Trace element distribution and enrichment patterns of Ediacaran-early Cambrian, Ziyang selenosis area, Central China: constraints for the origin of Selenium

Jie Long^{a,b}, Kunli Luo^{a,b,*}

^a Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101

^b University of Chinese Academy of Sciences, Beijing 100049

*Correspondence to: luokl@igsnrr.ac.cn & kunliluo@sohu.com

Abstract:

Ziyang County is one of the two major regions in Central China exposed to selenium (Se) poisoning. To understand the origin of anomalous Se enrichment strata of the Ediacaran-early Cambrian period (ca. 635-520 Ma) in the area of Ziyang affected by selenosis, major and trace elements were analyzed for 468 samples collected from the Lujiaping Formation in Ziyang County, Central China.

Se is the most highly enriched trace element in the Lujiaping Formation of the Ediacaran-early Cambrian period. Selenium concentrations vary from 0.03 to 303 ppm, with an average of 16 ppm, or more than 324 times the concentration found in the upper continental crust. The average Se content of Bed 6 (approximately 63 m thick) is the highest, at 49.20 ppm (1.45-154 ppm). The Lujiaping Formation is highly enriched in Cd ($\times 53$), S ($\times 31$), Mo ($\times 22$) and As ($\times 13$), compared to the upper continental crust. It is slightly enriched in V ($\times 8.07$), Ba ($\times 7.65$), Ga ($\times 7.24$), Zn ($\times 7.22$), U ($\times 5.43$), Cu ($\times 4.02$), Bi ($\times 2.55$), Tl ($\times 2.16$), Ni ($\times 1.75$), P ($\times 1.03$), and depleted in Pb (0.97), Cr (0.96), Sr (0.81), Li (0.79), In (0.69), Sc (0.69), Be (0.38), Cs (0.36), Co (0.30), Rb (0.29), and Th (0.27).

All Eu/Eu* for the forty anomalous Se-enrichment samples (Se=42-303 ppm) of the 1st Member (1.09-2.09, average=avg=1.40), 2nd Member (1.20-1.38, avg=1.29), 3rd Member (1.12-4.00, avg=2.38) and 4th Member (2.51-4.48, avg=3.56), show positive Eu anomalies and an increasing trend upward. However, Eu/Eu* of two samples are 0.90 (HSBY324, Bed 4 of 1st Member) and 0.95 (HSBY401, Bed 6 of 1st Member), which indicate that they are characterized by hydrothermal sediments, except HSBY324 and HSBY401 of 1st Member. Based on these elements' geochemical and petrographic characteristics, we conclude that these samples are of hydrothermal origin. There is also a strong positive correlation between Se and Ba ($R_{\text{Se-Ba}}=0.738^{**}$, $n=40$). In three point X-ray energy spectrometric analysis of black shale mineral anomalous Se-enrichment samples (HSBY601), the nor.C measurements of Ba (L Series) are 55.50 wt.%, 54.94 wt.% and 27.20 wt.%, respectively, with the corresponding Atom. C of 14.80, 14.50 and 5.72 at.%. Thus, the main Se source were derived from hydrothermal fluids, of anomalous Se-enrichment strata of Ediacaran-early Cambrian (ca. 635-520 Ma) of South Qinling Mountain.

Key words: Lujiaping Formation, Selenium, Hydrothermal activity, South Qinling Mountain.

48 1. Introduction

49 Selenium (Se) exists in low concentrations in the Earth's crust (~0.05 ppm) (Liu
50 et al., 1984), and it is not easily enriched to the extent that it can be of commercial
51 importance. Se is an essential trace element for animals and humans (Rosenfeld 1964;
52 Terry et al., 2000) but, in excess, can become toxic. For human consumption, this
53 toxicity threshold is 400 mg/day (Mac Farquhar et al., 2010), with possible
54 consequences including neurotoxicity, cancer and diabetes (Vinceti et al., 2014; Sun
55 et al., 2014). Trace elements enter soils primarily as a result of the weathering of
56 trace element-bearing rocks (Foth, 1978). Anthropogenic metal input and natural
57 geochemical sources of elements may influence trace element concentrations in soils
58 and edible plants (Thornton, 1993).

