CHINESE JOURNAL OF GEOCHEMISTRY Vol. 26 No. 4 2007

DOI: 10.1007/s11631-007-0439-2

Helium, lead and sulfur isotope geochemistry of the Gejiu Sn-polymetallic ore deposit and the sources of ore-forming materials

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Received December 10, 2005; accepted February 12, 2006

Abstract Studies on the helium, lead and sulfur isotopic composition were performed of the Gejiu super-large Sn-polymetallic ore deposit. The results indicated that the ore-forming materials came from different sources and the deposit is a product of superimposed mineralization. The deposit is characterized by multi-source and multi-period mineralization, which experienced submarine hydrothermal deposition and Late Yanshanian magmatic hydrothermal mineralization. It is held that the Gejiu super-large Sn-polymetallic ore deposit is a multi-genesis deposit.

Key words Gejiu; source of ore-forming material; multiple mineralizing process; hydrothermal deposition; magmatic hydrothermal activity

1 Introduction

The Gejiu Sn-polymetallic ore deposit is located in the Gejiu area, southeastern Yunnan Province, China, which is renowned as a super-large tin as well as large Cu, Pb, Zn, W and Ag deposit associated with numerous colored and rare metallic ores. The deposit is tectonically situated at the convergence of the Tethys tin ore belt and circum-Pacific tin ore belt, which are two important zones containing abundant tin ores in the world. Yanshanian magmatic-hydrothermal mineralization was once widely accepted as the genetic model of the Gejiu Sn-polymetallic ore deposit (Wang Zhifen, 1983; Li Jiahe, 1985; Wu Qinsheng and Liu Qinglian, 1985; Yu Chongwen et al., 1988; Wang Xinguang et al., 1992). Following the discovery of strata-bound tin deposits by Schwartz and Surjono (1990) and the rise of the concepts, some researchers began to take it into consideration the genesis of the Gejiu tin deposit and tried to set up the magmatic-hydrothermal model (Jin Zude, 1991; Peng Zhangxiang, 1992). In 1999, Zhou Jianping et al. (1999) found new evidence on the basis of which a submarine exhalative hydrothermal model was established, which aroused great concern with the genesis of the Gejiu Sn-polymetallic ore deposit again. In this paper we described the geochemical characteristics of helium, lead and sulfur isotopes with an attempt to constrain the sources of ore-forming materials for this deposit.

2 Geological setting

The Gejiu mining district is a location characterized by the convergence of the Yunnan-Xizang structure, the Nanling tectonic zone and the Sichuan-Yunnan structure. Other structures around the mining district are the Yuebei paleo-uplift, the Sichuan-Yunnan paleo-uplift and the Ailaoshan metamorphic belt. The mining district was a semi-closed ‘bay’, open only relative to the ancient sea in the northeast. Because of the influence of the deep giant Nanpanjiang fault, this area is located in the center of a sharp tensional down-warping region. From Proterozoic to Triassic, a layer measured at 24 km was deposited in the region, and only during the Middle Triassic had there been deposited about 3 km-thick carbonate rocks, which provided a wide space for later ore deposition. Developed in the mining district are four sets of faults which extend NE, EW, SN and NW. The most important structures in this area are the Wuzishan anticlinorium and the Jiasha synclinorium. The mining district is divided by the Gejiu fault into two sub-districts. In the eastern sub-distidct, the Wuzishan anticlinorium and other structures control the localization of five ore fields, i.e., Malage, Songshujiao, Gaosong, Laochang and Kafang. The main host rocks developed in the mining district are limestone, dolomitic limestone and

