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Geochemical characteristics and metallogenesis of Carlin-type gold deposits in the Sandu-Danzhai metallogenic zone, Guizhou Province, China

YAN Baowen[1,2], XIA Yong[1*], WANG Zepeng[1,2], TAN Qingping[1,2], WU Shourong[3], and FAN Erchuan[3]
[1] *State Key Lab. of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*
[2] *Postgraduate University of Chinese Academy of Sciences, Beijing 100039, China*
[3] *No.1 General Party of Bureau of Non-ferrous Geological Exploration of Guizhou Province, Guiyang 551400, China*
* *Corresponding author, E-mail: xiayong@vip.gyig.ac.cn*

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Abstract Geochemical studies of the Paiting and Miaolong Carlin-type gold deposits in the Sandu-Danzhai metallogenic zone, Guizhou Province, have shown that the mineralized-altered rocks show LREE-enrichment patterns, generally displaying negative Eu anomalies (δEu=0.51−0.97) and unobvious negative Ce anomalies (δCe=0.86−0.99). Calcite and fluorite in relation with metallogenesis show MREE-enrichment patterns, generally displaying rather weak negative Eu anomalies (δEu=0.74−0.93) and weak negative Ce (δCe=0.70−0.98) anomalies. The $\delta^{13}C_{PDB}$ values of carbon in calcite are -1.61‰− -5.82‰, the $\delta^{18}O_{SMOW}$ values of oxygen are 13.97‰−19.24‰, and the $\delta^{34}S_{CDT}$ values of sulfur in stibnite are 17.72‰−21.68‰. In regard to δD and $\delta^{18}O$, ore-forming fluids possess the characteristics of metamorphic water. The process of metallogenesis of the Carlin-type gold deposits is controlled by the Yanshanian tectonic activities. The Yanshanian movement promoted the migration and mobilization of metamorphic fluids in the extensively developed medium- to high-grade metamorphic rocks in this region, carrying primarily enriched gold and associated elements such as Hg, As, and Sb in the Sinian metamorphosed black shales and Lower Cambrian black shales. The ore-forming fluids found their way into a suitable metallogenic environment along the fault zone, followed by gold precipitation to form gold deposits.

Key words carlin-type gold deposit; geochemistry; Paiting and Miaolong gold deposits; Guizhou Province

1 Introduction

In Guizhou Province the gold deposits hosted in sedimentary rocks mainly occur in the Late Paleozoic to Early Mesozoic (southwestern Guizhou) and Early Paleozoic (southeastern Guizhou) sedimentary rocks and distributed along the southwestern margin of the Cambrian Yangtze Craton. The characteristics are similar to the Carlin-type gold deposits in Nevada, the United States, obviously enriched in As, Sb, Hg and Tl (Hu Ruizhong et al., 2002; Peters et al., 2007). The ore deposits are mainly controlled by strata and faults (Zhang Xingchun et al., 2003; Mao Shuihe, 1991). The typical characteristic includes impure carbonate or calcareous and carbonaceous rocks hosted rocks that contain disseminated pyrite and arsenopyrite. Gold occurs either as submicrometer-sized particles or invisibly as solid solution in As-rich rims of pyrite and arsenopyrite (Mao Shuihe, 1991; Zhang Xingchun et al., 2005; Su Wenchao et al., 2008). Hydrothermal alteration caused decarbonation, silicification, argillization, and sulfication (Hu Ruizhong et al., 2002; Zhang Xingchun et al., 2003; Su Wenchao et al., 2008), similar to the characteristics of the Carlin-type gold deposits in Nevada, the United States (Mao Shuihe, 1991; Zhang Xingchun et al., 2005; Su Wenchao et al., 2008). During the late stage of metallogenesis, it commonly developed stibnite, realgar and orpiment (Hu Ruizhong et al., 2002; Hofstra and Cline, 2000; Su Wenchao et al., 2009; Zhang Yu et al., 2010a).

Previous researchers investigated the Carlin-type gold deposits in the Sandu-Danzhai metallogenic zone from the angle of organic geochemistry and they considered that those deposits were closely related to the formation and evolution of fossil oil reservoirs (Chen Qingnian et al., 1998; Shi Jixi et al., 1995; Shao Shuxun et al., 1999). This study focuses on the trace elements and isotopes of altered-mineralized rocks and gangue minerals such as quartz and calcite, so as to explore the geochemical characteristics of the ore deposits and also primarily discusses the process of metallogenesis of the Carlin-type gold deposits.

2 Regionally geological characteristics

The Carlin-type gold deposits in the Sandu-Danzhai metallogenic zone are located in the Sandu-Danzhai region of Southeast Guizhou on the southern margin of the Jiangnan platform uprise of the Yangtze Block (on the northern margin of the Youjiang River rift), i.e., within the area where China's well-known "Sandu-Danzhai mercury ore zone" is located. The Hongfachang, Sixiangchang, Miaolong, Paihe, Paiting, Yangyong, Gaotong and other Carlin-type gold (Hg-Sb) deposits and occurrences constitute the Sandu-Danzhai Hg-Au-Sb mineralization belt (Fig. 1). Up to now, the Danzhai gold deposit is still a deep-seated small-sized gold deposit or an gold orebody in the medium-small-sized gold deposits, associated large-sized Hg deposits in the large-scale Hg orefield. Arsenopyrite is the most important Au-bearing mineral, followed by As-rich pyrite. Realgar and orpiment are rarely seen (Gao Zhenmin et al., 2002). The strata exposed in the mineralization belt include the Proterozoic Xiajiang Group and Upper Permian (Paleozoic) strata. The Upper Sinian-Lower Cambrian black rock series and Middle Cambrian-Early Ordovician carbonate rocks are most developed, with the Middle Cambrian carbonate strata constituting the major ore-hosted strata. The Sandan-Danzhai metallogenic zone has the advantages of good geological conditions for gold mineralization and excellent ore-searched prospect. It is another important metallogenic prospective zone following the discovery of the gold zone in southwestern Guizhou (Peng Yangqi, 1997).

The Sm-Nd dates of hydrothermal calcites from the Shuiyindong in Guizhou are 134±3 to 136±3 Ma (Su Wenchao et al., 2009), the Rb-Sr isochron age of the Hongfachang and Sixiangchang high-grade ores is 114±6 Ma (Chen Qingnian et al., 1998), and the fission track ages of quartz from the Paiting and Yangyong gold deposits are 66.7 and 65.4 Ma, respectively (Li Chaoyang et al., 2002), with the metallogenic ages being concentrated within the range of 140−75 Ma, indicative of metallogenesis during the Yanshanian movement (Hu Ruizhong et al., 2002).