59 In the 1960s, Se-poisoning was discovered in Shuang'an Town of Ziyang
60 County, located in Shaanxi province (Central China), and the area with the greatest
61 concern for selenosis in Shuang'an Town is very small, limited to Naore Village (Mei
62 1985). Luo et al (2004) suggested that the selenosis problem in Naore Village is due
63 to the 40-meter-thick package of carbonaceous slate, black shale and volcanic tuff of
64 the Ediacaran-early Cambrian (ca. 635-520 Ma) Lujiaping Formation (LFm), which
65 crops out in the floor of the valley and weathers to Se rich soils, and Se
66 concentrations vary from 0.324-42.3 ppm (average Se content= 20.48 ppm). However,
67 the origin of this high-Se strata is unclear. Se concentrations in the LFm strata range
68 widely from 0.324 to several hundred ppm (Luo et al., 1994, 1995a, 2001, 2004;
69 Fang et al., 2002; Wen et al., 2003), with the highest Se contents found in the
70 siliceous rocks, with a concentration of 278 ppm (Feng et al., 2004). The thickness of
71 the LFm is approximately 900 meters (Xiang et al., 1999); however, there has been
72 no systematic study of the Se contents in the LFm strata, and samples of the LFm
73 from previous studies are scattered. The distribution and enrichment patterns of Se
74 and other trace elements in whole stratigraphic sequences of the LFm are unclear.

75 Additionally, the Ediacaran-Cambrian transition represents an important event in
76 Earth's history (Knoll et al., 2006) and is a significant turning point in the radiation of
77 complex multicellular life on Earth (Fike, 2006). The concentrations of bio-essential
78 trace elements in the ocean, including Se, have had a major influence on evolutionary
79 processes throughout time (Knoll et al., 2006; Morel, 2008). From 700 to 540 Ma,
80 many of the trace elements (e.g., Se, Cr, Ag, Mo, Cu, Ni, and Mn) rose by 1 to 2
81 orders of magnitude in response to the Great Oxygenation Event 2 (Large et al.,
82 2014), accompanied by the diversification of phytoplankton and the appearance of
83 eukaryotic clades (Shields-Zhou and Och, 2011), which were the preludes to the
84 Cambrian Explosion (Large et al., 2014). Therefore, a study of the trace element
85 distribution and enrichment patterns, and Se in particular, of Ediacaran-lower
86 Cambrian strata in Ziyang selenosis will not only help us explore the Se resource and
87 understand Se origin of the strata in geological history (especially during the key time
88 of Ediacaran-early Cambrian) but also provide the basic data for further research on
89 the relationship between trace elements and the evolution of multicellular life in
90 earth's history.

91 In this paper, 468 fresh rock samples of LFm (Huoshibian sections in Ziyang
92 County, Shaanxi Province) were collected from Sep. 28th to Oct. 20th, 2013. We are
93 currently investigating the distribution and enrichment patterns of trace elements (in
94 particular Se) of the LFm of Ediacaran-early Cambrian and exploring the Se-origin of
95 anomalous Se enrichment strata.

2. Geological setting

The Qingling-Dabie-Sulun orogen, which stretches East–West for more than 2000 km between the North China Block and the South China Block (SCB), constitutes the geographic, geologic and cultural heart of China (Bader et al., 2013) (Fig.1.A and B). The Qingling Mountain (QM) is divided into two orogen, including North Qingling Mountain (NQM) and South Qingling Mountain (SQM) (Dong et al., 2011).