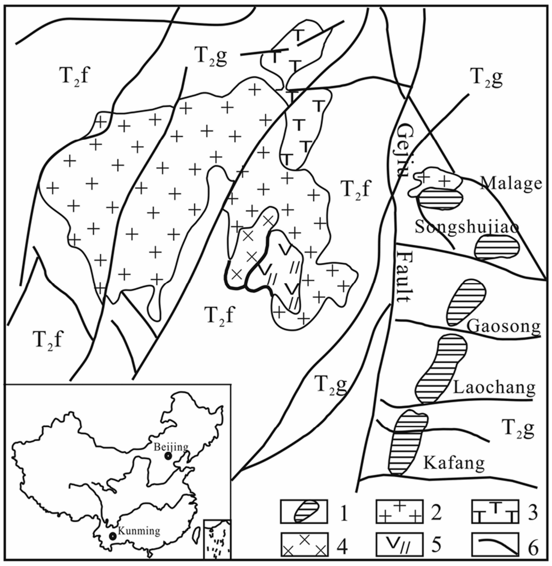

Fig. 1. Sketch map showing the distribution of main orefields in the Gejiu area (after Geological Survey Team 308 of Yunnan Province). 1. Main orefield; 2. granite; 3. alkalic rock; 4. gabbro; 5. monzonite; 6. main faults in the Gejiu area.

dolostone. It is found that above 90% of the total proven reserve was hosted in the layer of the lower Kafang member (T_2g) (Zhuang Yongqiu et al., 1996).

The Gejiu area lies in the center of multi-cycle and multi-source magmatic activities. There have been recognized three magmatic cycles known as the Variscian, the Indo-Chinese and the Yanshanian. The Variscian and Indo-Sinian cycles are marked by volcanic extrusion, which gave rise to the formation of alkalic and calc-alkalic basalts and acidic volcanic rocks representing deep magmatic series. The basic and alkalic intrusive rocks were produced in the Late Indo-Chinese and Early Yanshanian periods. The remelted granite series denoted the Yanshanian magmatic cycle.

3 Deposit type

There are three types of orebody in the Gejiu Sn-polymetallic ore deposit, which are stratiform sulphide, skarn sulphide and vein-like orebodies. Of them, the stratiform and skarn orebodies are more important ones, which are hosted in the contact zone of concealed granites or in the T_2g carbonate strata overlying the granites.

3.1 Stratiform sulphide orebodies

The distance between the orebodies and the granite may range from one meter to tens of meters. The attitude of the orebodies is controlled mainly by strata, lithology and structure, which contain stratiform and stratoid, with a single layer or several layers, lenticular, string-of-bead-like, banded, tubular and irregular orebodies. Most of the orebodies have been oxidized. The main ore minerals are pyrrhotite, pyrite, cassiterite, arsenopyrite, galena, marmatite and minor chalcopyrite. The oxide ore minerals are limonite, hematite, cerusite, pyrolusite, etc.

3.2 Skarn sulphide ores

Orebodeies of this type are distributed in the contact zones between granite, marble and dolostone. The orebodies are mostly subvertically dipped veined and columnar, gently dipped lenticular and stratoid, irregular saccate and nodular in shape. The attitude of the orebodies is controlled mainly by the configuration of contact plane between granite and host rock. On the other hand, it is also correlative with the faults in the contact zones as well as the lithology and attitude of host rocks. The ore minerals are dominated by pyrrhotite, arsenopyrite, chalcopyrite, pyrite, marmatite, cassiterite, galena and scheelite. The gangue minerals include diopside, garnet, plagioclase, fluorite, phlogopite, quartz and turquoise.

3.3 Vein-like orebodies

The vein-like orebodies can be sub-divided into quartz-veined tungsten orebodies and the tourmaline veined orebodies, which are controlled directly by structural fractures.

4 Helium isotope geochemistry

On the basis of microscopic observations, we picked out one piece of pyrite (TO2) and three pieces of pyrrhotite (T10-1, GL5, GS28) for He isotopic analysis in their fluid inclusions. Listed in Table 1 are the results of analysis and the description of the sample localities. By observing the specimens under the microscope, it is found that, except specimen T10-1, there exist typical oolitic pyrite and spherical colloidal pyrite and most of the oolites were fragmentized and suffered metasomatism by epigenetic pyrite, sphalerite and galena. Because the ores were disseminated, we can only grind the specimens and select single minerals of pyrite and pyrrhotite with high purity (>99%) by the electromagnetic method and it is impossible to separate the early pyrite and pyrrhotite from the later ones.

