Geological features and S isotope composition of tin deposit in Dachang ore district in Guangxi

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Abstract: The geological investigation of the Dachang ore field was carried out in detail, and the geological characteristics of the deposits, consisting of the Tongkeng and Dafulou deposits, were observed and researched systematically. It suggests that the mineralization types of Changpo ore are composed of cracking vein, thin vein, bedded vein and thin vein-net vein disseminated types. The cracking vein ore is usually lens-shaped in the vertical direction. The thin vein ore is always characterized by a stable trend and tendency. The bedded ore always occurs along the strata in the way of filling and metasomatism in the fracture system. In terms of Bali-longtoushan ore, it is characterized by complicated mineral components and a variety of minerals. More generally, ore textures consist of the anhedral-subhedral shapes and thin particle, and secondary with the interstitial texture, solid solution separation texture, dissolution texture, corona texture, and crushing texture, yet ore structures include the massive, veinlet, disseminated, banded, miarolitic, biological residual and brecciated structure. In addition, the sulfur isotopes of the metal sulfide were analyzed. The results show that the $\delta^{34}S$ values of Tongkeng ore range from −0.30% to 1.38% with more dispersed characteristics, yet in terms of Dafulou ore, the $\delta^{34}S$ values are from −0.15% to 0.22% which are characterized by more focused. This indicates that the sulfur isotope composition has large difference between the different deposits. The sulfur isotope values of the Dafulou ore are concentrated relatively, yet are dispersed for the Tongkeng ore. Likewise, there are also divergences of sulfur isotopes for the different minerals. The sulfur isotope values of pyrrhotine are dispersed, yet are homogeneous for pyrite. In short, the divergence of the sulfur isotope is reflected in both the different deposits and minerals, all of these may account for the difference of sulfur sources.
Key words: deposit geology; sulfur isotope; sulfur sources; Dachang tin deposit

1 Introduction

The world-famous Dachang tin ore deposit, which situates in Nandan county of Guangxi province, southern China, is one of the largest tin ore in the world [1−3]. The ore deposit is characterized by the large quantity of mineral assemblage, various mineralization types, and huge amounts of resource reserves [4−6]. It has been mined for nearly 1000 years, but the formal exploration work mainly began in earnest in the 1950s by No.215 geological team of nonferrous geological exploration company of Guangxi. Overall, the tin-polymetallic ores show fine veinlike, stock veinlet, dissemination and massive structures [7,8]. These orebodies are stratiform and stratabound which are composed of cassiterite, sphalerite, pyrite, pyrrhotite, arsenopyrite and jamesonite, with minor franckeite, boulangerite, zinckenite, marcasite, colloidal pyrite, chalcopyrite, stibnite and galena [9−11].

Currently, it generally agrees with the correlation between the shallow vein ore and the Longxianggai granite. However, there are three different views about the medium and deep layer ore [2,4−6,12−14]. The first view considers that the ore forms in Yanshan period and belongs to the epigenetic metasomatic-filled deposit,

which is relevant with granite. The second view considers that the deposit forms in Devonian period and belongs to the syndepositional exhalative deposit, which has no relationship with granite. However, some scholars proposed the view of superimposed mineralization, which has the characteristics of layer controlling and multiple ore sources.

About the genesis of the Dachang tin deposit, a lot of studies have been done since the deposit was found. HAN and HUTCHINSON [15] concluded that the ore source of the Dachang vein ore was relevant to the intrusive body, whereas the layer ore was irrelevant to the intrusive body. CAI et al [16] pointed out that the Tongkeng-Changpo vein and layer orebodies share the same material source based on the fluid inclusions and the He, Ar, and S isotopes, and the mineralization is relevant with the Yanshanian tectonic and magma thermal events. LIANG et al [17] thought that with regard to the different types of ore bodies in Dachang ore field, the prime sulfur source was identical, the changes of sulfur isotope rate were related with process and environment of mineralization, and in the process of down-up migration of the ore-forming fluid with the same source, the evolutionary mechanism of sulfur isotope was the same, which included the mix of wall rocks. Zinc−copper ore body was a typical source of magmatic sulfur, and tin ore body was characterized by the mixed sulfur. In the early stage, the magmatic sulfur was the main source, and latter was the mixed sulfur.