The South Qingling Mountain (SQM) is located in an important tectonic position linking the NQM and the SCB, and is characterized by thin-skinned structures which include south-vergent imbricated thrust-fold system (Dong et al., 2008), and redivided into (Southern of South Qingling Mountains) S-SQM and N-SQM (Northern of South Qingling Mountains). S-SQM consists of a pre-Sinian basement overlain by a thick pile of Neoproterozoic (Sinian) to early Paleozoic strata (Fig. 1C) (Lin et al., 2013).

The study area is located in the S-SQM (Fig. 1C). The main strata exposed in the S-SQM from older to younger are:

- The Yunxi Group (Ca.830-750 Ma (Cai et al., 2006; Ling et al., 2010) and Ca. 2500 m thick), composed of dacitic-rhyolitic lavas, pyroclastic tuffs, and basalt-andesites (Ling et al., 2010).

- The Yaolinghe Group (Ca.750-635 Ma (Cai et al., 2007) and Ca. 775 to 1500 m thick), mainly composed of (meta-) basic to acid volcanic rocks, tuffaceous rocks and fine-grained (meta-) sedimentary rocks, which is unconformably overlain by the Lujiaping Formation (Xia and Xia, 2008; Zhu et al., 2014).

- The Lujiaping Formation (LFm)(Ca.635-520 Ma and Ca. 900 m thick) is mainly composed of dark-black siliceous, shale, dolomite and interbedded with minor, barolite ore and volcanic tuff, which is conformably covered by the Jianzhuba Formation (Luo, 2006).

The other Lower Paleozoic strata is mainly composed of clastic and carbonate rocks (Zhang and Yu, 2000).

3. Sampling and analytical methods

3.1 Sample description

The LFm is divided into the following five members (Fig. 2 and 3) in ascending order: I=1st Member, II= 2nd Member, III= 3rd Member, IV= 4th Member, and V= 5th Member. The 1st Member, 2nd Member and 3rd Member are characterized by carbonate rocks interbedded with clastic rocks, including 6 series of carbonate and clastic rocks (series 1 to 6). The 4th Member is characterized by black or light-green siliceous rock interbedded with witherite ore (ca. 2-meter-thick). The 5th Member is characterized by gray or gray-black shale. Furthermore, based on the lithological features of the LFm from the lower to upper sections, it is also divided into 14 beds, which contain 6 beds of carbonate rocks (Bed 1, 3, 5, 7, 9 and 11) and 8 beds of clastic rocks (Bed 2, 4, 6, 8, 10, 12, 13, 14).

A detailed description of the LFm of the Southern Shaanxi Province is found in Table 1, including data regarding its thickness, sample location and lithology.

The bedding structure was observed on the dolomitic limestone. The structures of siliceous rocks and black shale are mainly bedded and laminated, respectively. Sharp-clasts were observed within the black shale.

Within the siliceous rocks, the crystal size of quartz tends to be quite variable, from several μm to several hundred μm . Individual quartz crystals have irregular crenulate crystal boundaries and a pronounced undulose extinction (Fig. 4A and B),

which is similar to typical micro-crystalline and meso-crystalline quartz, which results from the disordered crystallographic structure of individual grains (Knauth, 1994). The meso-crystalline quartz (20–50 μm) is the most common recrystallized quartz phase in the siliceous rock samples. Large pores and cavities within these siliceous rock samples are commonly filled with length-fast mega-crystalline quartz, and there are also a few quartz veins (Fig. 4C).

The orbicular and nodular structures were observed within the black shale of HSBY 382 (Fig. 4E). Sporadic pyrite and deposition of organic matter were observed within the black shale of HSBY 601 under orthogonal polarized light (Fig. 4D). Within the HSBY 370 sample, a typical black shale of drill hole with pyrite aggregates in a dark matrix of quartz, adularia and chlorite, and chlorite (Chl) appears as light-gray patches compared to the dark-gray quartz-adularia matrix (Fig. 4E).

