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# Ore-forming material of Dachang tin deposit in Guangxi, China: Lead isotope evidence

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**Abstract:** For revealing the ore sources of the Dachang tin−polymetallic ore deposit, the lead isotopes were analyzed systematically by using the single minerals of sulphides, including pyrite, pyrrhotite, sphalerite, and galena. Then, the mineral sources and their characteristics were discussed based on the classical lead isotope discriminating model. The results show that the lead isotope ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ range from 17.478 to 18.638, 15.440 to 15.858, and 37.556 to 39.501, respectively. According to Zartman lead model, the ore lead contains the upper crust composition; however, the granite does not provide all ore leads, and other material sources exist. Obviously, the ore deposit belongs to the result of the combined effect of crust−mantle. The source rocks are characterized by a certain degree of similarity with the island arc material. Moreover, its distant origin in the upper and lower crusts may be related to the subduction island arc material or oceanic crust. The mantle-derived material may have a certain status in the source region. Meanwhile, based on the lead isotope three-dimensional topology projection vectors, the ore leads are concentrated in zone *A*, which indicates the characteristics of Yangtze lead isotope province and a possible genetic relationship with Yangtze block.

**Key words:** lead isotope; ore source; ore genesis; Dachang tin-polymetallic deposit; Guangxi

## 1 Introduction

The Dachang tin deposit in Guangxi, China is a world-famous tin metal production base with several superlarge-scale tin−polymetallic ore deposits and is regarded as the best natural laboratory for investigating tin−polymetallic ore deposits [1,2]. The Tongkeng−Changpo tin−polymetallic ore deposit, which lies in the western ore belt of the Dachang ore field, consists of vein and layer ores [3,4]. The cassiterite−sulfide ores lie in the shallow part; however, the skarn zinc−copper deposits are located in the deep part [3]. Due to the super-large scale and the specificity of the Dachang ore deposit, plenty of geological researches have been done since its finding, i.e., the metallogenic prediction, the prospecting model, the mineralization mechanism, the mineralization age and the ore source [5,6]. Yet, considerable debate still exists mainly concerning the deposit mechanism in the geoscience field [7−9]. Of course, the central issues of the dispute are focused on the deposit model, mineralization age, and ore source, etc.

Undoubtedly, the sources of ore-forming materials of ore deposit have long been also the focus of argument in the academia and are difficult issue in researching on ore deposits, which is the key to understand the genesis of the ore deposit. In the Dachang ore field, the research results about the source of ore-forming materials are very abundant. Recently, LIANG et al [10] have investigated the isotopes of orebodies with different types and occurrences and believed that lead in the Dachang ore

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field originated from crust caused by magmatism, as well as partly from the upper crust and mantle. With the development of the analysis and measurement technology, the understanding to ore deposit is becoming deeper gradually than before.

Lead isotope composition is an effective geochemical tracer to crustal evolution, ore genesis, and ore-forming material source, among others [11−17]. Three different radiogenic lead isotopes are created by the wide half-life matrix, yet two of them are the same element, so it is a powerful tool for the studying of mantle or crust evolution [18,19]. By using different isotopes to the relevant event, the property of the differentiation events can not only be discriminated possibly, and there may be restrictions on their epochs. Lead isotope geochemical tracing system is very useful, which can not only indicate the crustal evolution but also reveal the origin and material sources of the ore deposit. The changes of lead isotopic composition are mainly due to the radioactive uranium, thorium decay reaction, and should not be affected by the changing of geochemical environment after its formation.

In minerals, without or extremely low U and Th, they can be ignored compared to the lead content. After the formation of mineral, there was no such circumstance of joining obviously for radioactive lead. It can reflect U−Th−Pb system, which supplies the metal material to original hydrothermal fluid, and characteristics of initial lead isotope composition. In addition, due to the big mass number of the lead isotope molecular and the slight difference of the relative mass between the different isotopic molecules, the isotope fractionation would not only occur when leaching from the source rocks, but also during transferring into the ore-forming hydrothermal fluid and migrating, even if the changing of physic-chemical condition of ore-forming hydrothermal fluid, their isotopic composition generally didn't change [20−23].

So, based on the recent samples, field investigation and lead isotope analysis, this study provides new data and material to strengthen the understanding to the ore sources of deposit and their genesis.

## 2 Regional geology

The world famous Danchi ore belt is located at the south margin of the Yangtze platform. It formed as a NW−SE trough, surrounded by shallow-water carbonate platform from two sides. The trough has an area of 3000 km$^2$ (100 km in length and 30 km in width) and includes many ore deposits (Fig. 1), of which cassiterite sulfide deposit is the most important deposit type [24,25].