About the sulfur isotope characteristic of Dchang tin-polymetallic ore deposit, much research works have been done and a lot of useful views were put forward with regard to the genesis, metallogenic mechanism, fluid evolution and material sources. Most of the sulfur isotope compositions of the vein ore and bedded ore show good consistency, indicating their similar sulfur source. Recently, LIANG et al [17] also analyzed and studied the sulfur isotope composition aiming at the different ore types and mineralized occurrences of the Dachang tin ore deposit. The result indicates that the δ^{34}S values of the sphalerite range from −0.79% to 0.26%, with an average value of −0.34%. Despite a lot of research results, a considerable debate still exists mainly concerning the deposit mechanism in the field of earth science. Of course, the central issues of the dispute were focused on the deposit model, mineralization age and ore source [10,13,14,16,17]. Undoubtedly, with the development of the analysis and measurement technology, the understanding of the ore deposit gradually becomes more and more thorough.

Recent mining exposures of the Dachang tin deposit provided an ideal opportunity for detailed underground investigation and systematic sampling. So, based on the previous academic results, some representative samples of the recently developed area were studied, ore body and new geologic phenomenon were newly found, the geological features of the ore deposit were described, moreover the ore sources and ore genesis were discussed based on the sulfur isotope geochemistry of the sulfide. The research results can supply new data to the ore genesis of Dachang tin-polymetallic deposit.

2 Geological setting

The Danchi ore belt lies in the southern border from the Proterozoic to the early Paleozoic, yet it is located in the second rifting basin of the Youjiang basin [4]. A partially restricted sea basin was formed in this area during late Paleozoic as a result of depression along the NW-striking basement fault, with the fast depressing sector developed into the middle-late devonian Nandan-type basin in Guangxi. The belt formed as a NW−SE trough, surrounded by shallow−water carbonate platform from two sides [9]. The trough has an area of 3000 km^2 (100 km in length and 30 km in width) and includes many ore deposits, of which the tin–polymetallic sulfide deposits in the Dachang ore field are the most important. This area experienced three great historical phases: the intracontinental and continental margin rifting stages from the Proterozoic to the early Paleozoic, the intracontinental and continental margin rifting stages from the Devonian to the early Permian, and the back-arc rifting stage from the late Permian to the Triassic [1,8]. The Danchi ore belt belongs to a fault basin, which is located in the Youjiang passive continental margin-rifting basin in the Hercynian−Indosinian phase.

In the Dachang metal district, the most important structures are the NW-trending faults (Fig. 1), such as overthrust fault, which developed parallel with the axis of the Dachang anticlinorium [3,4]. In addition, the NE-trending and SN-trending structures are also very important, especially at the intersection of the NW-trending and the NE-trending structures. The Longxianggai anticline and the Longxianggai fault are the major structural systems in this area, together with a series of parallel small folds. The main fold is asymmetrical with a tight north-west limb that is affected by the north east trending Longxianggai fault [17].