It was reported that the contents of He in the atmosphere are too low to affect the He abundance and isotopic composition of crustal fluids (Stuart et al., 1994; Marty et al., 1989). It is believed that the cosmogenic production of ^{3}He is not significant

Table 1. Helium isotopic composition of fluid inclusions in pyrite and magnetite from the Gejiu Sn-polymetallic deposit (^4He in cm^3STP/g, $Ra=1.4\times10^{-6}$)

Sample No.	Locality	Mineral	$^3He/^4He$ ($\times10^{-7}$)	^4He ($\times10^{-6}$)	^3He ($\times10^{-13}$)	R/Ra
TO2	Orebody 32-3 in the Laochang orefield (exo-contact zone of skarn orebody)	Pyrite	2.89±1.12	3.25	9.39	0.21
T10-1	Orebody 32-3 in the Laochang orefield (endo-contact zone of skarn orebody)	Pyrrhotite	0.78±0.46	1.83	1.43	0.06
GL5	Orebody 5 in the Laochang orefield (skarn orebody)	Pyrrhotite	6.22±2.88	0.64	3.98	0.47
GS28	Orebody 1-3 in the Gaosong orefield (stratiform orebody)	Pyrrhotite	1.94±0.57	2.31	4.48	0.14

Analysis was performed at the Institute of Deposit Geology, Ministry of State Land and Resources, China.

(Simmons et al., 1987; Stuart et al., 1995) in this study because all the samples were collected from underground mines. Therefore, the helium in fluid inclusions of the deposit has only two possible major sources, i.e., the mantle and the crust. The Gejiu granite is a Yanshanian S-type crust-remelting granite (Zhuang Yongqiu et al., 1996). Only a little data is available on the $^3He/^4He$ ratios of granites in the literature. For example, some granite samples taken from Ukraine gave $^3He/^4He$ ratios of 0.07×10^{-7}–0.14×10^{-7} cm^3 $STP\cdot g^{-1}$ (Mamyrin and Tolstikbin, 1984), indicating typical radiogenic crustal helium. In this work, sample T1, collected from the endo-contact zone of ore bodies, has a ten times lower $^3He/^4He$ ratio than the samples collected from the exo-contact zone, which implies that the $^3He/^4He$ ratio of the Gejiu granite is lower and thus the helium should be radiogenic crustal helium. Therefore, it is considered that helium in the Gejiu granite may have come from meteoric water and radiogenic crustal helium. Except that it is 0.06 Ra for sample T1, $^3He/^4He$ ratios in the mineralizing fluid for other samples range from 0.14 to 0.47 Ra, which are far higher than those of the radiogenic crustal helium, indicating that there does exist mantle helium in the fluid. By projecting the ratios onto the concentration diagram of He isotopes, it is shown in Fig. 2 that the data points lie between radiogenic helium and mantle-source helium, which indicates that part of He in the mineralizing fluid came from the mantle, obviously distinguished from that derived from the Gejiu granite. We were unable to separate the later minerals from the early minerals before we got the results of sample analysis. So our isotopic analysis results showed that the mantle helium is a very important source. As viewed from the results of He isotopic analysis, it is learned that the helium in early mineralizing fluid from the Gejiu deposit came mainly from the mantle. Therefore, the mineralizing fluid should be the mixture of seawater and mantle fluid. Furthermore, the early source bed or orebody had been superimposed and reworked by later mineralizing fluid of the Yanshanian granites, and the fluid was very rich in radiogenic crustal helium.