According to the fact that the Hg-Au deposits in Guizhou are controlled by Yanshanian tectonic activities, it is commonly accepted that their metallogenesis is synchronous with the most recent and most intense regional tectonic activity (Yan Junping et al., 1989; Hua Yongfeng and Liu Youping, 1996), and this is also an important evidence suggesting that the Hg-Au deposits in Guizhou are the products of Yanshanian tectonic activities (Hu Ruizhong et al., 2007).

3 Geological characteristics of the ore deposits

The Paiting gold deposit is located in the southeastern part of Danzhai County (10 km in diameter) and it was discovered by the Bureau of Non-ferrous Geological Exploration of Guizhou Province (Peng Yangqi, 1997). It is an independent micro-disseminated gold deposit discovered for the first time in the Middle-Lower Cambrian stratum, following the discovery of the Miaolong Sb-Au deposit and the Sixiangchang-Hongfachang Hg-Au deposit. The main orebodies have an average grade of 4.05×10^{-6} g/t. It is a medium-sized gold deposit (Dong Guanggui, 2007; Wu Shourong, 2008). At present, the Paiting gold deposit is the largest-scale gold deposit in the metallogenic zone.

The strata exposed in the mining district (Fig. 2) include the Precambrian Xiajiang Group Longli Formation (Ptxjl) medium- to thick-layered, fine- to mediun-grained biastopsammite, the Upper Sinian Doushantuo Formation (Zbds) thin- to medium-thick limestones, the Liuchapo Formation (Zblc) thin to medium thick siliceous rocks with phosperite nodules. The Lower Cambrian Jiumenchong Formation ($\in_1$j), the Bianmachong Formation ($\in_1$b) and the Wuxun Formation ($\in_1$w) are dominated by mudstone and silty mudstone.

In addition, there are the Middle Cambrian Duliujiang Formation ($\in_2$d) medium- thick mudstone, muddy limestone and dolomite and the Upper Cambrian Yangjiawan Formation ($\in_3$y) limestone, dolomite and other strata. The Bianmachong Formation ($\in_1$b), the Wuxun Formation ($\in_1$w) and the Duliujiang Formation ($\in_2$d) are the principal ore-hosted strata.

In the region, there are three groups of faults, i.e., NNE, NE and NEE. According to the sizes of the faults, three classes can be distinguished: the Wuwan fault belongs to the first class, the Xiongqi fault belongs to the second class, jointly constituting the basic tectonic framework within the mining district. The faults of class III include NEE-, NE-, SN- and NW-trending faults, most of which are ore-hosted faults (Fig. 2).

The Miaolong gold deposit is located (about 7 km in diameter) in the north part of Sandu County and it was discovered in 1979, with an average gold grade of 5.32×10^{-6} g/t, it is a medium-scale gold deposit (Peng Yangqi, 1997; Wang Shangyan et al., 2006). The mining district is located within the Miaolong synclinorium, where there are developed the SN-, EW-, NW- and NE-trending faults, of which the F2 fault (Fig. 3) controls gold mineralization in this region (Wang Shangyan et al., 2006). The orebodies are hosted mainly in the Cambrian Sandu Formation ($\in_3$S) and the Yingshangpo member of the Ordovician Guotang Formation (Ogt^y). Thin-layered banded limestone, laminated marlite and thick-layered calcirudite are the major lithological types.

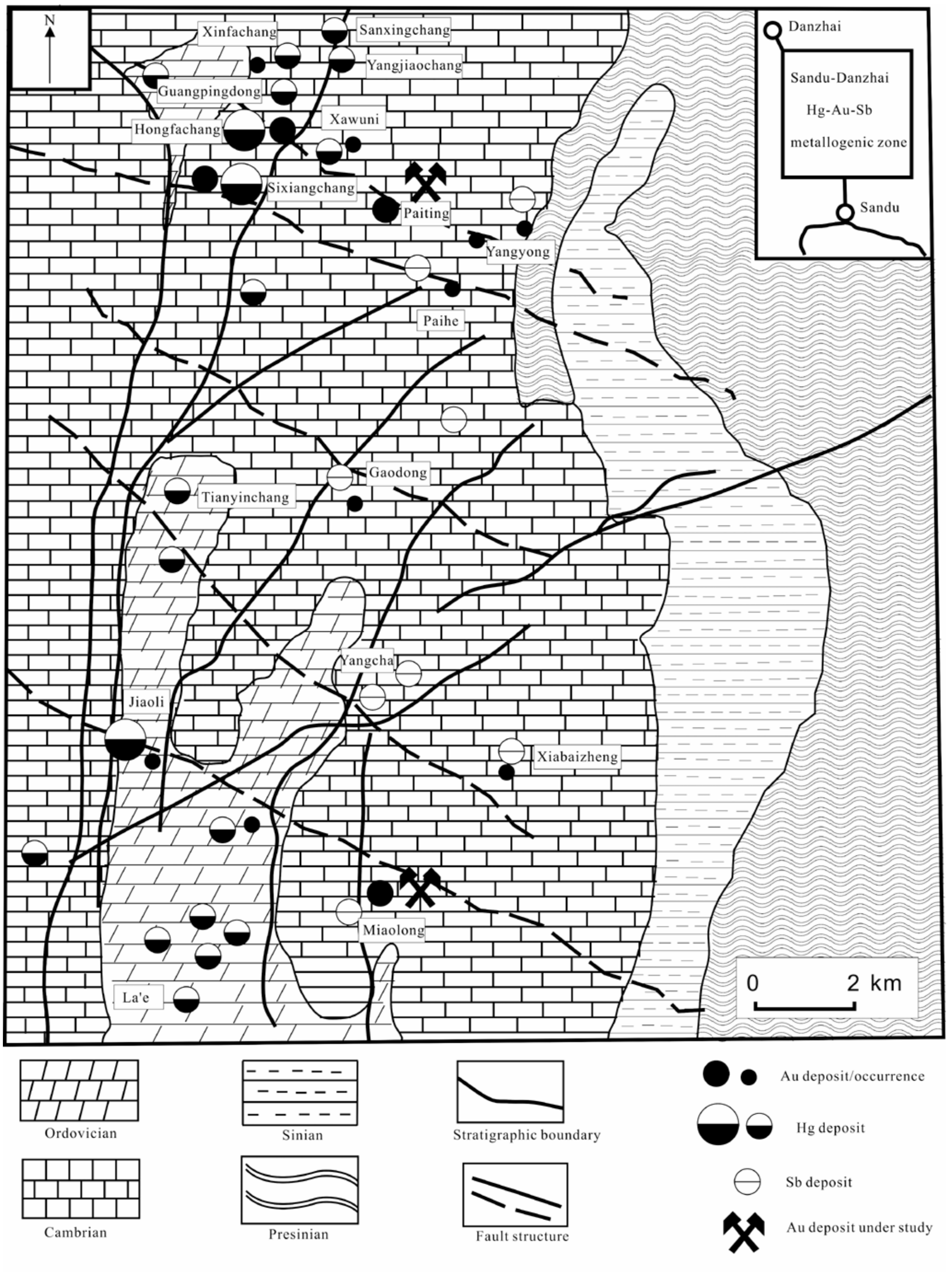

Fig. 1. Sketch map showing the geological structure of the Sandu-Danzhai Hg-Au-Sb mineralization zone in Guizhou Province (Gao Zhenmin et al., 2002).