In the Danchi district, the tin-polymetallic ore belt spreads in the northwest-southeast for more than 100 miles, with the northwestern part of the ore belt beginning from the Guizhou and Guangxi border, and the southeastern border beginning from the southern Wuxu county. The southwestern border begins from the Yilan mercury deposit and the northeast border spreads along the Lama−Layi−Beixiang−Hongsha. As the main part of the Danchi ore belt, the Dachang tin ore field is rich with
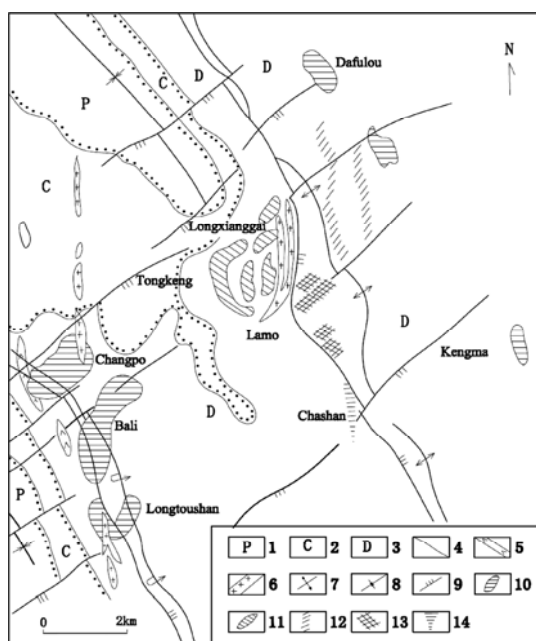
Fig. 1 Mineralization zoning of Dachang ore field (compiled from China Nonferrous Metals Industry Corporation, 1987): 1 — Permian limestone and siliceous; 2 — Carboniferous limestone; 3—Devonian limestone, shale and siliceous; 4—Parallel unconformity stratigraphic contact; 5 — Diorite porphyrite; 6—Granite and granite porphyry; 7—Anticline axis; 8—Syncline axis; 9—Faults; 10—Tin orebody; 11—Zn−Cu orebody; 12—Scheelite veins; 13—Wolframite veins; 14—Antimony veins

Sn, Zn, Pb, Sb, Hg, Cu and W. The orebodies lie within 4000 m thick sedimentary rocks from Devonian to Permian [4].

The host rocks of the deposit are Devonian carbonates, siliceous rocks [18] and shales (Fig. 1), which were characterized by typically banded, consisting mainly of siliceous rock and limestone, with lesser, but significant amounts of alternating thin beds of sulfides, K-feldspar-rich rocks. Major strata are composed of C- and S-rich black shales and argilloealeareous or silty sediments with a total thickness of over 1700 m [9]. The world-famous deposits of Tongkeng, Changpo and Gaofeng occur in middle and upper Devonian (Fig. 1). In the east belt, the deposits of Dafulou, Huile and Kengma are located in lower Devonian (Fig. 1), yet Lamo zinc−copper ore and Chashan stibium ore in the medium belt occur in upper Devonian [2].

3 Economic geology of tin-polymetallic deposit

3.1 Changpo deposit

The Changpo ore is the primary tin-polymetallic deposit that is famous for its large scale, and its vertical mineralization array from top to bottom is in the sequence of the cracking vein, thin vein, bedded vein, and thin vein-net vein disseminated types (Fig. 2). The Changpo deposit has 9 types of mineral combinations
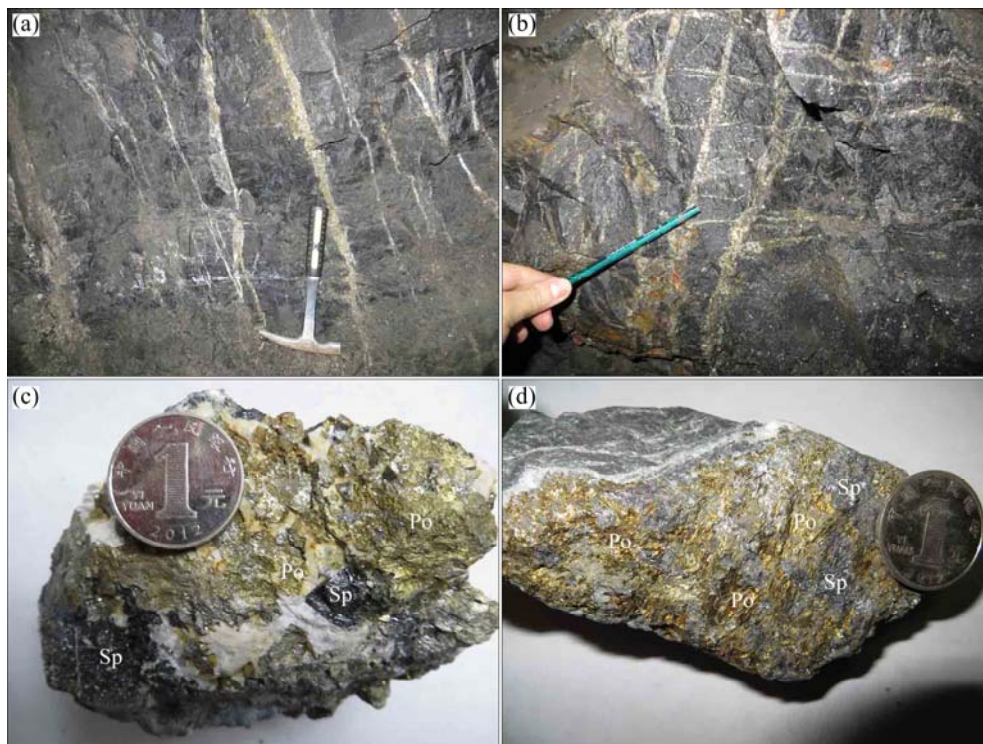