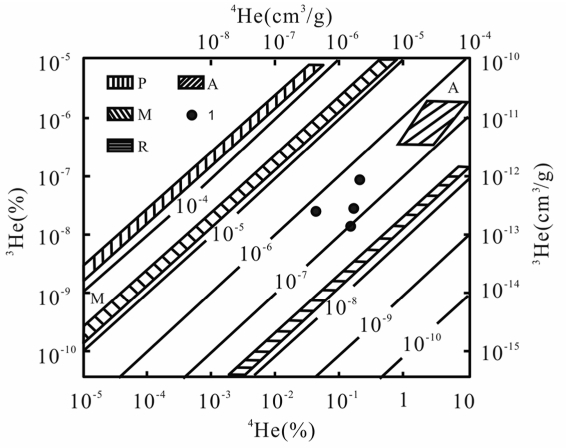

Fig. 2. Concentrations of helium isotopes in the Gejiu Sn-polymetallic deposits. P. Primitive He; M. mantle He; R. radiogenic He; A. old ultrabasic rocks of Kola Peninsula. 1. Helium isotopes from the Gejiu Sn-polymetallic deposits.

5 Lead isotope geochemistry

Listed in Table 2 are the Pb isotopic compositions of the Gejiu tin deposit. In combination with the above 300 sets of Pb isotope data from the above 30 strata-bound deposits in China, Chen Haoshou (1981) divided the Pb isotopes into three types as ‘normal’, ‘abnormal’ and ‘complex’. According to his work, the results of Pb isotopic analysis for the Gejiu tin deposit are comparable with those for ‘the complex’, though some abnormal results such as negative age were found in a few samples.Since the 1990s, it has been widely supported that the origin of ore lead should be investigated in terms of synthetical studies of Pb isotopes in ores, magmatic rocks and strata. Ore source of a deposit should not be simply considered as a sphere of the Earth (Zhang Qian et al.

Table 2. Lead isotopic composition of the Gejiu Sn-polymetallic deposit

Item	Locality and geological setting	Mineral	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
Ore	Vein-like PbS in the Longshujiao fault	Galenite	17.986	15.655	38.102
	2000M from Bainidong	Galenite	18.401	15.674	38.884
	Stratiform oxide orebody in Bainidong	Galenite	18.524	15.761	39.082
	Stratiform veined orebody in Lutangba	Galenite	18.411	15.661	38.875
	Stratiform veined orebody in Lutangba	Galenite	18.417	15.671	38.894
	Stratiform stripped orebody in Songshujiao	Galenite	18.416	15.626	38.523
	Ag , Pb deposit No.102 in Gaosong	Galenite	18.400	15.636	38.776
	Stratiform sulfide orebody No.10-14 in Gaosong*	Galenite	18.398	15.636	38.785
	Stratiform sulfide orebody No.1-3 in Gaosong*	Galenite	18.446	15.658	38.336
	Stratiform oxide orebody in the Falang Formation	Galenite	18.399	15.615	38.787
	Stratiform oxide Pb orebody in Baoshan	Galenite	18.422	15.631	38.791
	Stratiform oxide orebody in Banshan	Galenite	18.617	15.563	38.661
	Stratiform oxide orebody in Daaozi	Galenite	18.491	15.664	38.431
	Stratiform oxide orebody in Daaozi	Galenite	18.484	15.653	38.386
	Stratiform oxide orebody	Galenite	18.385	15.606	38.775
	Stratiform oxide orebody far from the contact zone	Galenite	18.357	15.624	38.647
	Oxide ore in the middle of orebody 2165 in Laochang	Galenite	18.348	15.538	38.712
	Pb-rich oxide ore in orebody 2-4-7 in Laochang	Galenite	18.447	15.715	38.092
	Oxide ore in orebody 2138-25 in Laochang	Galenite	18.65	15.942	39.766
	Outer contact zone in orebody 5 in Laochang	Galenite	18.005	15.513	37.848
	Contace zone in orebody 1-5 in Laochang	Galenite	18.188	15.643	38.267
	Stratiform oxide orebody in Laochang*	Galenite	18.410	15.63	38.740
	Ore outside the Shenxianshui mass	Galenite	18.410	15.622	38.721
	Veined PbS in the faults outside the Malage orefield	Galenite	18.467	15.643	38.770
Enclosing rock	Limestone in the strata of T_2g in Malage	Pyrite	18.551	15.619	38.63
	Limestone in Qidaoxiang, Malage	Pyrite	19.068	15.644	38.583
Granite	Biotite granite along the Longcha River	K- felspar	18.359	15.613	38.723
	Biotite granite in Beipaotai	K- felspar	18.445	15.640	38.741
Lava	Lava developed from Tabai to Niushizhai	Galenite	18.368	15.540	38.567

Note: * The data analyzed at the Institute of Mineral Resources, Chinese Academy of Geological Sciences, and the others from Zhuang Yongqiu et al. (1996).