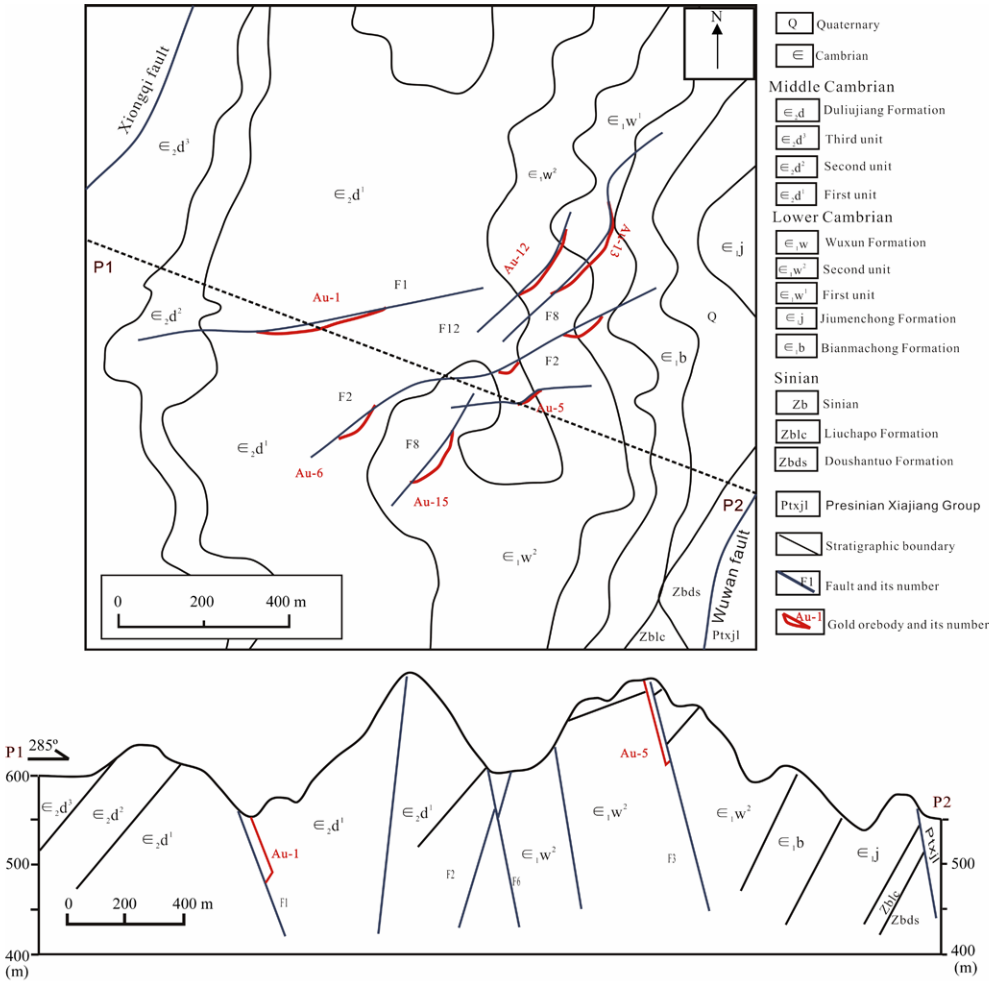

Fig. 2. Geological sketch map of the Paiting gold orefield (after Fan Erchuan, 2010).

In the Miaolong and Paiting gold deposits, Ore minerals are mainly arsenopyrite, pyrite and stibnite with minor amounts of associated minerals such as sphalerite and pyrrhotite. Arsenopyrite and pyrite are the major Au-bearing minerals, micro-disseminated in mineralized rock. The gangue minerals are mainly quartz, dolomite and calcite, and subordinately are barite and fluorite. Fluorite is relatively developed in the Miaolong gold deposit, and white and light green fluorites formed at the late stage of mineralization. No fluorite has been found in the Paiting gold deposit. Hydrothermal alterations include silicification, calcitiation, dolomitization, baritization, pyritization, arsenopyritization, etc. From the Miaolong deposit to the Paiting deposit organic carbonation tends to develop progressively. Silicification and organic carbonation represent the important alteration assemblage of the Paiting gold deposit.

4 Samples and testing methods

The samples were collected from drill hole, adit and tunnel, those of the Paiting gold deposit were taken from core and adit (sample codes ZK and PD), and those of the Miaolong gold deposit were collected from tunnel (sample code ML). On the basis of systematic field investigation and rock/mineral identification, the samples were treated and analyzed.

(1) REE analysis method: Calcite and fluorite samples were crushed as fine as 20−40 mesh and impurities were picked out under binocular to make the purity of calcite reach more than 99%. Then, the purified calcite was ground as fine as 200 mu by means of an agate mortar. REE analysis was conducted on an element-type high-resolution ICP-MS made by Finnigan MAT Co. at the ICP-MS Room under the State Key Lab. of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The relative standard deviation for the repeatability test of trace elements is less than 10%. Altered-mineralized rock samples were crushed as fine as 200 mμ and tested and analyzed in the company of ALS by using the ME-MS81 analysis method.