3.2 Sample collecting

The Huoshibian section is located in Maoba Town, which is the southernmost town of Ziyang County, Southern Shaanxi Province (in the southernmost edge of South Qinling Mountains), China, and exhibits an unusually complete and expanded stratigraphic column spanning the interval from the Neoproterozoic (Sinian) to the Lower Paleozoic sediments. Stratigraphic ordering of the whole horizons appears identical to the East-West's auxiliary roadside (Fig. 2 and Fig 4A). The Global Positioning System (GPS) locations and elevations (height above sea level) of the cross section from the start to the end point are $32^{\circ}18.179'\text{N}$ - $108^{\circ}13.929'\text{E}$ 586 m and $32^{\circ}18.188'\text{N}$ - $108^{\circ}13.415'\text{E}$ 613 m, respectively.

A total of 497 fresh rock samples in 593.7 m thick strata were collected from the Huoshibian sections, including 29 samples of the Yaolinghe Group (underlain strata of the LFm) and 468 samples of the Lujiaping Formation. To ensure the investigated samples could reflect the overall characteristic of the Ediacaran and early Cambrian strata, the rock samples were collected densely over intervals of approximately 0.1 m to 3 m in this stratum. The positions of these samples in the stratigraphic column are shown in Figure 1C and 2B.

3.3 Analytical methods

Prior to chemical analyses, all the Lujiaping Formation rocks were firstly cleaned by deionized water to eliminate weathered surfaces, and secondly air-dried at room temperature, then fresh parts were chipped and ground into powder (less than 200 mesh) for analyses. All samples were analyzed at Laboratory of Analytical and Testing Center (LATC) of the Institute of Geographic Sciences and Natural Resources Research (IGSNRR), Chinese Academy of Sciences (CAS), Beijing, China.

Major and trace elements analysis

Major and trace element compositions were analyzed by Elan DRC-e Inductively Coupled Plasma Optical Emission Spectrometer, standard X-ray fluorescence spectrometry methods and Perkin-Elmer Optima 5300DV Inductively Coupled Plasma Mass Spectrometry. Analyses of the Chinese national rock standards GBW07112 indicated that precisions and accuracies were both better than 5%. Parallel samples, blank experiment, and repeated measurements were also used. Se and As were determined by Hydride Generation Atomic Fluorescence Spectrometer (Beijing Haiguang Instruments Co. Ltd). The procedures detailed for sample dissolution and calibration with international rock standards have been documented by Ni (2015) and Wang (2015) to which the reader is referred.

The ratios of Eu/Eu^* and Ce/Ce^* were calculated by using published formulae (Bau and Dulski, 1999; $\text{Eu}/\text{Eu}^* = 2\text{Eu}_N/(\text{Sm}_N + \text{Gd}_N)$, $\text{Ce}/\text{Ce}^* = 2\text{Ce}_N/(\text{La}_N + \text{Pr}_N)$, “N” refers to normalized concentrations against the shale standard PAAS (Taylor and McLennan, 1985).

Loss on ignition (LOI) analysis

A clean porcelain-crucible was placed in a muffle furnace and was heated to 900°C for 30 minutes. The porcelain crucible was removed from the furnace when the temperature fell to 500°C , and was quickly placed in a desiccator. After 10-20 minutes, the weight of the porcelain crucible (m_1) was measured. 1.0 g of powdered sample (m_2) was put in the known-weight of porcelain-crucible and then heated again as described above. The weight of the heated sample was measured (m_3). The calculated LOI values are as follows: $\text{LOI} (\%) = [(m_1 + m_2) - m_3]/m_2 \times 100$.

Pearson correlation method

The method of Pearson correlation analysis was used in this paper. The “*” represent that correlation is significant at the 0.05 level (2-tailed), while the “**” represent that Correlation is significant at the 0.01 level (2-tailed).

4. Results

4.1 Major elements

The major elements of the LFm of Ziyang County of southern Shaanxi Province, China, are given in Appendix as Supplementary Data. The average and range contents are listed into Table 2, of Carbonates and Clastics’ major elements from the LFm of southern Shaanxi Province.