Fig. 2 Typical mineralization type and ore textures of Dachang tin ore field from Tongkeng ore deposit: (a) Steep thin vein ore (405 level); (b) Stockwork mineralization type (405 level); (c) Massive ore structure (355 level); (d) Disseminated mineralization type (505 level)

and more than 80 mineral kinds, among which more than 10 types of minerals have economic value.

3.1.1 Cracking vein ore

The cracking vein ore lies in the axis and eastern wing of the Changpo anticline, filling along the northeastern crack zone. The ore vein has a horizontal length in the range from 50 m to 500 m, but most has length in the range from 100 m to 250 m. The ore vein crowd is lens-shaped in the vertical direction.

3.1.2 Thin vein ore

The thin vein ore is located in the secondary anticline axis of the Changpo anticline eastern wing, which belongs to the spreading part of the horizontal cracking zone. It is characterized with a stable trend and tendency, but gradually disappears along both sides.

3.1.3 Bedded ore

With the representative Nos. 91 and 92 ores (Fig. 3), the No. 91 ore lies in the secondary anticline axis of the Dachang anticline eastern wing. The tin-polymetallic ore always occurs along the strata in the way of filling and metasomatism in the fracture system. The No. 92 ore is located in the deep parts of the northeastern direction horizontal cracking zone. Moreover, the Liujiang group siliceous hosts the No. 92 ore, and the ore occurrence is closely similar to the strata, which strikes in the E−W direction with a northern tendency. Moreover, thinning is obvious from the center outwards.

3.2 Bali-longtoushan deposit

The Bali-longtoushan deposit consists of mainly the Nos. 100 and 105 orebodies, which are characterized by complicated mineral components and various types of minerals. Aside from cassiterite, the metallic minerals consist of pyrrhotite, jamesonite, marmatite, pyrite, arsenopyrite, and marcasite, and a little of chalcopyrite, galena, stannite, herzenbergite, gudmundite, freibergite, miargyrite, boulangerite, polybasite, ultrabasite, discrasite and native antimony. They also include a little of gangue minerals, including quartz, calcite, fluorite and asphalt. The mineral texture mainly involves the anhedral to subhedral shapes, thin particle, and secondary with the interstitial structure, solid solution separation structure, dissolution structure, corona texture and crushing structure. Moreover, the ore is characterized by the construction of the massive structure, veinlet structure, disseminated structure, banded structure, miarolitic structure, biological residual structure and brecciated structure.