(2) Stable isotope analysis method: Carbon and oxygen isotopic measurement of calcite and sulfur isotopic measurement of stibnite were accomplished

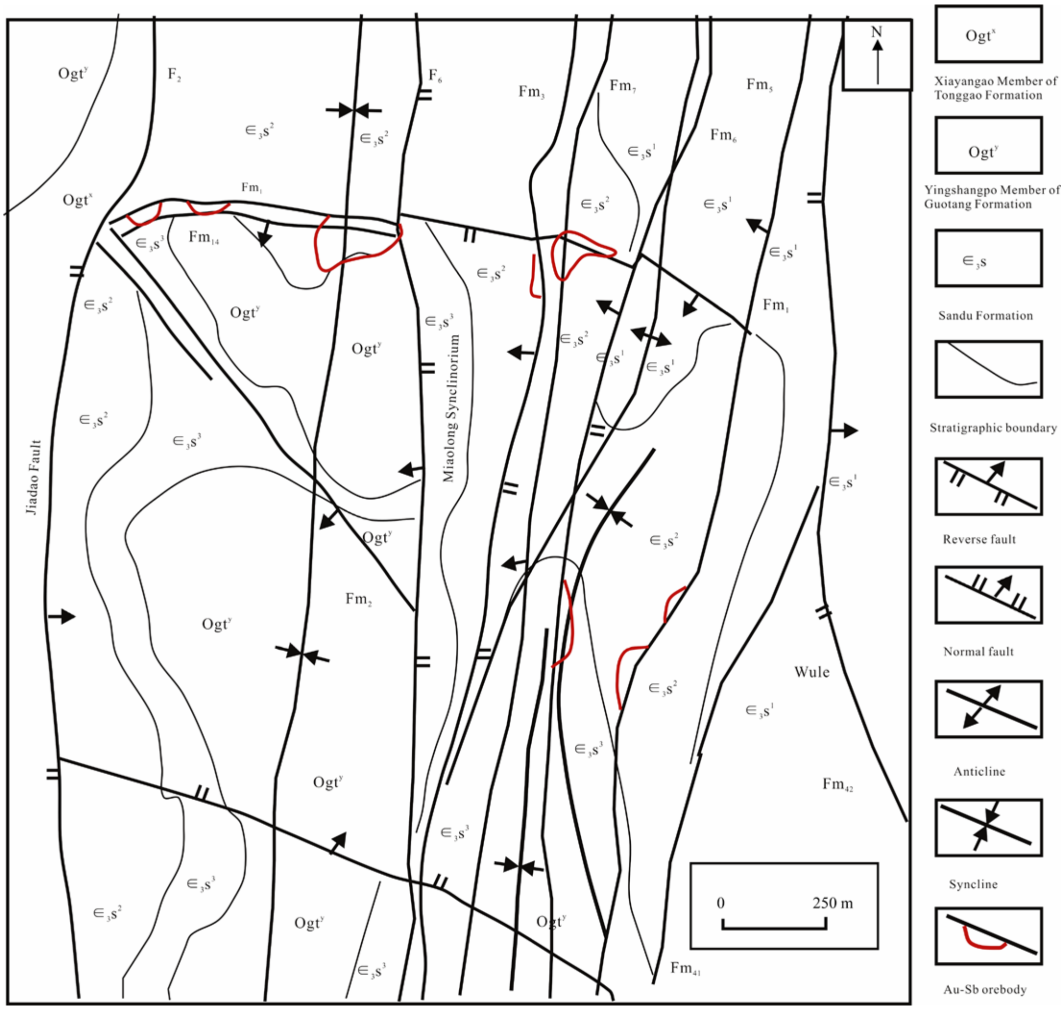

Fig. 3. Sketch map showing the geological structure of the Miaolong Au-Sb deposit (after Wang Shangyan et al., 2006).

at the State Key Lab. of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The 100% phosphoric acid method was adopted for C and O isotopic analysis of calcite and the instrument used for the purpose was a MAT0252 mass spectrometer. PDB was used as the standard for $\delta^{13}C$ and PDB and SMOW were adopted as the standards for $\delta^{18}O$, with the relative errors involved in the analysis being less than ±0.2‰. Sulfur isotopic measurement was conducted on the MAT252-Model mass spectrometer and the method of determination was the SO_2 method. The standard sample was CDT and the relative analysis error was less than ±0.2‰.

4.1 REE characteristics

REE standardization was done by using the data of Sun and McDonough (1989).

(1) As can be seen from Table 1 and Fig. 4, the alteration-mineralization rocks of the Paiting and Miaolong gold deposits display LREE-enrichment patterns and generally show negative Eu anomalies (δEu=0.51−0.97) and unobvious negative Ce anomalies (δCe=0.86−0.99).

(2) As can be seen from Table 2 and Fig. 5, the calcite and fluorite in relation to the metallogenesis of the Paiting and Miaolong gold deposits display MREE-enrichment patterns and generally show rather weak negative Eu anomalies (δEu=0.74−0.93), but nearly unobvious negative Ce anomalies (δCe= 0.70−0.98).

These MREE patterns are consistent with those of calcite in relation to the mineralization of the Carlin-type gold deposits in southwestern Guizhou (Su Wenchao et al., 2009; Zhang Yu et al., 2010a, b). That would be related to ore-forming hydrothermal solutions, but the forming mechanism is still unclear. Fluorite and calcite in relation to mineralization of Sb deposits were also reported to show MREE-enrichment patterns (Peng Jiantang et al., 2002, 2004). It is considered that the REE distribution patterns are mainly controlled by crystallochemical factors. In the process of metallogenesis of hydrothermal fluids, the calcite formed in a relatively reducing environment would show weak negative Eu anomalies (Liang Ting et al., 2007) and unobvious weak negative Ce anomalies (Wang Jiasheng et al., 2010), indicating that the processes of transport and metallogenesis of hydrothermal fluids under relatively reducing conditions. It is in consistency with the regionally geological background of metallogenesis. The strata in this region commonly present reducing organic matter, the total contents of organic carbon in the high-grade ore zone are within the range of 0.11%−4.43% (Chen Qingnian et al., 1998), thus providing a reducing environment for the evolution of ore-forming fluids.

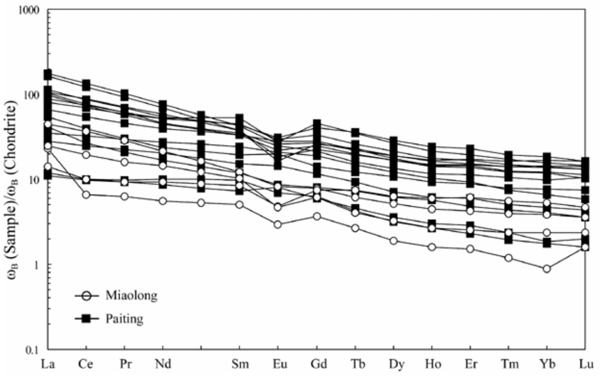

Fig. 4. The REE distribution patterns of altered-mineralized rocks at Paiting and Miaolong.

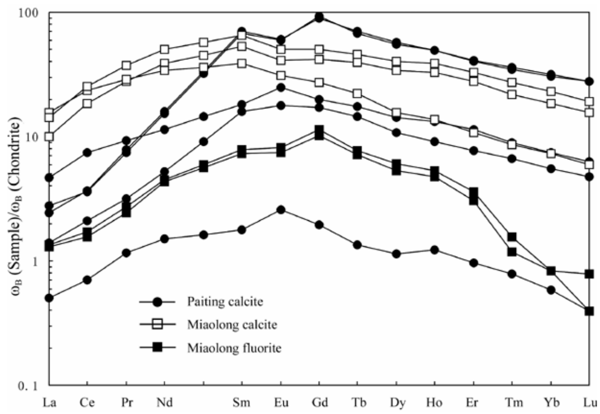

Fig. 5. REE distribution patterns of calcite in relation to mineralization at Paiting and Miaolong.