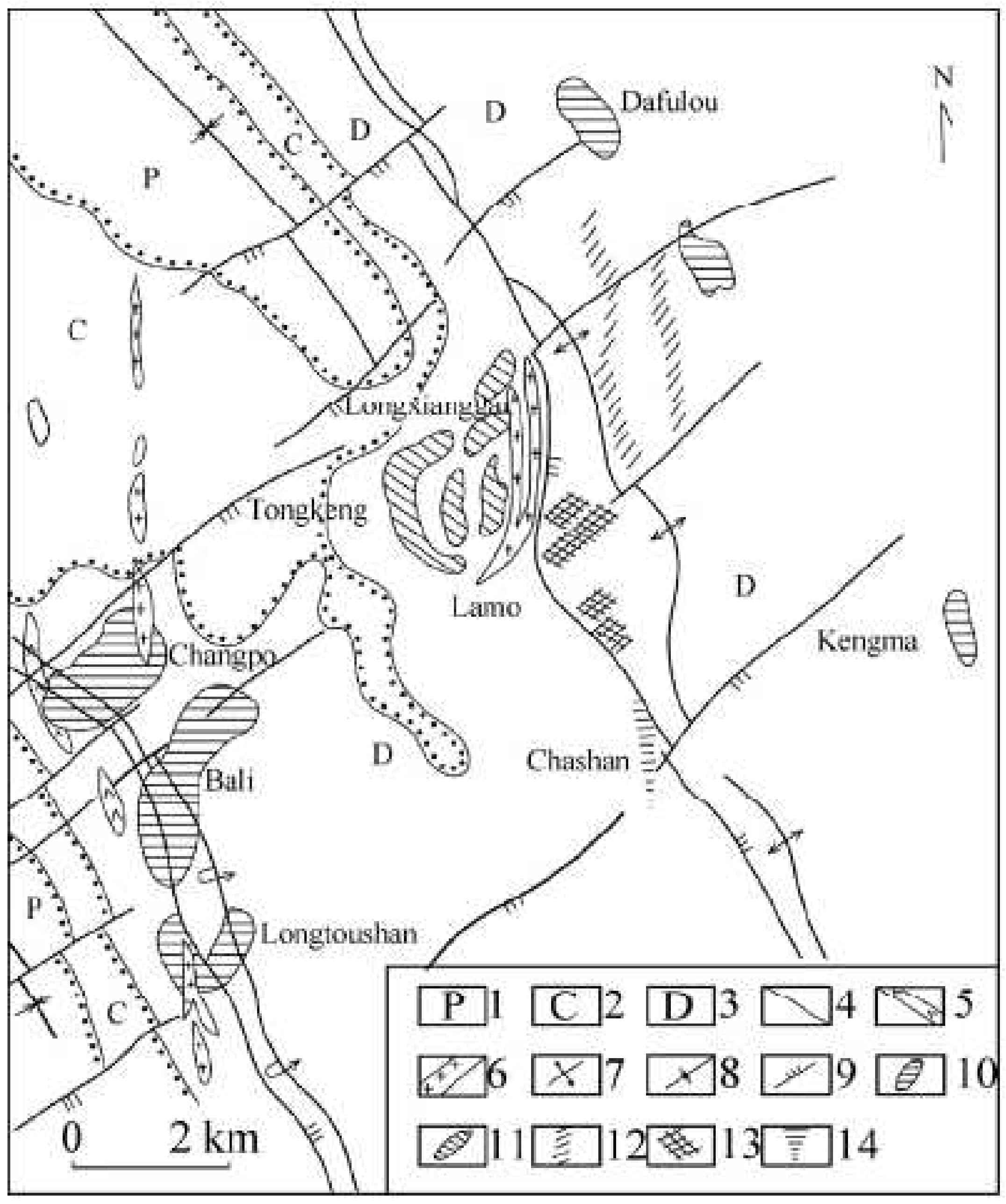


**Fig. 1** Mineralization zoning of Dachang ore field (compiled from China Nonferrous Metals Industry Corporation, 1987): 1 — Permian limestone and siliceous; 2 — Carboniferous limestone; 3—Devonian limestone, shale and siliceous; 4—Parallel unconformity stratigraphic contact; 5 — Diorite porphyrite; 6—Granite and granite porphyry; 7—Anticline axis; 8—Syncline axis; 9—Faults; 10—Tin ore; 11—Zn−Cu ore; 12—Scheelite veins; 13—Wolframite veins; 14—Antimony veins

The Longxianggai anticline and Longxianggai fault constitute the major structural systems in the zone, 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. And, affected by compression, there exist plenty of NW-trending pressure (or twisting) fractures that are parallel to the axis of Danchi anticline. The restricted sea basin formed 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, China. Major strata are composed of C- and S-rich black shales and argilloealeareous or silty sediments with a total thickness of over 1700 m [7].

On the basis of the regional structure, the Danchi mineralization belt is usually divided into three metallogenic belts [26], including the west ore belt (e.g. Changpo−Tongkeng tin−polymetallic ore), the middle ore belt (e.g. Lamo zinc−copper ore deposit, Chashan antimony−tungsten ore deposit), and the east ore belt (Dafulou cassiterite sulfide ore deposit and Kengma tin−zinc ore deposit) (Fig. 1).

The main magmatism occurs in the medium and late

Yanshanian, belonging to (super) shallow igneous rocks, which distributes in Longxianggai, Dachang and Mangchang in the form of dykes, rock strain, rock bed, etc. The intrusive rocks are composed of biotite granite, granite porphyry, quartz porphyry, fraidronite, diorite porphyry, and so on. The rocks are always characterized by small size and tremendous depth, and intruded along both sides of the Danchi fault. The current study shows that there is close relationship between intrusive rock and regional structure [27,28].

The Dachang tin−polymetallic ore field, which is one of the largest tin ore field in the world, situates in Danchi ore belt, Guangxi province, China. And, it is also just located at the joining part between Guangxi platform and Jiangnan uplift in northwest Guangxi, China [24]. The host rocks of the Dachang deposit are typically banded, consisting mainly of Devonian carbonate, siliceous rock and shale, with lesser but significant amounts of alternating thin beds of sulfides and K-feldspar-rich rocks. The ore bodies lie within a 4000 m thick succession of Devonian to Permian sedimentary rocks (Fig. 1).

## 3 Lead isotope analysis

### 3.1 Methodology

Lead isotope analysis was carried out in Wuhan Institute of Geology and Mineral Resources, Ministry of Land and Resources of China. After crushing and sieving the ore and rock samples, the fresh rock particles and single minerals, with purity of more than 98%, were picked out under the binocular microscope. Sulfide samples were washed with 0.15 mol/L HCl and high purity water. All of these samples were ground to below 74 mm, and decomposed in the Teflon PFA bottle using HCl and $HNO_3$. After complete decomposition, they were evaporated to nearly dry and transformed into 0.15 mol/L HCl and 0.65 mol/L HBr medium, then separated in Bio-RadAG 1×8 anion exchange column and leached with 1.0 mol/L $HNO_3$ and heated to dry. Lead isotope ratios were tested using a thermal ionization MAT−262 mass spectrometer with Si gel as the transmitter agent. The test was under the static model, controlling the mass fraction through the standard sample SRM 981 mass spectrometer. Moreover, the reported data were corrected for per-quality fractionation. Finally, the results were referred to the international standard sample NBS−981 [29,30].

### 3.2 Results

As shown in Table 1, the lead isotope compositions of the sulphide minerals in the Dachang ore district range from 17.478 to 18.638, from 15.440 to 15.858, and from 37.556 to 39.501 for the ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$, respectively. Yet, for different minerals, the isotope ratios have a certain variation range. As for pyrite, the ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ are from 17.478 to 18.630, from 15.525 to 15.705, and from 37.849 to 38.988, respectively. The ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ of pyrrhotite samples range from 17.517 to 18.269, from 15.440 to 15.647, and 37.556 to 38.515, respectively. And with regard to the sphalerite samples, the ratios of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ are from 18.438