2000). Instead, it should be localized in a concrete rockbody and a stratum. Based on the illustration in the literature (Zartman and Doe, 1981), we compared the Pb isotopes of ores, strata, granites and volcanic rocks in the Gejiu tin mining district. It is shown in Fig. 3 that the ores in the mining district are not homogenous in Pb isotopic composition. Three quarters of the projecting points lie between the Pb curve of the upper crust and that of the orogenic belt, and the other points are dispersed, indicating the ore lead in the deposit was not supplied merely by Yanshanian magmatic hydrothermal solutions. So we believed that the lead of this type of ore deposits did not come from one source only. The Pb isotopic ratios of the ores, determined to be ^{206}Pb/^{204}Pb=18.385–18.450, ^{207}Pb/^{204}Pb=15.606–15.671 and ^{208}Pb/^{204}Pb=38.386–38.894, is in consistency with those of the granite in the mining district, determined to be ^{206}Pb/^{204}Pb=18.359–18.445, ^{207}Pb/^{204}Pb=15.613–15.64 and ^{208}Pb/^{204}Pb=38.723–38.741, which indicates most of the ore lead came from the Yanshanian magmatic hydrothermal solutions. The Pb isotopic composition of the ores, determined to be ^{206}Pb/^{204}Pb=18.005–18.617, ^{207}Pb/^{204}Pb=15.513–15.563 and ^{208}Pb/^{204}Pb=37.848–38.809, is partially close to that of Indo-Sinian volcanic rocks, determined to be ^{206}Pb/^{204}Pb=18.368, ^{207}Pb/^{204}Pb=15.540 and ^{208}Pb/^{204}Pb=38.567. And their projecting points lie on the

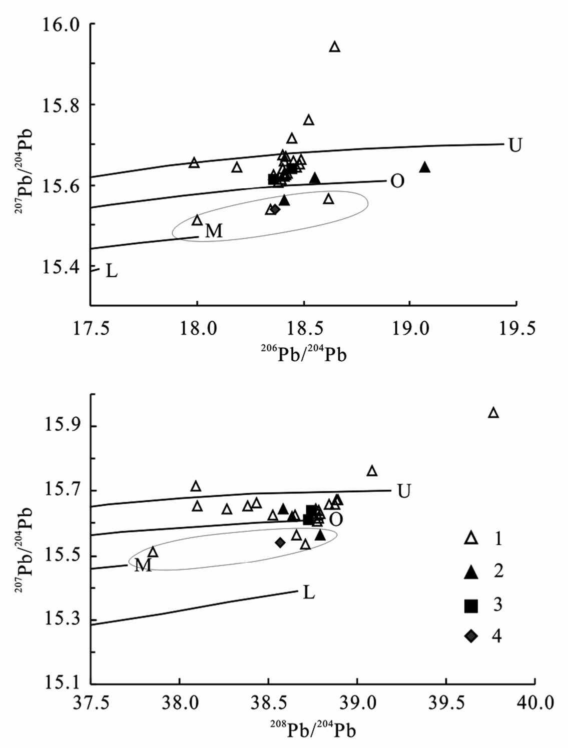

Fig. 3. Lead isotopic composition of the Gejiu Sn-polymetallic deposit (after Zartman et al., 1981). M. Upper mantle lead; L. lower crustal lead; O. orogenic belt lead; U. upper crustal lead. 1. Orebody; 2. enclosing rock; 3. granite; 4. lava.