4.2 Stable isotopic characteristics

4.2.1 Sulfur isotope

Sulfur isotopic composition is the most direct and most effective approach to trace the source of sulfur in ore-forming fluids. Studies by Zhang Xingchun et al. indicated that the Au-bearing mineral-pyrite in the Carlin-type gold deposits exhibits rims-texture. The sulfur isotopic composition of hand-picked pyrite could not represent that of ore-forming fluids. Some scholars made use of the sulfur isotopic compositions of minerals formed at the late stage of metallogenesis, such as realgar and stibnite, to investigate the sulfur isotopic composition of ore-forming fluids (Su Wenchao et al., 2009; Stephen et al., 2005; Zhang Yu et al., 2010b). The sulfur isotopic values of five stibnite samples taken from Sandu-Danzhai gold deposits vary within the range of 17.72‰−21.68‰, in consistency with the results obtained by our predecessors (Li Chaoyang et al., 2002; Chen Qingnian et al., 1998). The fact that the sulfur isotopic values are within the range of those of marine sulfates (Fig. 6, Table 3) reflects that the sulfur in ore-forming fluids was derived from the Cambrian strata. The case is different from the sulfur isotopic analysis data of pyrite, realgar and orpiment from the Carlin-type gold deposits both in the United States and in southwestern Guizhou. Those sulfur isotopic values are characteristic of magma-sourced sulfur (Fig. 6, Table 3), demonstrating that the sulfur in ore-forming fluids was derived from magmas (Stephen et al., 2005; Zhang Yu et al., 2010b).

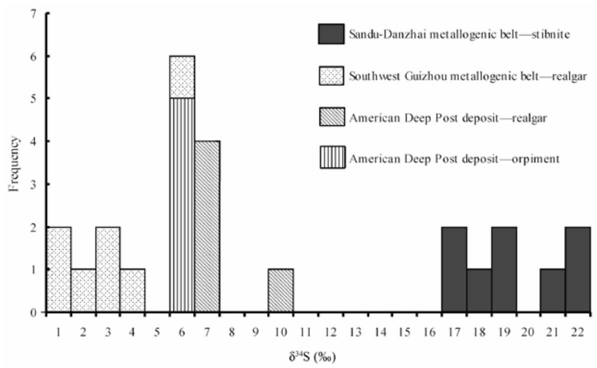

Fig. 6. Sulfur isotope histograms of stibnite, realgar and orpiment in the Carlin-type gold deposits both in Guizhou Province of China and the United States.

4.2.2 Carbon and oxygen isotopes

The carbon and oxygen isotopic characteristics of the Carlin-type gold deposits in the Sandu-Danzhai metallogenic zone (Table 4, Fig. 7). Liu Jianming et al. (1997) summarized the ranges of carbon and oxygen isotopic values for the three major sources in crust-source fluids (organic source, marine carbonate rock source, magma-mantle source) and the variational trends of carbon and oxygen isotopic compositions came from five major processes. As can be seen from Fig. 7, carbon ($\delta^{13}C_{PDB}$=-1.61‰−-5.82‰) and oxygen ($\delta^{18}O_{SMOW}$=13.97‰−19.24‰) in the calcite related to the mineralization of gold deposits in the study region were both derived from the dissolution of marine carbonate rocks. At the same time, the possibility could not be ruled out that carbon and oxygen derived from dehydroxylation of sedimentary organic matter.

Table 1 REE contents of altered-mineralized rocks at Paiting and Miaolong (×10^{-6})

Sample No.	Sampling location	Sample type	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	ΣREE	LREE	HREE	LREE/HREE	LaN/YbN	δEu	δCe
ZK1-5	Paiting	Pyritized carbonaceous mudstone	38.30	74.30	8.77	32.30	5.74	1.06	4.65	0.73	4.21	0.83	2.46	0.36	2.48	0.36	22.90	176.55	160.47	16.08	9.97	11.07	0.60	0.95
ZK5-7		Pyritized carbonaceous mudstone	22.90	44.60	5.40	20.60	5.14	1.62	5.76	0.83	4.51	0.81	2.37	0.32	2.08	0.29	23.10	117.23	100.26	16.97	5.90	7.89	0.90	0.94
ZK7-7-1		Carbonaceous mudstone	6.60	15.30	2.11	9.40	2.34	0.83	2.38	0.35	1.80	0.35	1.00	0.13	0.80	0.11	11.50	43.50	36.58	6.92	5.28	5.91	1.06	0.99
ZK7-7-2		Pyritized carbonaceous mudstone	8.30	19.80	2.79	12.90	3.68	1.21	3.92	0.56	3.11	0.58	1.54	0.19	1.11	0.15	18.70	59.84	48.68	11.16	4.36	5.36	0.96	1.00
ZK31-5		Pyritized carbonaceous mudstone	41.60	81.70	9.66	35.80	6.50	1.50	5.52	0.82	4.75	0.95	2.83	0.42	2.83	0.41	25.50	195.29	176.76	18.53	9.53	10.54	0.74	0.96
ZK32-5		Pyritized carbonaceous mudstone	24.20	46.60	5.84	21.40	5.28	1.43	4.35	0.60	3.44	0.65	1.88	0.27	1.64	0.27	17.80	117.85	104.75	13.10	7.99	10.58	0.88	0.93
ZK33-5		Pyritized carbonaceous mudstone	27.00	53.20	6.57	25.40	6.66	1.78	8.39	1.34	7.33	1.38	3.83	0.49	3.13	0.41	38.70	146.91	120.61	26.30	4.58	6.18	0.72	0.94
PD-2-1		Pyritized mudstone	13.00	23.90	2.87	11.00	2.96	1.15	2.93	0.46	2.72	0.52	1.48	0.20	1.31	0.19	15.20	64.69	54.88	9.81	5.59	7.11	1.18	0.91
PD-2-2		Carbonaceous siltstone	24.70	53.90	6.78	27.30	5.72	0.94	5.37	0.86	4.78	0.92	2.52	0.36	2.33	0.33	25.30	136.81	119.34	17.47	6.83	7.60	0.51	1.00
PD-2-3-1		Pyritized mudstone	18.90	42.50	5.48	24.20	8.12	1.58	9.34	1.31	6.84	1.21	3.20	0.44	2.67	0.37	34.40	126.16	100.78	25.38	3.97	5.07	0.55	1.01
PD-2-4		Carbonaceous siltstone	2.60	6.00	0.89	4.00	1.11	0.46	1.23	0.17	0.90	0.17	0.47	0.06	0.31	0.05	6.20	18.42	15.06	3.36	4.48	6.01	1.19	0.96
PD-2-5		Stibnitized argillaceous limestone	2.80	6.10	0.93	4.70	1.50	0.40	1.30	0.16	0.81	0.15	0.38	0.05	0.30	0.04	4.50	19.62	16.43	3.19	5.15	6.69	0.85	0.92
PD-2-6		Stibnized siliceous mudstone	9.80	16.40	2.00	7.90	1.82	0.50	1.64	0.27	1.56	0.32	0.80	0.11	0.69	0.09	9.20	43.90	38.42	5.48	7.01	10.18	0.86	0.85
PD-3-1		Argillaceous siltstone	21.00	45.40	5.85	24.40	6.83	1.70	6.84	0.98	5.38	1.00	2.80	0.38	2.42	0.33	29.10	125.31	105.18	20.13	5.22	6.22	0.75	0.98
PD-3-2		Pyritized argillaceous siltstone	15.50	33.30	4.34	18.20	5.14	1.28	5.12	0.74	4.29	0.80	2.29	0.31	2.01	0.26	23.20	93.58	77.76	15.82	4.91	5.53	0.75	0.97
ML-28-2	Miaolong	Stibnitized limestone	10.60	22.60	2.71	10.10	1.88	0.48	1.62	0.23	1.32	0.25	0.71	0.10	0.65	0.09	6.70	53.34	48.37	4.97	9.73	11.69	0.82	1.00
ML-28-4-2		Stibnized siliceous limestone	3.30	6.10	0.89	4.30	1.29	0.28	1.52	0.28	1.61	0.34	1.02	0.14	0.89	0.12	10.60	22.08	16.16	5.92	2.72	2.65	0.61	0.85
ML-28-5		Stibnized siliceous limestone	5.40	4.00	0.60	2.60	0.78	0.17	0.76	0.10	0.48	0.09	0.25	0.03	0.15	0.04	2.70	15.45	13.55	1.90	7.13	25.82	0.66	0.44
ML-28-6		Stibnized siliceous limestone	5.80	11.80	1.52	6.80	1.55	0.27	1.26	0.15	0.83	0.15	0.42	0.06	0.40	0.06	4.00	31.07	27.74	3.33	8.33	10.40	0.57	0.95