**Table 1** Lead isotope compositions of metal sulfides from Dachang ore field in Guangxi, China

| Ore deposit | Sample No. | Mineral | Isotope ratio | | | Parameter | | |
|---|---|---|---|---|---|---|---|---|
| | | | $^{206}Pb/^{204}Pb$ | $^{207}Pb/^{204}Pb$ | $^{208}Pb/^{204}Pb$ | $\Phi$ | $\mu$ | Th/U |
| Tongkeng | Y015 | Pyrite | 18.630±0.001 | 15.683±0.001 | 38.866±0.004 | 0.578 | 9.60 | 3.81 |
| Tongkeng | Y016 | Pyrite | 18.630±0.001 | 15.705±0.002 | 38.941±0.006 | 0.580 | 9.65 | 3.85 |
| Tongkeng | Y024 | Pyrite | 18.454±0.001 | 15.647±0.001 | 38.623±0.001 | 0.585 | 9.55 | 3.80 |
| Tongkeng | Y026 | Sphalerite | 18.638±0.005 | 15.858±0.005 | 39.501±0.015 | 0.596 | 9.95 | 4.10 |
| Tongkeng | Y038 | Pyrite | 18.491±0.006 | 15.696±0.004 | 38.988±0.009 | 0.588 | 9.64 | 3.94 |
| Tongkeng | Y040 | Sphalerite | 18.438±0.004 | 15.621±0.005 | 38.738±0.010 | 0.583 | 9.50 | 3.85 |
| Dafulou | Y01-3 | Pyrrhotite | 18.269±0.011 | 15.647±0.008 | 38.515±0.026 | 0.597 | 9.57 | 3.85 |
| Dafulou | Y03-1 | Pyrite | 17.478±0.006 | 15.510±0.005 | 37.849±0.017 | 0.638 | 9.41 | 3.97 |
| Dafulou | Y03-2 | Pyrite | 18.044±0.007 | 15.525±0.006 | 38.026±0.014 | 0.599 | 9.36 | 3.74 |
| Dafulou | Y11-3 | Galena | 18.431±0.016 | 15.717±0.010 | 38.839±0.040 | 0.594 | 9.69 | 3.91 |
| Dafulou | Y21-1 | Pyrrhotite | 17.566±0.008 | 15.468±0.007 | 37.687±0.015 | 0.626 | 9.31 | 3.84 |
| Dafulou | Y29-2-1 | Pyrite | 18.369±0.003 | 15.667±0.002 | 38.678±0.006 | 0.593 | 9.60 | 3.87 |
| Dafulou | Y29-4 | Pyrite | 18.304±0.001 | 15.624±0.001 | 38.505±0.002 | 0.592 | 9.52 | 3.82 |
| Dafulou | Y30-2 | Pyrrhotite | 17.517±0.007 | 15.440±0.006 | 37.556±0.016 | 0.627 | 9.26 | 3.80 |

$\Phi$ is slope of initial isochron; $\mu$ is $w(^{238}U)/w(^{204}Pb)$.

to 18.638, from 15.621 to 15.858, and from 38.738 to 39.501, respectively.

The values of $\Phi$, $\mu$ and Th/U range from 0.578 to 0.638, from 9.26 to 9.95, and from 3.74 to 4.10, respectively, among which the sphalerite sample has the maximum values of $\mu$ and Th/U. Yet, the sample of pyrite has the maximum value of $\Phi$. According to the scatter diagram of $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$, overall, the data are characterized by the linear feature (Figs. 2 and 3).

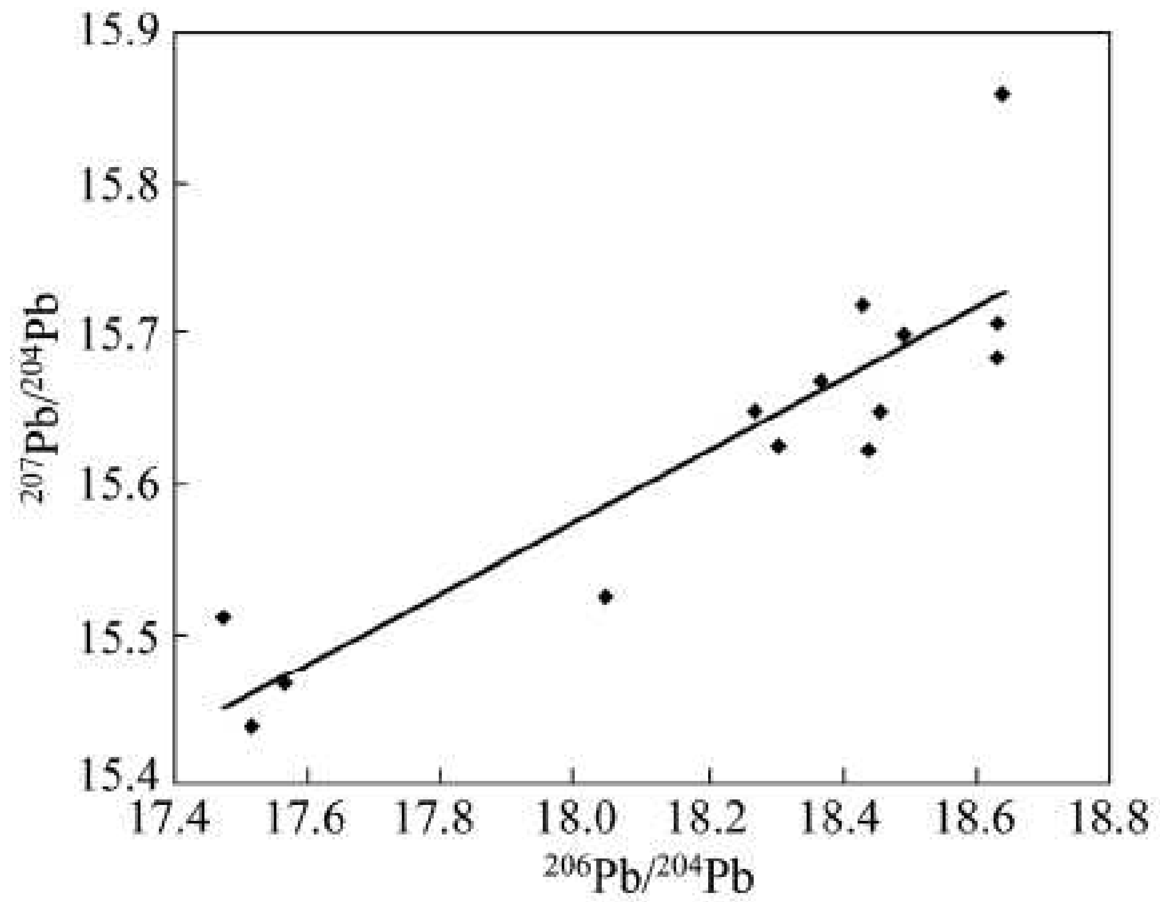


**Fig. 2** Scatter diagram of $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ of minerals from Dachang ore field, Guangxi, China