4 Methodology

The sulfur isotope research in identifying the genesis of the ore deposit is very useful. Yet, the composition of sulfur isotope is very complicated, which partly because of the various forms of sulfur, such as the natural sulfur and its four valence states of +6, +4, −1 and −2. Each valence forms a significant number of compounds, among which isotope fractionation always occurs [19]. In hydrothermal deposit, the sulfurs are mainly found in all kinds of sulfide minerals, mainly including sulfides and secondary sulfate minerals, and the sulfur sources in hydrothermal solution consist of the mantle sulfur, deep source sulfur, gypsum salt mineral and biogenic sulfur. The sulfur isotope composition of
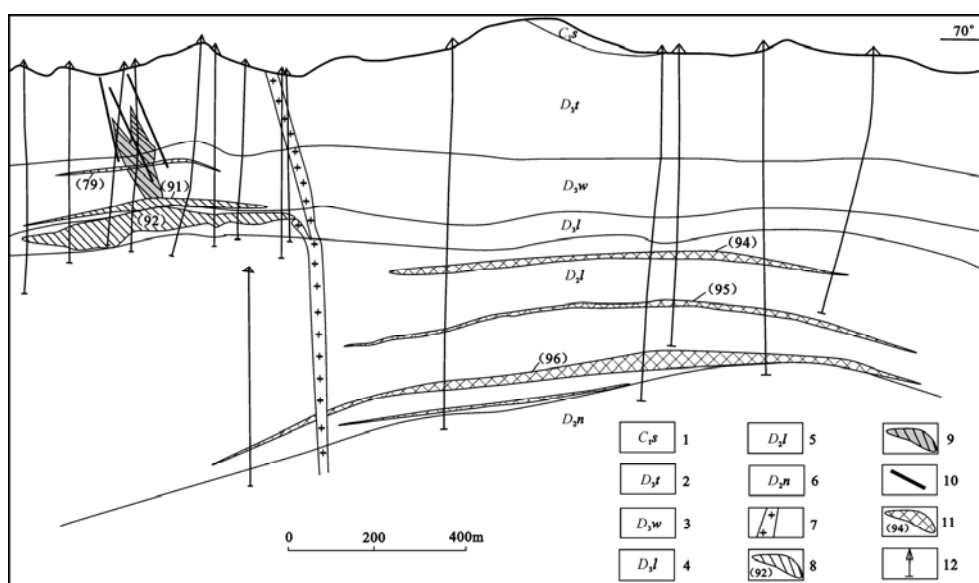

Fig. 3 Geologic cross-section of Changpo deposit (compiled from the Geology Team of Guangxi No. 215, 2007): 1—Lower carboniferous Simen group; 2—Upper Devonian Tongchejiang group; 3—Upper DevonianWuzhishan group; 4—Upper Devonian Liujiang group; 5—Middle Devonian Luofu group; 6—Middle Devonian Nabiao group; 7—Granite porphyry; 8—Tin-polymetallic ore; 9—Small vein tin-polymetallic ore; 10—Large vein tin-polymetallic ore; 11—Zn−Cu ore; 12—Drilling

crystalline mineral depends on the concentration of the total sulfur in hydrothermal, isotope composition, physical and chemical parameters, types of crystalline minerals and relative quantity [20].

In this study, 13 sulfur isotope samples (consisting of one galena, seven pyrite, and five pyrrhotite samples) were collected from the latest tunnel. Samples for analysis, which can reflect the new phenomenon and feature of the mined ore body recently, were collected from Tongkeng tin-polymetallic ore deposit of the west ore belt (5 samples) and Dafulou tin ore deposit of the east ore belt (8 samples). The metal minerals for analysis are composed of galena (1 sample), pyrrhotite (5 samples) and pyrite (7 samples). Samples of veinlike, stock veinlet, stratiform, disseminated and massive sulfide were collected, and their ore petrography and mineralogy were observed and described carefully by optical sheet and thin slice using light microscopy at Central South University, China. These samples were cleaned using distilled water, and then crushed to 180−250 μm. Specific minerals were then singled out (purity of higher than 98%).

Sulfur is an important element in most ore deposits [21−23]. Through analysis of sulfur isotope geochemistry, some problems can be studied, such as ore source, deposit model and mineralization age [24−28]. If mineral assemblages are simple, the value of $\delta^{34}S$ could represent the total sulfur value, which is usually expressed as $\delta^{34}S_{CDT}$ [29]. So, in order to discuss the genesis of Dachang tin ore, the sulfur isotope analysis was performed.

