z. (1984) Research on the genesis of the Mashan gold deposit in Tongling, southern Anhui. *Geological Review*, **30**, 467-476 (in Chinese with English abstract).

Received January 1, 2003

Accepted May 7, 2003

附表 1 地名对照表

Ceshui Formation	測水組
Dachang mine	大廠
Dangping mine	蕩坪
Guilin	桂林
Huangshaping mine	黃沙坪
Jinjiyan	金鷄岩
Lamo mine	拉麼
Lianhuashan mine	蓮花山
Liuxiashan mine	劉下山
Luoboling	蘿卜嶺
Luotuoshan Park	駱駝山
Makeng	馬坑
Mashan mine	馬山
Ningwu basin	寧蕪盆地
Qianlishan	千里山
Qingkeng mine	青坑
Qixingyan Park	七星岩
Sanjiaowo mine	三角窩
Shidengzi Carb. Formation	石磴子組
Shizhuyan mine	柿竹園
Shuimei mine	水美
Taipingli	太平里
Tashan mine	塌山
Tiandong mine	田東
Tongshan mine	銅山
Wuhengtian mine	烏橫田
Xihuashan	西華山
Yangshan	陽山
Yangshuo	陽朔
Yinshan	銀山
Yinkengshan	銀坑山
Zhuxi	朱溪
Zijinshan	紫金山

## 華南における2・3のマグマ-熱水性鉱床の硫黄の起源

石原舜三・王 平安・梶原良道・渡辺 寧

### 要 旨

華南褶曲帯に貫入するジュラ紀花崗岩類に成因的に関係したマグマ-熱水性鉱床から、花崗岩母岩(西華山)、炭酸塩岩母岩(柿竹園と黄沙坪)の3例を選び、硫黄同位体比の研究を実施した。華南褶曲帯は“ミオ地向斜”の古生代中期の堆積岩類からなり、デボン紀-石炭紀を中心に炭酸塩岩に富む。鉱床の平均値を知るために各鉱床の選鉱産物の $\delta^{34}\text{S}$ 値を分析すると第2表の結果、すなわち平均値で西華山鉱床(W)-0.9 ‰ (n=3)、柿竹園鉱床 (Sn, Cu, Pb, Zn) +7.0 ‰ (n=3)、黄沙坪鉱床(+13.2 ‰, n=3)が得られた。柿竹園鉱床では花崗岩(-1.0 ‰)から南東(+10.4 ‰)へゾーニングが著しい。西華山および柿竹園鉱床の生成に関与した花崗岩マグマは+2 ‰程度の $\delta^{34}\text{S}$ 値を持つものと考えられ、従って炭酸塩岩類を母岩とする柿竹園、黄沙坪鉱床は極めて高い $\delta^{34}\text{S}$ 値を持つと言える。

$^{34}\text{S}$ に富む岩石として炭酸塩岩に注目してそのSSS(構造置換態硫酸塩)硫黄の含有量と $\delta^{34}\text{S}$ 値を測定した。デボン紀の炭酸塩岩は低い含有量(平均1.8ppm S)と高い $\delta^{34}\text{S}$ 値(平均+30.9 ‰)を示した。この $\delta^{34}\text{S}$ 値は上部デボン系に与えられる一般値+24.1 ‰より高い。一方上部石炭系の値は+25.7 ‰であり、これも一般値+15.7 ‰よりも高く、華南の炭酸塩岩類のSSSの $\delta^{34}\text{S}$ 値は世界のその他の地域と比べて一般に高い値を持つと言えるが、今後のさらなるデータの蓄積が必要である。SSS硫黄含有量は現世の炭酸塩岩の含有量(0.1 ~ 1 ‰S)よりも著しく低い。以上の結果から西華山鉱床は+2 ‰前後の $\delta^{34}\text{S}$ 値を持つ花崗岩マグマから分離した熱水から生成したが、柿竹園鉱床の主要部分と黄沙坪鉱床は母岩の炭酸塩岩類のSSSが続生作用や花崗岩類の貫入に伴う熱水鉱化変質作用により溶出し、鉱床に移動・濃集したものと推察される。