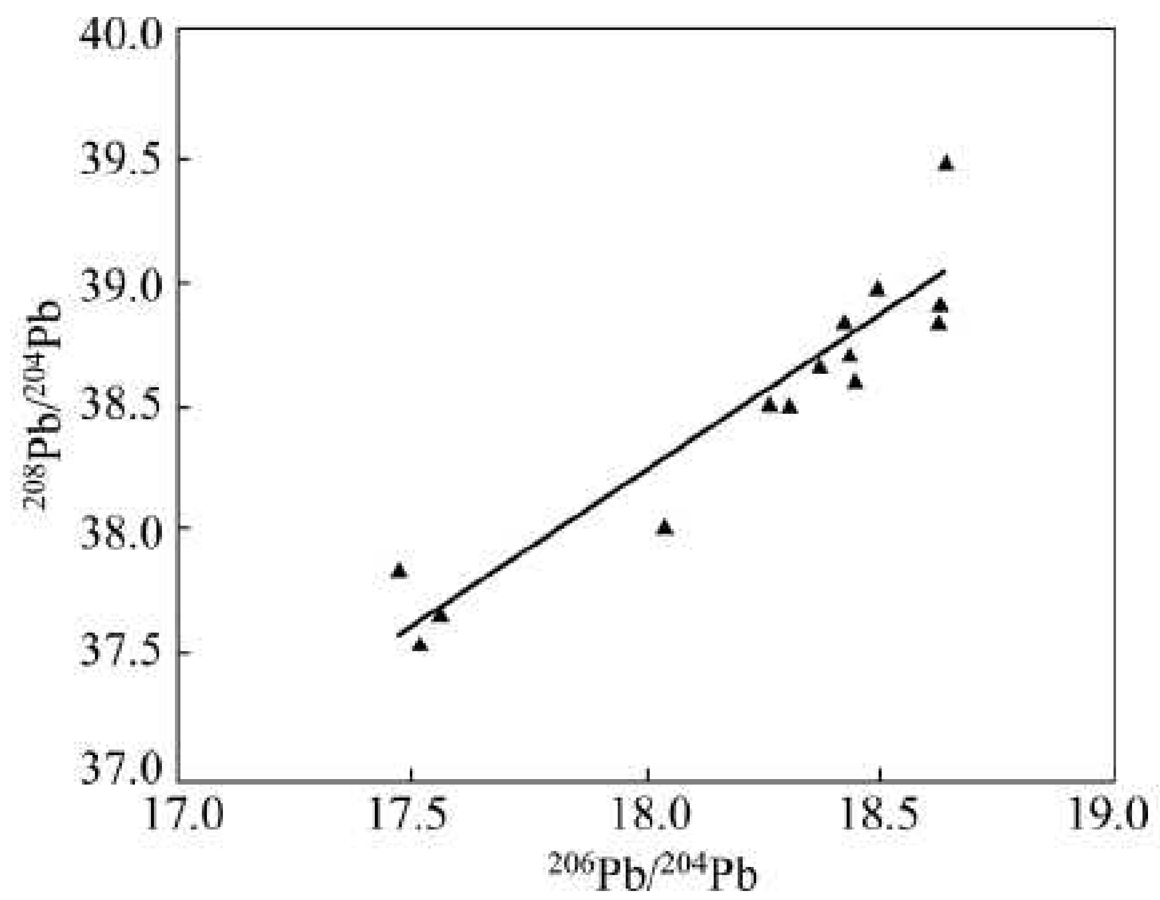


**Fig. 3** Scatter diagram of $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ of minerals from Dachang ore field, Guangxi, China

## 4 Discussion

### 4.1 Metal source(s)

The ore lead refers to ore minerals deposited in the environment of various hydrothermal, excluding U, Th, such as lead in the galena and pyrite. Its component is mainly constrained by the original lead in the source area, U/Pb, Th/U, namely $\mu(^{238}U/^{204}Pb)$, $v(^{235}U/^{204}Pb)$, $\omega(^{232}Th/^{204}Pb)$, Th/U and formation time, are basically not affected by the geochemical environment after its formation. By analyzing the composition of ore lead isotope, the characteristics of U−Th−Pb system of source area could be deduced, and then information about the source of ore-forming materials could be gained [23].

Geochemical tracing of ore-forming fluid activity has become a new trend. Through the fluid tracer of source, migration and its positioning, the whole process of fluid activity could be monitored, which is of great significance to recover the history and evolutional process of the fluid flow [31−33]. According to the characteristics of lead isotopic composition of ore minerals, wall rocks and Zartman lead model, it is of vital significance, such as tracing the source of ore-forming material, investigating the genesis and vertical zoning of the ore deposit [34].

The Zartman tectonic pattern is the most commonly used lead isotope tracer diagram [35,36]. In accordance with this model, the projecting points are mainly located between the orogenic belt and upper crust or on the top of the upper crust growth curve (Fig. 4) [35], suggesting that the ore lead contains the upper crust composition or is originated from the upper crust. Moreover, the granite does not provide all ore leads, and other material sources exist. In accordance with $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ growth curve pattern, the projection points are characterized by the concentrated distribution and locate between the lower crust and the orogenic belt, indicating that the upper crust provides a part of some lead for mineralization (Fig. 5) [35].