4.2 Trace elements

The trace elements of the LFm of Ziyang County of southern Shaanxi Province, China, are given in Appendix as Supplementary Data. The variation of the Se, Cd, Mo, S and As contents of the most enrichment five trace elements of 14th Bed of the LFm of southern Shaanxi Province are shown in Table 3. Enrichment patterns of trace elements of 14th Bed of the LFm are shown in Figure 6. The trace element with a Concentration Coefficient ($\text{CC} = \text{ratio of element concentration in the LFm vs. upper continental crust}$ (Taylor and McLennan, 1985) is divided to five interval: $\text{CC} > 1000$, $1000 > \text{CC} > 100$, $100 > \text{CC} > 10$, $10 > \text{CC} > 1$, $\text{CC} < 1$, which represent anomalous enrichment, supper enrichment, remarkable enrichment, slight enrichment and depletion of the corresponding elements, respectively.

The only trace element with a concentration coefficient (CC) > 100 is Se ($\text{CC} = 324$). Trace elements with a CC of 10 to 100 included Cd ($\text{CC} = 53$), Mo (31), S (22) and As (13). Other elements are slightly enriched in the LFm, including V (8.07), Ba (7.65), Ga (7.24), Zn (7.22), U (5.43), Cu (4.02), Bi (2.55), Tl (2.16), Ni (1.75), P (1.03). However, Pb (0.97), Cr (0.97), Sr (0.81), Li (0.78), In (0.69), Sc (0.69), Be (0.38), Cs (0.35), Co (0.30), Rb (0.29) and Th (0.26) are depleted (Fig. 9 A and B).

The Se contents of analysed samples are presented in Table 3; Selenium concentrations vary from 0.03 (HSBY607, dolomitic limestone) to 303 ppm (HSBY601, black shale), with average value of 16.40 ppm and concentration coefficient of 324.

Results shows that Se is the most highly enriched trace elements among the 27

analyzed trace elements of the LFm in the Ediacaran-early Cambrian period. Among the 14th Bed of the LFm, the average Se content of Bed 6 (1st member) is the highest, reaching to 49.20 ppm (1.45-154 ppm) and it more than 947 times of the UCC (0.05 ppm, Taylor and McLennan, 1985) and 84 times of the world shale average value (0.6 ppm, Turekian et al., 1961), respectively.

Among the 14th Bed of the LFm, the average Se value of the ordering sequence is as follows: B6 (49.20 ppm) > B4 (33.57 ppm) > B12 (21.72 ppm) > B 13 (19.82 ppm) > B 10 (17.88 ppm) > B 5 (10.07 ppm) > B 8 (9.90 ppm) > B 11 (9.25 ppm) > B 2 (6.90 ppm) > B 9 (6.24 ppm) > B 3(5.34 ppm) > B 7(2.75 ppm) > B 14 (2.29 ppm) > B 1 (0.30 ppm), respectively (Fig. 7A and B).

Additionally, Se, Cd, S, Mo, As, Ba, V, Ga and Bi are enriched in the Yaolinghe Group (Ca.750-653 Ma) and the LFm (Ca.635-520 Ma), however Co, Cs, Rb, Be and Th are depleted (Fig. 9A). Se, Cd, S, Mo, As, Ba, V, Ga and Bi contents of the LFm (Ca.635-520 Ma) are more than 206.77, 46.03, 1.45, 19.53, 11.40, 3.95, 5.71, 2.12 and 1.81 times of those elements of the Yaolinghe Group (Ca.750-653 Ma) (Fig. 9A). Tl is enriched in the LFm (CC=2.16), and depleted in the Yaolinghe Group (CC=0.65). Ni, Cu and U are enriched in the LFm (Ca.635-520 Ma), but depleted in the Yaolinghe Group (Ca.750-653 Ma) (Fig. 10A).