The sulfur isotopic compositions of 13 sulfide samples were analyzed on the MAT−251 gas mass spectrometer at the Isotope Geology Laboratory of Wuhan Institute of Geology and Minerals Resources, Chinese Ministry of Land Resources. Sulfur in the sulfide was oxidized directly into SO_2, and the values of $\delta^{34}S$ were measured by the isotope mass spectrometer MAT−251, which was made by the Finnigan Company. Results were expressed using the International Standard CDT. The analytical procedure usually yielded an in-run precision of ±0.02% under a given conditions of 20 °C and 30% humidity. The calibrations were performed with regular analyses of internal $\delta^{34}S$ standard samples.

5 Results

In this study, the data listed in Table 1 show that the $\delta^{34}S$ values of sulfides from the Dachang tin deposit vary from −0.30% to 1.38%, but are mainly within the range of −0.30% to 0.22% (Fig. 4).

Specifically, in terms of the Dafulou ore, the $\delta^{34}S$ values range mostly from –0.15% to 0.22%, yet the Tongkeng ore deposit is characterized by a larger scope

of $\delta^{34}S$ values than Dafulou ore (Table 1), ranging from −0.30% to 1.38%.

Table 1 Sulfur isotope composition of sulfides of Dachang ore field in Guangxi province

| Order No.	Ore deposit	Sample No.	Mineral	$\delta^{34}S_{V\text{-}CDT}$ /%
1	Dafulou	Y28-7	Galena	0.22
2	Dafulou	Y29-4	Pyrrhotite	0.09
3	Dafulou	Y03-1	Pyrrhotite	0.21
4	Dafulou	Y16-4	Pyrrhotite	−0.15
5	Dafulou	Y03-2	Pyrite	−0.02
6	Dafulou	Y29-6	Pyrite	0.22
7	Dafulou	Y05-3	Pyrrhotite	0.18
8	Dafulou	Y05-3	Pyrrhotite	0.17
9	Changpo	Y015-100	Pyrite	1.38
10	Changpo	Y016	Pyrite	1.12
11	Changpo	Y028	Pyrite	−0.08
12	Changpo	Y024	Pyrite	−0.30
13	Changpo	Y017	Pyrite	0.87
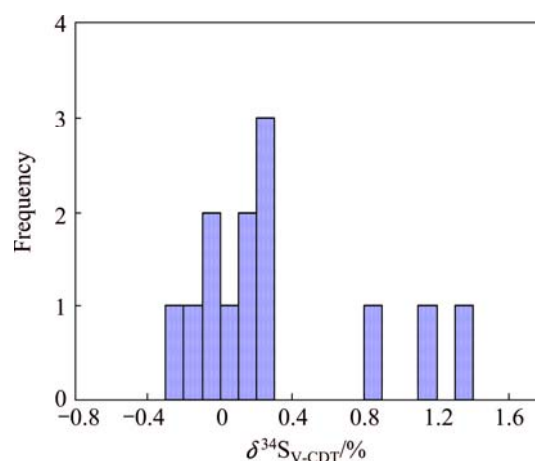
Fig. 4 Sulfur isotope composition histogram of Dachang tin deposit, Guangxi province

But, the differences of $\delta^{34}S$ for galena, pyrrhotite and pyrite also exist obviously (Table 1). The $\delta^{34}S$ values of pyrrhotite range from −0.15% to 0.21% (Table 1), showing more positive values. Likewise, the pyrite is characterized by large positive values. Although the ranges of $\delta^{34}S$ values obtained for different sulfides at each individual site overlap, the pyrite is typically more enriched in ^{34}S than coexisting galena and pyrrhotite (Table 1).

6 Discussion

In any event, case by case, the sulfur isotope composition, associated with metallogenic and

geological observations, allows distinctions to be drawn between the various types of deposits and then allows the potential mechanism for the origin of mineralization to be limited [30]. When tracing the ore-forming material source according to the sulfur isotope, the key is how to determine the sulfur isotope composition of possible source rock, and it can not simply use the sulfur isotope composition of a particular mineral to take the place of the sulfur isotope of the hydrothermal solution and speculate the sulfur isotope sources of ore deposit, especially in the ore deposit with complex mineral paragenesis [31].