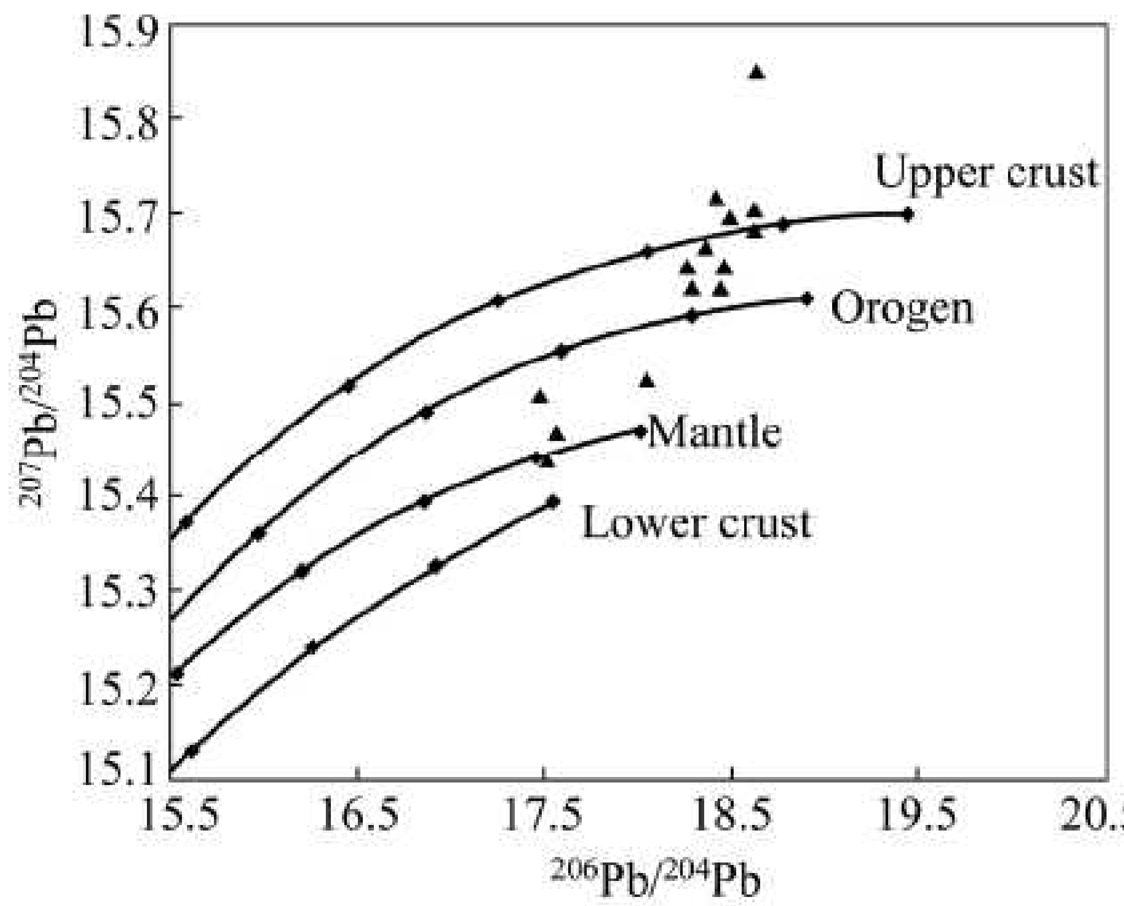


**Fig. 4** $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram of sulfides from Dachang ore field in Guangxi, China [35]

Many research results on the lead sources of the Dachang ore field play an important role in explaining some divergences, such as ore genesis and ore mechanism. LIANG et al [10] pointed out that different types and occurrences of orebodies are characterized by similar lead isotope compositions, which are mostly composed of crustal lead and a small amount of mantle-derived lead. The tectonic setting discrimination diagram of the lead isotope is a familiar method for investigating the lead source. The ore lead is relatively concentrated in the lead isotope tectonic pattern and projects onto the island arc zone, which is away from the upper crust, lower crust, and oceanic island volcanic (Figs. 6 and 7), indicating that the source rocks are similar to the island arc material. Moreover, its distant origin in the upper and lower crusts may be related to the subduction island arc material or oceanic crust. The mantle-derived material may occupy a certain position in the source region. The upper crust is the main tin−polymetallic ore source, but the mantle-derived material is also involved in mineralization. In general, metallogenesis is influenced jointly by the crust and mantle.

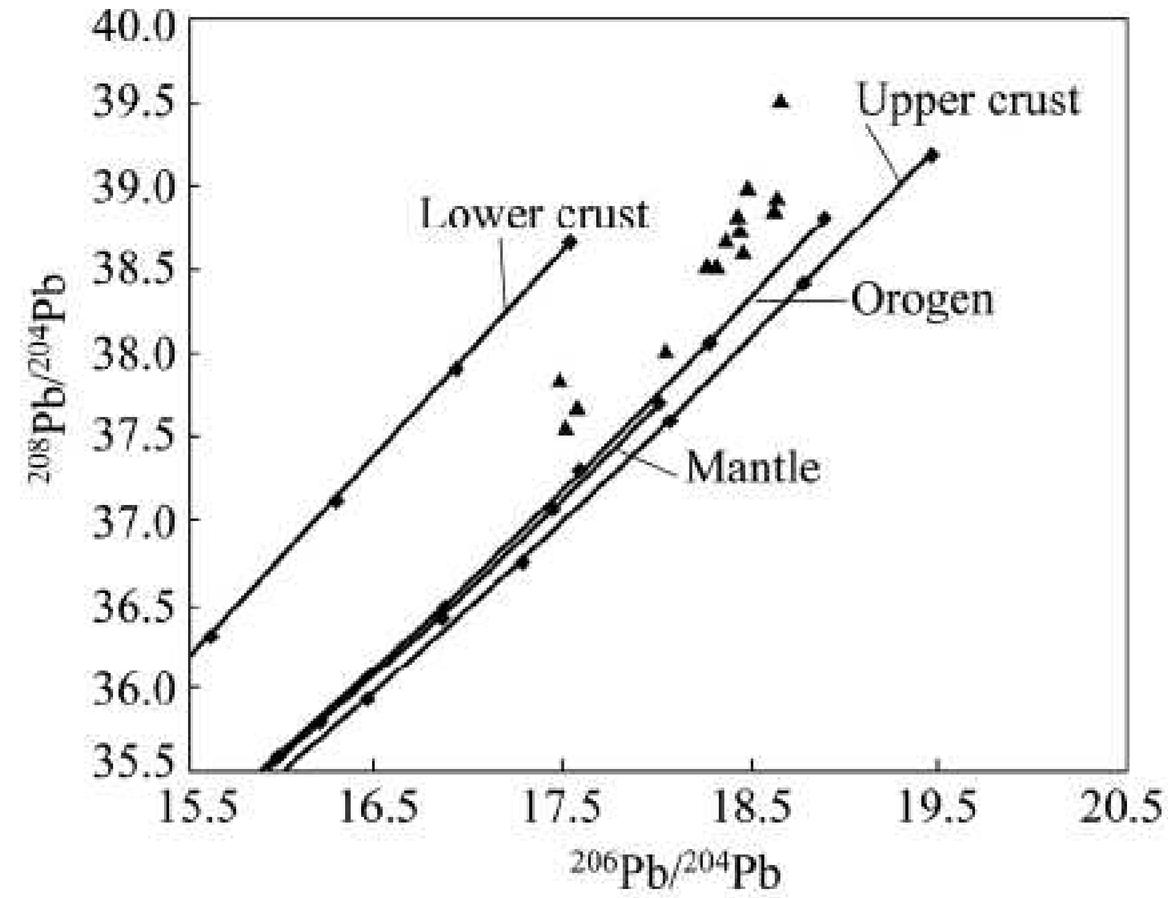


**Fig. 5** $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram of sulfides from Dachang ore field in Guangxi, China [35]