Table 2 REE contents of calcite in relation to mineralization at Paiting and Miaolong (×10^{-6})

Sample No.	Sample type	Sampling location	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	ΣREE	LREE	HREE	LREE/HREE	LaN/YbN	δEu	δCe
ZK5-7-1	Calcite	Paiting	0.58	2.23	0.75	7.38	10.7	3.51	18.23	2.64	14.5	2.81	6.83	0.92	5.34	0.7	72.4	77.12	25.2	51.97	0.48	0.07	0.76	0.7
ZK5-7-2			0.66	2.22	0.7	7.22	10.4	3.46	18.96	2.52	14	2.8	6.69	0.88	5.19	0.71	68.4	76.41	24.7	51.75	0.47	0.091	0.74	0.71
ZK7-7-1			1.11	4.52	0.88	5.33	2.77	1.44	4.05	0.65	3.6	0.75	1.88	0.23	1.27	0.16	21.4	28.64	16.1	12.59	1.27	0.62	1.31	1.05
ZK7-7-2			0.12	0.43	0.11	0.7	0.27	0.15	0.4	0.05	0.29	0.07	0.16	0.02	0.1	0.01	2.19	2.88	1.78	1.1	1.61	0.86	1.39	0.84
PD-2-3-1			0.33	1.28	0.3	2.44	2.44	1.04	3.52	0.54	2.76	0.52	1.27	0.17	0.93	0.12	13.4	17.66	7.83	9.83	0.79	0.25	1.08	0.91
ML-28-1	Calcite	Miaolong	2.38	11.3	2.65	18	8.11	2.38	8.63	1.47	8.62	1.87	4.63	0.56	3.14	0.4	48.8	74.14	44.8	29.32	1.52	0.54	0.86	0.97
ML-28-3-1	Fluorite		0.32	1.04	0.26	2.12	1.2	0.47	2.32	0.29	1.53	0.3	0.6	0.04	0.14	0.02	23.4	10.65	5.41	5.24	1.03	1.63	0.84	0.83
ML-28-3-2	Fluorite		0.31	0.96	0.23	2.03	1.12	0.43	2.1	0.27	1.35	0.27	0.5	0.03	0.14	0.01	17.6	9.75	5.08	4.67	1.08	1.58	0.84	0.84
ML-28-5	Calcite		3.71	14.3	2.72	15.8	5.92	1.79	5.64	0.83	3.97	0.77	1.79	0.22	1.24	0.15	20.6	58.85	44.2	14.61	3.02	2.14	0.93	1.05
ML-28-6	Calcite		3.38	15.5	3.55	23.4	9.89	2.9	10.35	1.72	10.2	2.18	5.39	0.69	3.95	0.49	55.5	93.59	58.6	34.97	1.67	0.61	0.86	0.98

Table 3 The sulfur isotopic compositions of stibnite, realgar and orpiment in the Carlin-type gold deposits both in Guizhou Province of China and the United States

Sample No.	Location	Determined mineral	$\delta^{34}S_{CDT}$ /10^{-3}	Data source
PD-2-6	Paiting	Stibnite	20.46	This study
ML-28-1	Miaolong		21.65	
ML-28-2	Miaolong		21.68	
ML-28-3	Miaolong		17.72	
ML-28-4-2	Miaolong		18.47	
PHZ-2-2	Paihe	Stibnite	16.58	Li Hongyang et al., 2002
YY-2	Yangyong		18.16	
DZ-2	Hongfachang		16.07	
ZK27403-3	Bojitian	Realgar	1.04	Zhang Yu et al., 2010b
ZK27403-4	Bojitian		3.02	
ZK27403-5	Bojitian		0.79	
ZK27403-6	Bojitian		2.87	
ZK27403-7	Bojitian		0.73	
ZK27408-1	Bojitian		5.86	
SYD	Shuiyindong		2.14	
DP-03-02-RL	Deep post	Realgar	6.00	Kelsler et al., 2005
DP-03-03-RL	Deep post		6.00	
DP-03-04-RL	Deep post		6.30	
DP-03-05-RL	Deep post		6.70	
SJ-552-1093-RL	Screamer		9.90	
DP-03-03-OR	Deep post	Orpiment	5.70	
DP-03-04-OR	Deep post		5.30	
P-175-1327-OR	Deep post		5.50	
P-175-1330-OR	Deep post		5.80	
P-208-1584-OR	Deep post		5.50	