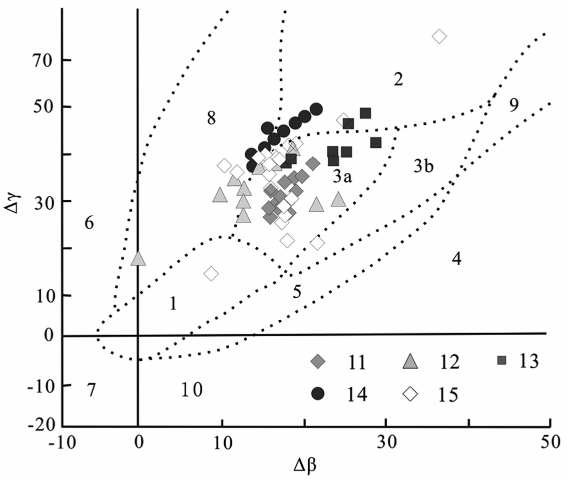

Fig. 4. Δβ-Δα genetic schematic diagram of ore lead isotopes of the Gejiu Sn-polymetallic deposits. 1. Mantle lead; 2. upper crustal lead; 3. mixed lead from upper crust and mantle in the subduction zone (3a. magmatism, sedimentation); 4. chemical sediment lead; 5. lead in hydrothermal sediments on the sea floor; 6. lead from moderate- to high-grade metamorphism; 7. lower crust lead from high-grade metamorphism; 8. orogenic belt lead; 9. upper crust lead of old shale; 10. retrograde metamorphism lead (after Zhu et al., 1998; and the Δβ-Δα genetic schematic diagrams of Dachang, Bainiuchang, Daxiangping and Dulong after Liu Yuping, 2000). 11. Dachang; 12. Bainiuchang; 13. Dajiangping; 14. Dulong; 15. Gejiu.

evolution line of mantle lead or in its extending direction, which shows that part of the ore-forming materials of the deposit came from the upper mantle. In previous studies, Zhou Jianping et al. (1999) discovered hydrothermal sedimentary tin ores and Zhang Huan et al. (2004) found cassiterites in the oolitic pyrites representing hydrothermal sediments in interlayer orebodies, so it is believed that hydrothermal sedimentation had supplied part of the ore-forming materials for the deposit. Above the evolution curve of upper crustal lead, there are spread a few projecting points representing the Pb isotopic composition ($^{206}Pb/^{204}Pb$=18.447–18.650, $^{207}Pb/^{204}Pb$ =15.715–15.942 and $^{208}Pb/^{204}Pb$=38.082–39.766), which is the result of involvement of more radiogenic Pb, so the strata lead should also be one of the sources for the deposit.

As is shown in Fig. 4, on the basis of the Δγ-Δβ diagram of ore lead isotopes (Zhu Bingquan, 1998), we can see that ore lead of the Gejiu tin deposit falls mainly in the lead field of the upper crust, that of the orogenic belt and that of magmatism, compared with the Pb data points from four Sedex and magmatic hydrothermal superimposed deposits such as Dachang, Bainiuchang, Dulong and Dajiangping (Chen Duofu et al., 1998) for comparison, which indicates that the Gejiu tin deposit is genetically consistent with the four deposits mentioned above. During the forming processes of the five deposits, rock associations in the hydrothermal sediments as well as later superimposed and reworked geological processes may control the diversity of lead (e.g. ore lead and submarine hydrothermal lead).

Therefore, it is thought that the lead in the Gejiu tin deposit came from a number of sources. A part of the ore lead is consistent in source with ore lead in mantle-source volcanic rocks, indicating a good correlation with the Indo-Sibuan hydrothermal sedimentation. The remaining ore lead possesses similar Pb isotopic characteristics to those of the Yanshanian granites, which indicates that the lead came from the Yanshanian granites.