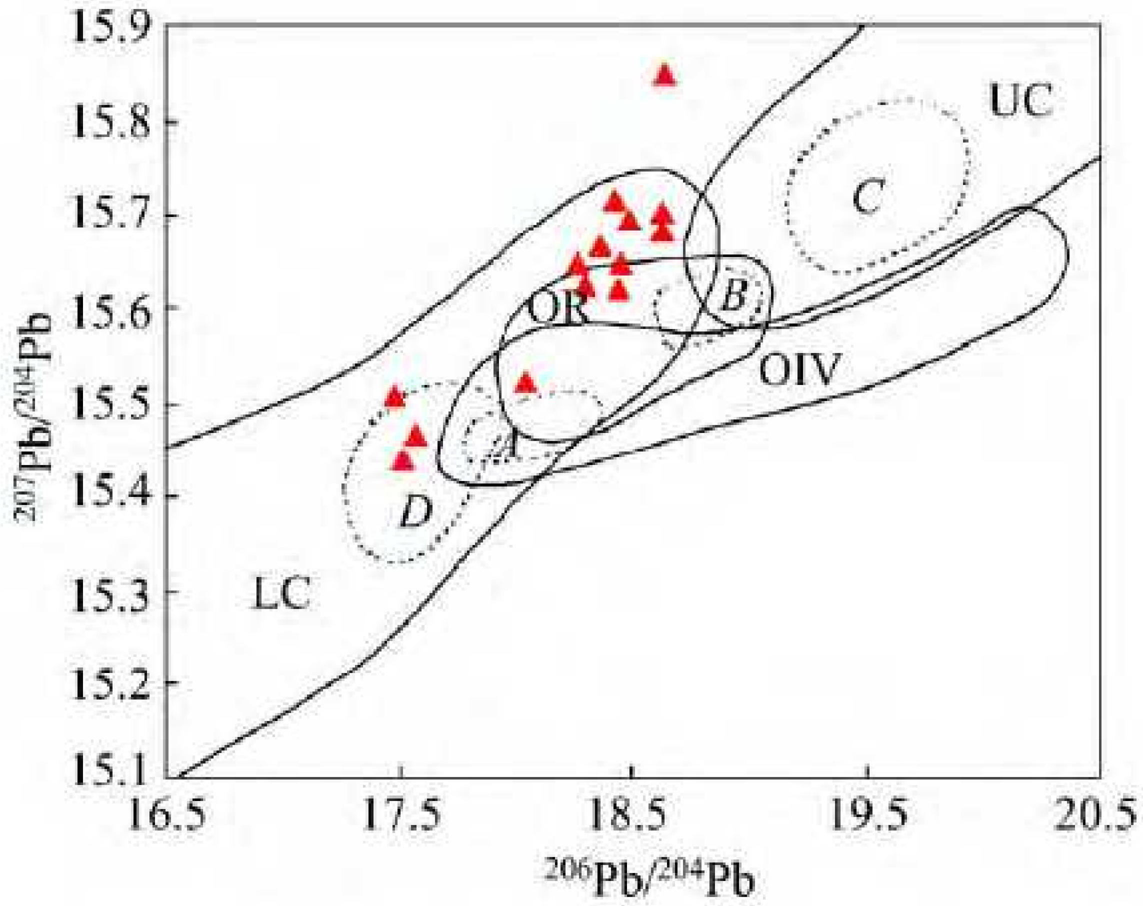


**Fig. 6** $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram for discriminating tectonic settings: LC—Lower crust; UC—Upper crust; OR—Orogen; OIV—Oceanic island volcanic [35]

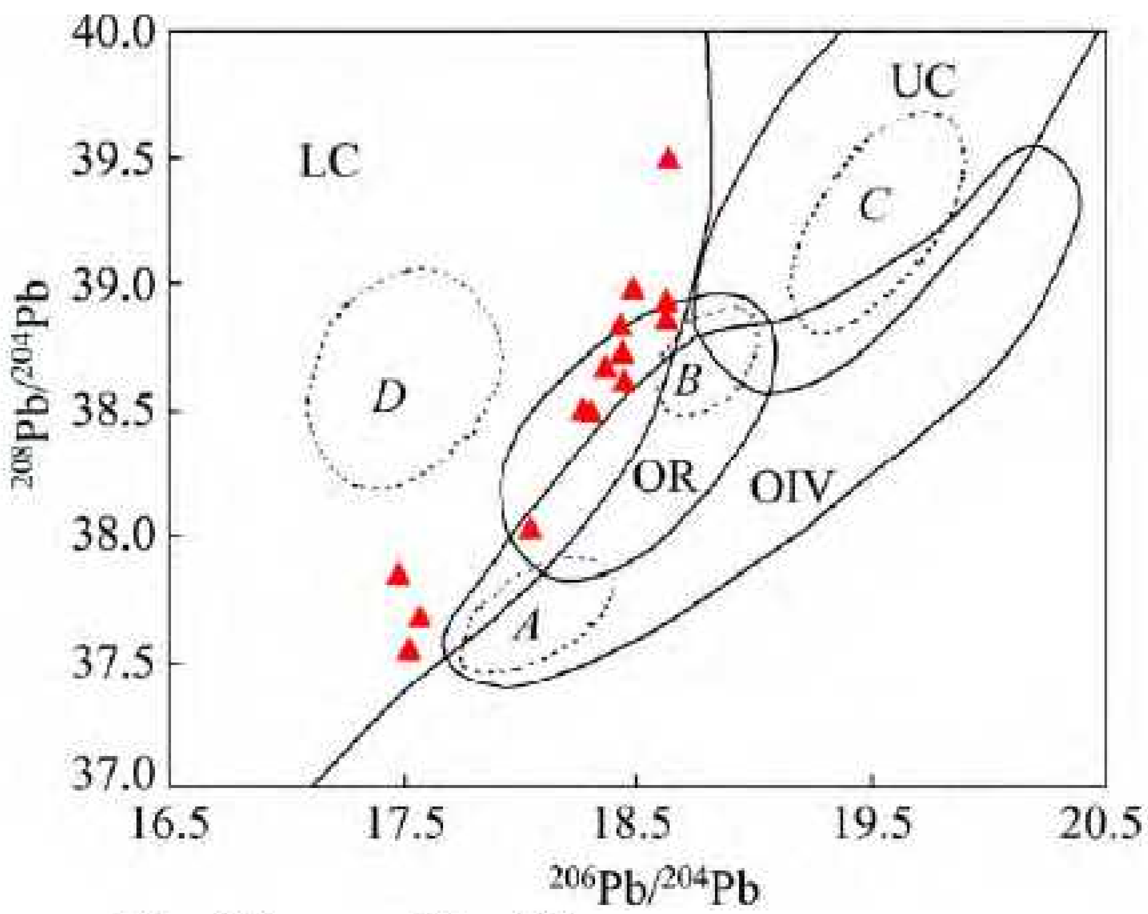


**Fig. 7** $^{208}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ diagram for discriminating tectonic settings: LC—Lower crust; UC—Upper crust; OR—Orogen; OIV—Oceanic island volcanic [35]

Overall, in accordance to the lead isotope analysis, in the Dachang ore field the upper crust is one of the lead sources; however, the mantle-derived material is involved in metallogenesis. In general, the ore formation is influenced by both the crust and mantle.

**4.2 Ore genesis**

The Danchi ore belt locates at the southwest side of the Jiangnan ancient land and the northeast of the Youjiang basin, just being the superimposed site of the Paleotethys and Pacific tectonic domain. And, the Dachang super large scale tin deposit situates at the deep fault between the southern China active block and the Yangtze stable platform, which experienced multicycle tectonic-magmatic activity [37].