FU et al [32] had analyzed sulfide samples (such as pyrite, sphalerite, arsenopyrite, pyrrhotite and chalcopyrite) of Changpo, Dafulou, Huile and Kengma deposited by analysis of sulfur isotope, which indicated that these deposited differ significantly in the sulfur isotope composition. LIANG et al [17] thought that the main ore mineral in Dachang ore field was sulphide, which was the main form of sulfur, yet the sulfate minerals were seldom seen. XU [33] classified the sulfur source of tin ore deposit, including the magma source and the mixture sources of magma and stratum, and also pointed out the percentage of the total sulfur isotope for the typical magmatic sulfur deposit was from −0.2% to 0.6%, but the mixed source sulfur was generally greater than 1.2%, and the value of δ^{34}S has lager positive value and bigger variation range. HAN and MA [34] pointed out that the sulfur source of ore deposit was diverse, which could be divided into three types roughly, such as the mantle sulfur, crust sulfur and mixed sulfur.

The sulfur isotope composition of the Dafulou deposit is in the range from −0.15% to 0.22%, which indicates the typical magmatic sulfur source. Yet, the sulfur isotope values of the Tongkeng deposit range from −0.30% to 1.38%, with the larger positive value (e.g. 1.38%, 1.12%, 0.87%) and a greater range of values, which suggests the typical characteristics of mixed sulfur source. It is not difficult to find out that the sulfur source shows surprising differences to the cassiterite sulfide deposits, which locates at the east and west ore belts, respectively.

In the Dachang ore field, it exists certain difference between the Tongkeng deposit in the west ore belt and the Dafulou deposit in the east ore belt for the sulfur isotope composition. The sulfur isotope values of the Dafulou ore are concentrated relatively, yet are dispersed for the Tongkeng ore which occupy the maximum and minimum values (Fig. 5). The sulfur isotope compositions of the different metal minerals have different characteristics, among which the sulfur isotope values of pyrrhotite are dispersed, but are homogeneous for pyrite (Fig. 6). In the Dachang ore field, the different deposits and metal minerals possess different sulfur
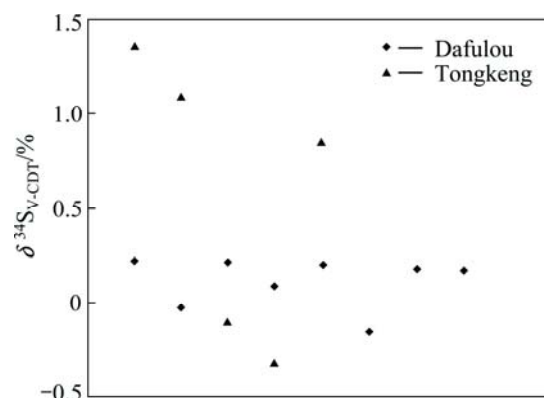

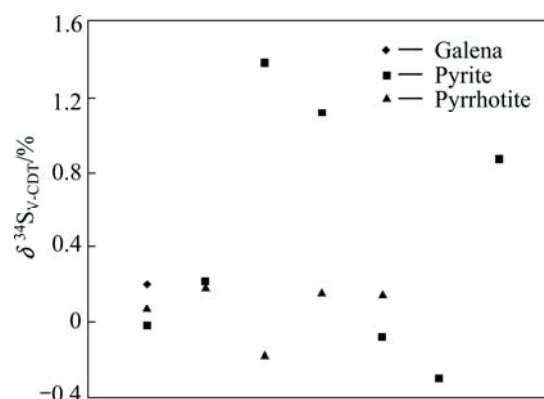**Fig. 5** δ^{34}S scatter diagram of sulfide from different deposit of Dachang ore field, Guangxi province

Fig. 6 δ^{34}S scatter diagram for different sulfide of Dachang ore field, Guangxi province

isotope compositions, indicating that the sulfur source may not be the same.