Table 4 Carbon and oxygen isotopic compositions of calcite in relation to mineralization at Paiting and Miaolong

Sample No.	Sampling location	$\delta^{13}C_{PDB}$ /‰	$\delta^{18}O_{PDB}$ /‰	$\delta^{18}O_{SMOW}$ /‰
zk5-7-2	Paiting	-4.03	-11.64	18.91
zk7-7-1		-3.08	-13.97	16.51
zk7-7-2		-1.66	-16.43	13.97
pd-2-3-1		-5.82	-12.50	18.02
pd-2-3-2		-5.72	-12.29	18.24
ml-28-1	Miaolong	-1.74	-11.32	19.24
ml-28-3		-1.98	-11.40	19.16
ml-28-5		-1.61	-11.44	19.12
ml-28-6		-1.79	-11.55	19.00

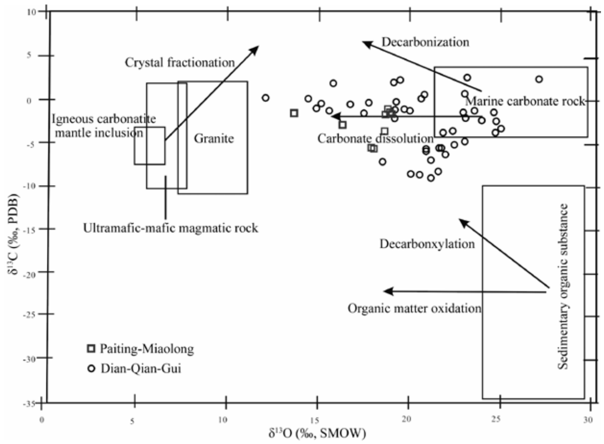

Fig. 7. Projection diagram of carbon and oxygen isotopic compositions of calcite in relation to mineralization at Paiting and Miaolong (after Liu Jianming and Liu Jiajun, 1997).

4.2.3 Hydrogen and oxygen isotopes

The Hg deposits in the Sandu-Danzhai metallogenic zone are an important part of the Hg deposits in Guizhou Province. Yan Junping et al. (1989) pointed out from the hydrogen and oxygen isotope data of ore-forming fluids for the Hg deposits and of spring water and fissure water basically representing meteoric waters (Table 5, Fig. 8) that ore-forming fluids for the Hg deposits in Guizhou were derived from meteoric water or mixed water dominated by meteoric water. A comparison between the H and O isotope data of ore-forming fluids from the Carlin-type gold deposits (Table 5) and the research data of Hg deposits (Fig. 8) reveals that the H and O isotope data of ore-forming fluids for the Carlin-type gold deposits (Table 5) are concentrated in two fields, i.e., in the field of magmatic and metamorphic waters and below the first field. As compared with the first field, the second field occurs to strong δD excursion.

In this region there have not been found magmatic rocks associated with metallogenesis, so it is considered that the ore-forming fluids were derived mainly from metamorphic water came from metamorphism. This conclusion is in consistency with the geological fact that there are large quantities of medium- to low-grade metamorphic rocks in this region (Wang Shangyan et al., 2006). The phenomenon of strong H isotope excursion is mainly due to H isotope exchange between ore-forming fluids and sedimentary rocks (the δD values of crude oil-related organic matter are -85‰− -181‰ Hsueh-Wen Yeh and Samuel Epstein, 1981), which promoted H isotope excursion. The fluids are different from those of Hg deposits derived mainly from meteoric water or mixed water dominated by meteoric water.

Table 5 The hydrogen and oxygen isotopic compositions of ore-forming fluids for Au and Hg ore deposits in the Sandu-Danzhai metallogenic zone

Sample No.	Sample location	Determined mineral	Metallogenic temperature (℃)	$\delta^{18}O$ /10^{-3}	$\delta^{18}O_{H2O}$ /10^{-3}	δD_{H2O} /10^{-3}	Data source
DZ-2	Hongfachang	Stibnized carbonate dyke	200	+19.8	+8.25	-47	
W005-2	Paiting	Gold mineralized quartz vein	242	+19.9	+10.49	-62	Li Hongyang et al.,2002
YY-2	Yangyong	Stibnite-calcite quartz vein	224	+19.4	+9.14	-102	
H(Hong)653	Hongfachang	Quartz from Au(Hg) deposit	220	+19.59	+8.38	-97.7	
S(Si)504	Sixiangchang	Quartz from Au(Hg) deposit	220	+23.10	+11.89	-61.50	Chen Qingnian et al.,1998
H(Hong)	Hongfachang	Quartz from Au deposit	217	+20.0	+8.62	-66	
S(Si)	Sixiangchang	Quartz from Au deposit	217	+23.10	+11.72	-110	
K1	Xinfachang	Dolomite from Hg deposit	140	+14.34	-1.0	-51.9	
K16a	Hongfachang	Calcite from Hg deposit	130	+19.81	+6.11	-59.5	
TBC-11	Dadongla, Tongren	Quartz from Hg deposit	135	+18.84	+1.5	-55.03	
WBW-48	Muyouchang, Wuchuan	Calcite from Hg deposit	136	+17.37	+4.15	-67.7	
II-1	Yanhe hot spring	Hot spring water			-9.44	-54.21	
II-2	Tianling, Yinjiang	Hot spring water			-10.56	-56.7	Yan Junping et al.,1989
II-5	Shiqian hot spring	Hot spring water			-9.63	-57.58	
W2	Muyouchang, Wuchuan	Fissure water from tunnel			-9.06	-46	
W3	Ganxigou, Wuchuan	Underground river water			-4.99	-46.6	
W4	Sanjiatian, Wuchuan	Dolomite fissure water			-7.4	-48.6	
W5	Sanjiatian, Wuchuan	Slope water			- 6.59	- 44.3	
W6	Longjingpo, Wuchuan	Limestone interstitial water			- 6.69	- 44.7	

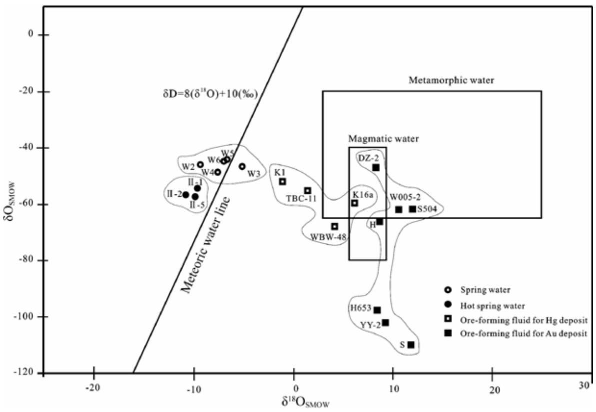

Fig. 8. Projection diagram of hydrogen and oxygen isotopic compositions of ore-forming fluids for Au and Hg deposits in the Sandu-Danzhai metallogenic zone.