Based on the study of lead isotopic composition of geologic body with various origins, ZHU [38−40] found that the lead sources of different origin geological bodies are significantly different, and according to the lead isotopic composition of a variety of geological bodies, he proposed the $\Delta\gamma$−$\Delta\beta$ ($\Delta\gamma$ is the relative deviation of $^{208}Pb/^{204}Pb$ with contemporary mantle; $\Delta\beta$ is the relative deviation of $^{207}Pb/^{204}Pb$ with contemporary mantle) lead source classification diagram. ZHU [38] pointed out that the lead isotope is characterized by the obvious block effect and the same composition in the same block, which can be used as bases for the continental lithosphere tectonic blocks division. And, in accordance with different types of rock leads and the known genetic ore lead, he also provided a $\Delta\gamma$−$\Delta\beta$ range for different ore leads. So, based on the $\Delta\gamma$−$\Delta\beta$ diagram, the ore lead of the Dachang ore deposit lies in the subduction zone of the upper crust and mantle, and only a small amount is located in the upper crust zone (Fig. 8) [38].

In addition, by using the 3D topology projection of lead isotope, the continent of China is divided into five main lead isotope provinces. The change of lead isotopic composition of ore is related to the time sequence of the evolution of crust, mantle and the mineralization epoch, moreover, with evident regional characteristic, and is closely related to the types of the mineral and deposit. In $V_1$−$V_2$ diagram (Fig. 9), not only the differences of the tectonic province of the ore lead isotopic composition, but also the significant differences in different minerals and deposit exist [38]. So, according to the lead isotope three-dimensional topology projection vectors $V_1$ and $V_2$, the ore leads of the Dachang ore field are concentrated in zone *A*. $V_1$ ranges from 69 to 105, mainly in the 69−82 range, with an average value of 80, whereas $V_2$ ranges from 53 to 68, with a mean value of 59 (Fig. 9).

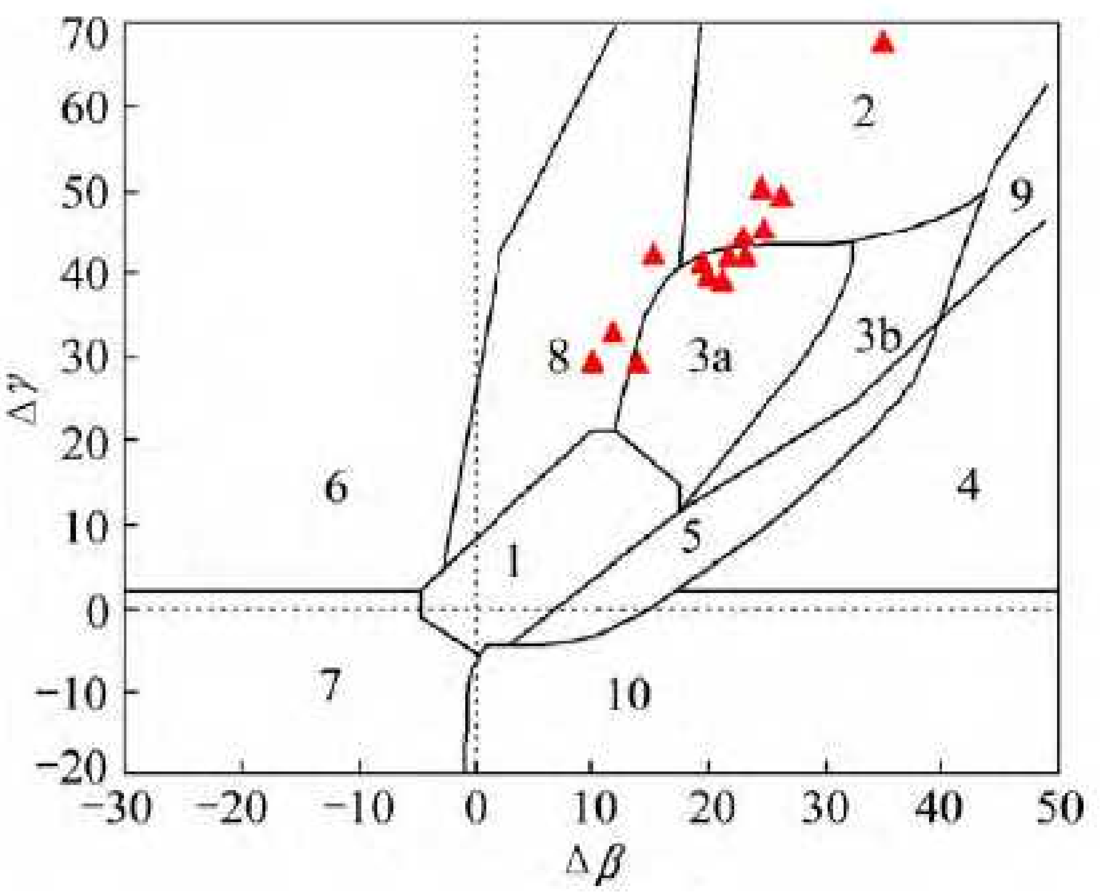


**Fig. 8** $\Delta\gamma$−$\Delta\beta$ diagram of ore lead from Dachang ore field, Guangxi, China [38]: 1—Mantle-derived lead; 2—Upper crust lead; 3—Mixed crust and mantle subduction zone lead (3a — Magmatism, 3b — Sedimentation); 4 — Chemical sedimentation lead; 5—Submarine hydrothermal lead; 6—Medium metamorphic lead; 7—High-grade metamorphic lower crust lead; 8—Orogenic lead; 9—Ancient shale upper crust lead; 10—Retrograde metamorphic lead