The composition of sulfur isotope in hydrothermal minerals is not only determined by the δ^{34}S value of the source materials, but also the physical and chemical conditions, which influence the migration and deposition of minerals [29,34]. Similarly, ZHENG and CHEN [31] also pointed out that sulfur isotope composition of hydrothermal sulfide depends on not only their source area but also the features of the closed system. Under the condition of a closed system, the precipitation of mineral sulfur results in the decrease of content of dissolved sulfur in hydrothermal. As long as it is different in the sulfur isotope composition between the precipitation mineral and total sulfur, the residual part of the sulfur isotope composition will also change, leading to the following mineral sulfur isotope composition of precipitation change, the direction of change is also related to hydrothermal redox condition, and in this case deposit occurs. So, the difference of sulfur isotope in the Dachang ore field may be related with the metallogenic environment [35,36], mineralization process and metallogenic dynamics.

7 Conclusions

1) The Changpo ore is composed of various mineralization types, such as the cracking vein, thin vein, bedded vein and thin vein-net vein disseminated types. The cracking vein ore is usually lens-shaped in the vertical direction. The thin vein ore is characterized by a stable trend and tendency. The bedded ore always occurs along the strata in the way of filling and metasomatism in the fracture system.

2) Bali-longtoushan ore is characterized by complicated mineral components and a variety of minerals. Ore textures consist of the anhedral to subhedral shapes and thin particle, and secondary with the interstitial texture, solid solution separation texture, dissolution texture, corona texture, and crushing texture. Ore structures include the massive, veinlet, disseminated, banded, miarolitic, biological residual and brecciated structure.

3) The sulfur isotope composition has certain difference to the different deposits. The sulfur isotope values of the Dafulou ore are concentrated relatively, yet are dispersed for the Tongkeng ore. Likewise, with regard to the different metal minerals, there are differences to sulfur isotopes. The sulfur isotope values of pyrrhotite are dispersed, but are homogeneous for pyrite.

4) The different deposits and metal minerals are characterized by the different sulfur isotope compositions, which probably indicate their different sulfur sources. To the Dafulou deposit, it is characterized by the typical magmatic sulfur source, yet it shows the mixed sulfur source for the Tongkeng deposit. The results probably indicate their distinctive metallogenic environment, mineralization process and metallogenic dynamics.

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广西大厂矿区锡矿床地质特征及硫同位素组成

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摘 要：对大厂矿田进行详细地质调查并对铜坑和大幅楼矿床进行系统观察与研究，结果表明：长坡矿床主要由裂隙脉型、细脉型、似层状、细脉－网脉浸染状等矿化类型组成。裂隙脉型矿化在垂向上通常呈透镜状，细脉型矿化具有稳定的走向与倾向，似层状矿化一般沿地层中的断裂系统充填和交代变化；巴力－龙头山矿床矿物组分复杂、种类繁多。矿石结构以他形－半自形以及细粒为主，其次为填隙结构、固溶体分离结构、溶蚀结构、反应边结构以及压碎结构等；矿石构造包括块状、细脉状、浸染状、条带状、晶洞状、生物残余和角砾状等构造。同时，对金属硫化物的硫同位素进行分析，结果表明：铜坑矿床的硫同位素 δ^{34}S 值较分散，介于−0.30%~1.38%之间；而大福楼矿床硫同位素 δ^{34}S 值较集中，变化范围为−0.15%~0.22%，说明不同矿床的硫同位素组成存在较大的差异。大福楼矿床相对铜坑矿床而言，硫同位素组成具有更为集中的特点。同样，不同类型金属矿物的硫同位素组成也不同，磁黄铁矿的硫同位素较为分散，而黄铁矿的硫同位素组成更为均一。总体来看，硫同位素组成的差异既体现在矿床尺度上也表现于不同类型的矿物上，这可能受到矿床不同的硫来源影响。

关键词：矿床地质；硫同位素；硫源；大厂锡矿

(Edited by Chao WANG)