6 Sulfur isotope geochemistry

In combination with previous studies on the Gejiu deposit, the sulfur isotopic composition of ores in the five ore fields is illustrated in Fig. 5, which shows that the $\delta^{34}S$ values of the Gejiu tin deposit range from -3.1‰ to +9.4‰, with a variation of 12.5‰ and a mean value of +2.2‰. As a quasi tower-style distribution, the illustration shows that the $\delta^{34}S$ values show a positive shift and the peak values are around zero, characteristic of meteorite sulfur. The

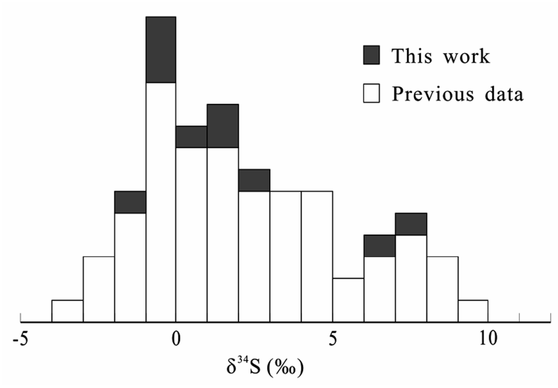

Fig. 5. Histogram of sulfur isotopic compostions of the Gejiu Sn-polymetallic deposit (previous data after Zhuang Yongqiu et al., 1996).

meteorite sulfur is a product at high temperature in the interior of the Earth, which represents a deep-source sulfur. Large-scale magmatism in the Yanshanian and later superimposition and reworking by magmatic hydrothermal solutions should be a reason why deep-source sulfur is dominant in the Gejiu tin deposit. However, even if the $\delta^{34}S$ values are around zero, it could not be considered that the sulfur involved in ore deposition only came from the Yanshanian hydrothermal solutions. According to the studies of modern submarine hydrothermal sediment associations and a number of previously discovered ore deposits of hydrothermal sedimentary origin, the occurrence of the interior magma chamber is the most important reason for the hydrothermal cycle, so the $\delta^{34}S$ values around zero suggest that the sulfur might have come from the interior magma chamber. On the other hand, deoxidization of the crustal rocks and submarine sulfates can produce such a kind of sulfur that has $\delta^{34}S$ values around zero (Ohmoto and Rye, 1979). Zeng Zhigang et al. (2001) analyzed 1264 sets of sulfur isotope data for global modern submarine hydrothermal sediments and found that the sulfur isotopic compositions of sulfide and sulfate minerals range from 1‰ to 9‰, with a mean of 4.5‰ (n=1042) and from 19‰ to 24‰, with a mean of 21.3‰ (n=217), respectively. In this work, sulfides were selected to analyze their sulfur isotopic composition, and their $\delta^{34}S$ values are consistent with those of sulfides present in the submarine hydrothermal sediments. So it is suggested that the sulfur in the Gejiu tin deposit came partly from the interior magma chamber and submarine sulfates, indicating that hydrothermal sedimentation played a very important role in ore deposition.

7 Conclusions

(1) Lead in the Gejiu tin deposit came from a number of sources. The lead was derived largely from Yanshanian magmatic hydrothermal solutions, and a part of the lead came from the upper mantle, and the strata supplied a minor amount of lead for the deposit.

(2) The sulfur was derived partly from the interior magma chamber and submarine sulfates and partly from large-scale Yanshanian magmatic hydrothermal solutions.

(3) Helium in early mineralizing fluid came mainly from the mantle. As a result of the interfusion of mantle fluid, the mineralizing fluid should be a mixture of seawater and mantle fluid. The early source beds or orebodies were superimposed and reworked by later mineralizing fluid of the Yanshanian granites rich in radiogenic crustal helium.

(4) On the basis of isotope geochemical studies, it has been proved that the ore-forming materials of the Gejiu Sn-polymetallic ore deposit came from different sources and the deposit was formed by different mineralizing processes. The deposit is the result of multi-source and multi-period mineralization, which suffered submarine exhalative hydrothermal sedimentation in the Middle Triassic and was superimposed and reworked by late Yanshanian magmatic hydrothermal mineralization.

Acknowledgements This work is financially supported jointly by the National Natural Science Foundation of China (Grant No. 40603013) and the Cooperative Project (Grant No. 2000YK-04) Conducted by Universities in Yunnan Province and the Chinese Academy of Sciences.

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