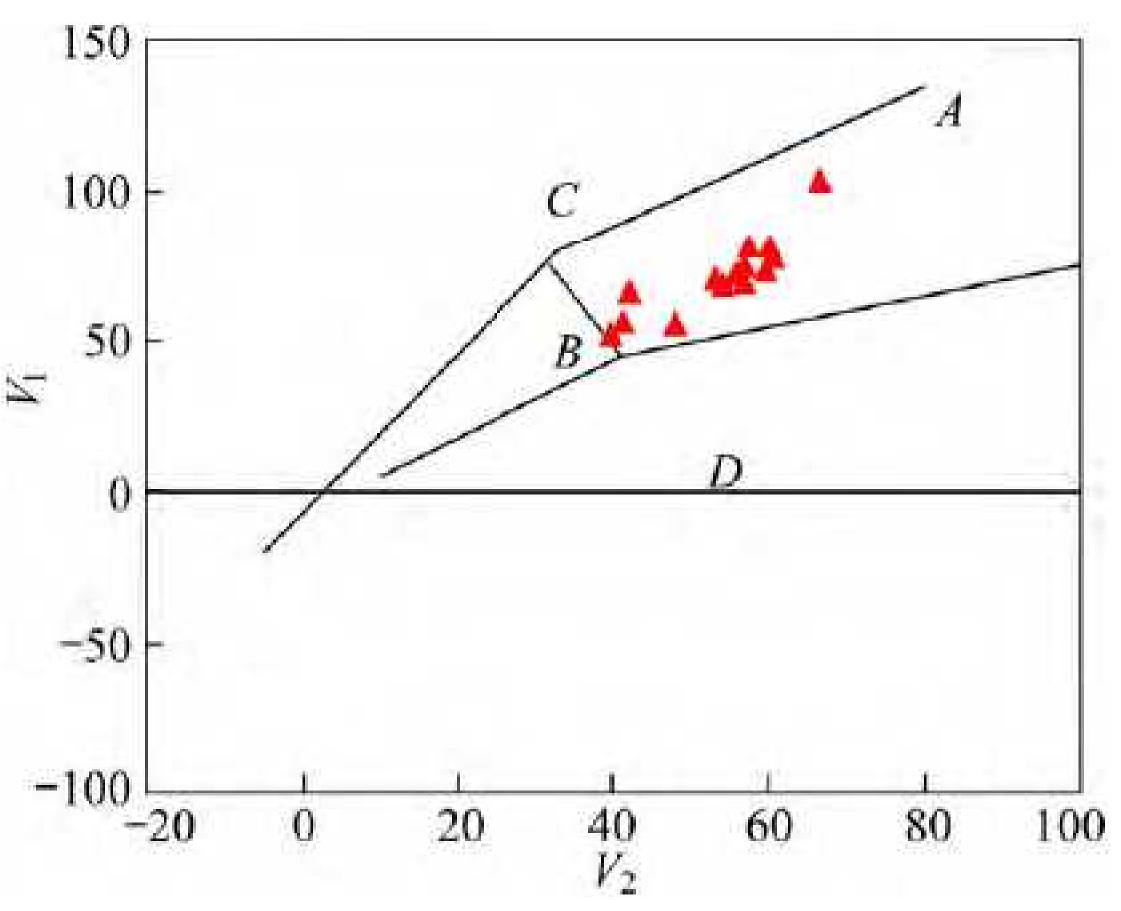


**Fig. 9** $V_1$ vs $V_2$ diagram of ore lead from Dachang ore field in Guangxi, China

According to $\Delta\gamma$−$\Delta\beta$ diagram [39], most of the previous data consistently show the upper crust source or the mixed source of the upper crust and the mantle, indicating a close relationship between the ore lead and magmatism, which also agrees well with the results of this study overall.

The dating of granite indicates that the conversion period from orogeny to extensional thinning was the time of late Yanshanian in the Dachang ore field. And, that is fairly crucial to the Dchang ore field from the collision to intraplate. In addition, the conversion of the regional tectonism lagged far behind its eastern region, which may be related to the stress transferring of the eastern pacific plate collision, implying the dynamic source for the tectonic transition and the diagenesis and mineralization to some extent [41]. The magmatism and tin−polymetallic deposit were controlled by the same structural condition in the Danchi ore belt, the mineralization and magmatism occurred in the late Yanshanian, representing the typical tectonic−magmatic−metallogenic event [42]. Especially, since Mesozoic area experienced the strong compression in the Indosinan period and later extensional shearing, some unique tectonic styles formed, such as the closed linear folds, thrust faults, extensional shear and transtensional fault.

Overall, the intrusive rock was controlled by the SN-trending tension−torsional fault and the interlayer gliding fracture, indicating different magmatism intrusions yet in the same tectonic environment, which should be in different stages but in the same phase [43]. The tin−polymetallic mineralization was mainly controlled by the extensional shear structure of the late Yanshanian, yet the diagenesis occurred in the board extensional tectonic environment [41]. Obviously, in the late Yanshanian, the tectonic transition led to the magmatism and large scale mineralization, being the favorable dynamic condition for the mineralization of the Danchi ore belt and even the whole south China. The above results indicate that the lead isotope is characterized by the Yangtze lead isotope province and shows the genetic relationship between the Danchi zone and Yangtze block. Perhaps, a certain kinship exists between the Danchi area and Yangtze block. The granite mainly formed during the collision and intraplate tectonic settings, and more likely in the tensional tectonic setting in the transition periods from the collision to intraplate.

## 5 Conclusions

1) In the Dachang ore field, the upper crust is the main tin−polymetallic ore source, or the ore lead contains the upper crust composition or is originated from the upper crust, but the mantle-derived material is also involved in mineralization. Moreover, the granite does not provide all ore leads, and surely other material sources exist. The formation of ore deposit is influenced by both the crust and mantle.

2) The source rocks are characterized by a certain degree of similarity with the island arc material. Moreover, its distant origin in the upper and lower crust may be related to the subduction island arc material or the oceanic crust. The mantle-derived material may have

a certain status in the source region. The ore lead lies in the subduction zone of the upper crust and mantle, and only a small amount of samples locate in the zone of upper crust.

3) $V_1$ ranges from 69 to 105, mainly in the range of 69−82, and with an average value of 80; whereas $V_2$ ranges from 53 to 68, with a mean value of 59. The lead isotopes are characterized by the Yangtze lead isotope province, which shows the genetic relationship between the Danchi zone and Yangtze block. Probably, a certain internal relation exists between Danchi area and Yangtze block.

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# 广西大厂矿区锡矿床成矿物质来源：铅同位素证据

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**摘 要**：为了揭示广西大厂锡多金属矿床的成矿物质来源，利用黄铁矿、磁黄铁矿、闪锌矿以及方铅矿等金属硫化物单矿物，开展铅同位素分析与研究。根据经典铅同位素判别模型，探讨矿质来源及其特点。结果表明，铅同位素比值 $^{206}Pb/^{204}Pb$、$^{207}Pb/^{204}Pb$ 和 $^{208}Pb/^{204}Pb$ 分别为 17.478~18.638、15.440~15.858 和 37.556~39.501。根据 Zartman 铅构造模式，矿石铅含有上地壳成分；然而，并非所有的铅都由花岗岩提供，还存在其他的铅来源形式。显然，该矿床属于壳−幔联合作用的产物，原岩与岛弧物质具有一定的相似性；而且上地壳和下地壳中的远源可能与俯冲岛弧或洋壳有关。幔源物质在源区发挥着重要作用；同时，基于铅同位素三维拓扑投影向量，矿石铅主要集中于 *A* 区域，表明其具有扬子铅同位素省的特征，也暗示了可能与扬子板块具有一定的亲缘关系。

**关键词**：铅同位素；成矿物质来源；矿床成因；大厂锡多金属矿床；广西

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