5 Ore-forming materials and ore-forming fluids

Studies by Lu Huanzhang, Yan Junping, Cheng Dunmom, et al. on inclusions in carbonate minerals and quartz indicated that the ore-forming fluids for the Danzhai deposits are characteristic of brines with the salinities being 16 or 18− >26 NaCl wt%. No homogenization salinity was obtained in the study by Chen Qingnian et al. (1998). In the inclusions the contents of cations increased in the order of K^+ >>Na^+>>Ca^{2+}, Mg^{2+} and the anions were rich in Cl^- and F^- and their contents tended to increase in the order of Cl^-＞F^-. The ore-forming solutions were weakly alkaline (pH=6.5), with Eh= +412.6− +432.6 mV, indicative of the KCl-NaCl system. Moreover, the inclusions have the characteristics of brines. All this indicates that the ore-forming fluids for the Danzhai gold deposit are characterized as being high in salinity. Hydrogen and oxygen isotopic studies indicated that gold ore-forming fluids were derived from metamorphic fluids. The metamorphic fluids with a high salinity (30 wt%−40 wt% NaCl) can promote the mobilization and migration of gold in the ore bed (Fan Hongrui, 1991; Xie Yihan and Fan Hongrui, 2000).

The coexistence of gold and organic matter in the Carlin-type gold deposits in the Sandu-Danzhai metallogenic zone is one of the characteristic features of gold deposits. Some authors once pointed out that organic matter and ore-forming elements in the Danzhai region may have been derived from the Sinian black light-grade metamorphic shales and Lower Cambrian black rock strata (Chen Qingnian et al., 1998; He Lixian, 1993). The contents of ore-forming elements in the black rock strata are shown in Fig. 9. It can be seen from Fig. 9 that the contents of gold are usually 10×10^{-9}, partly up to 250×10^{-9}; those of As are usually within the range of 20×10^{-6}, partly up to $10^{4}\times10^{-6}$; those of Sb are usually 10×10^{-6}, in some cases up to 200×10^{-6}. The contents of Au in the black rock strata come up to more than 5×10^{-9}, an amount in source rocks, which is required for the formation of a gold deposit (Hofstra and Cline, 2000; Ross et al., 2011). It is suggested that the Sinian black light-grade metamorphic shales and Lower Cambrian black rock strata may be the source beds.

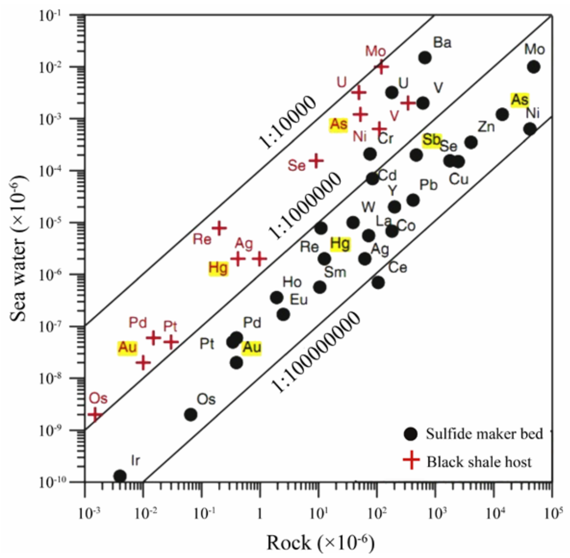

Fig. 9. The element contents of Early Cambrian black shales on the Yangtze platform (after Lehmann et al., 2007).

6 Discussion on the metallogenesis of gold deposits

In discussion on the genesis of gold deposits at Danzhai Prof. Tu Guangchi (1990) proposed such an understanding that “Metallogenesis has a long history, it at least involves two events. The first event is syngenetic sedimentation, producing ore bed” and “Metallogenesis occurs during the second event and this event involves the last phase of most Yanshanian movement in China”. This understanding is of great guiding significance. The Sinian black light-grade metamorphic shales and Lower Cambrian black rocks constitute the ore beds. The Rb-Sr isochron age of the Hongfachang and Sixiang high-grade ores is 114±6 Ma (Chen Qingnian et al., 1998), and the fission track ages of quartz from the Paiting and Yangyong ore deposits are 66.7 and 65.4 Ma, respectively (Li Chaoyang et al., 2002), indicating that metallogenesis occurred at the late stage of Yanshanian movement (Hu Ruizhong et al., 2002).

The metallogenesis of the Carlin-type gold deposits in this region is controlled by Yanshanian tectonic activities, and the Yanshanian movement promoted the migration and mobilization of metamorphic fluids in the extensively developed medium- to low-grade metamorphic rocks (Fig. 1) and the fluids carried preliminarily enriched Au and associated elements such as Hg, As and Sb in the Sinian black light-grade metamorphic shales and Lower Cambrian black rocks. The ore-forming fluids found their way into the suitable metallogenic environment along the fault zone, followed by the precipitation of gold to form gold deposits. The ores are obviously controlled by regional fault structures and the fault structural space provided an environment favorable for the precipitation of ore-forming fluids, promoting the precipitation of gold minerals, finally resulting in the formation of the Carlin-type gold deposits in the Sandu-Danzhai metallogenic zone.

7 Conclusions

(1) The mineralized-altered rocks in the Carlin-type gold deposits of the Sandu-Danzhai metallogenic zone display LREE-enrichment patterns. Calcite and fluorite in relation to metallogenesis show MREE-enrichment patterns, in consistency with those of calcite in relation to mineralization in the Carlin-type gold deposits in southwestern Guizhou.

(2) Hydrothermal calcite in relation to metallogenesis shows weak negative Eu and Ce anomalies, indicating that there occurred metallogenesis of hydrothermal fluids under a relatively reducing environment.

(3) As viewed from the carbon and oxygen isotope geochemical characteristics of calcite and the sulfur isotope geochemical characteristics of stibnite, it is considered that carbon, oxygen and sulfur were derived from ore-hosted wall-rocks. δD and $\delta^{18}O$ of ore-forming fluids are characteristic of metamorphic water.

(4) The process of metallogenesis of the Carlin-type gold deposits in this region is controlled by Yanshanian tectonic activities. The Yanshanian movement promoted the migration and mobilization of metamorphic fluids and the fluids carried preliminarily enriched Au and associated elements such as Hg, As and Sb in the ore beds into a suitable metallogenetic environment along the fault zone, followed by the precipitation of gold minerals, finally resulting in the formation of gold deposits.

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