5. Discussion

5.1 Anomalous Selenium significance

5.1.1 Anomalous Selenium availability

Se belongs to a rare and dispersed group of elements, and it is not easily enriched to the extent that it can be of commercial importance. The Clarke value (Taylor, 1964) of Se in the crust and its concentration in all geological bodies are notably low and the occurrence of selenide minerals is scarce. It is difficult to extract selenium independently from other resources of industrial interest because of its low Clark value. Selenium comes primarily from selenium-containing deposits (Simon et al., 1997; Förster and Tischendorf, 2001; Buttermann and Brown, 2004). Some Se-containing deposits have been described (Table 4), such as the La'erma-Qiongmo Au-Se deposit in West Qinling Orogenic (Wen and Qiu, 1999; Liu et al., 2000) and the Yutangba Se deposit in Enshi, Hubei Province (Song, 1989; Yao et al., 2002; Zhu, 2000; Feng et al., 2004). China is rich in selenium resources, which can be distinguished as different associated deposits as follows: magmatic, porphyry, skarn, hydrothermal and sedimentary. Se demand has been increasing year after year in international trade, and because global selenium resources are limited and not broadly distributed, the inconsistency between supply and demand of selenium is notable. Therefore, it is urgent for selenium resources to be reinforced through exploration, exploitation and utilization.

The Yutangba Se deposit in Southwest Hubei province is located in the northeast segment of the upper Yangtze platform. This location contains a rare highly concentrated Se deposit and is well known for high levels of Se which reach up to 8590 ppm (Feng et al., 2004). Deposits are approximately 6 m thick, and Se content ranges from 47 to 350 ppm, with an average of 84 ppm (Table 4). However, Se content varies from 1120 to 5400 ppm within the Se containing rocks specifically (Peng 1997). Se content is approximately 15.4 ppm of some very large Au-Se deposits (Dexing, Jiangxi Province of China) (Table 4). The average Se content is

approximately 50 ppm, of the Se-V Ore deposits of Zhoumafeng, in Hefeng County of Hubei province (Liu et al., 2001). Based on the specifications for rare metal mineral exploration (DZ/T0203-2002) and industrial grade metallic ore deposits (DZ/T02142002) from the Ministry of Land and Resources of the People's Republic of China, both deposit industrial indexes DZ/T0203-2002 and DZ/T02142002 show that the minimum Cu and Se contents are 0.5 wt% and 0.001 wt%, respectively, and the minimum exploration thickness of a Cu-Se deposit is 4 m, for open-pit mining. Results shows that among the 14th Bed of the LFm, the average Se value of the ordering sequence is as follows: B6 (49.20 ppm) > B4 (33.57 ppm) > B12 (21.72 ppm) > B 13 (19.82 ppm) > B 10 (17.88 ppm) > B 5 (10.07 ppm) > B 8 (9.90 ppm) > B 11 (9.25 ppm) > B 2 (6.90 ppm) > B 9 (6.24 ppm) > B 3(5.34 ppm) > B 7(2.75 ppm) > B 14 (2.29 ppm) > B 1 (0.30 ppm), respectively (Fig. 7 A and B). Additionally, the LFm are widely distributed in southern Shaanxi Province. Therefore, based on the specifications of DZ/T0203-2002, DZ/T02142002 and the grade of the Se deposit presently being explored, Bed 6 (Se=49.20 ppm, range from 1.45 to 154 ppm, ca. 63.7- meter-thick, (Table 3 and 4) may be utilized as a Se source.

5.1.2 Anomalous Selenium in the carbonate and clastic rocks of the LFm

Enrichment patterns of trace elements in carbonate and clastic rocks of the LFm are shown into Figure 10B.

S, Mo, Se, Cu, Ga, V, As, Ba, Bi, Cd and Zn are enriched in clastic and carbonate rocks of the LFm. Concentrations of S, Mo, Se, Cu, Ga, V, As, Ba, Bi, Cd and Zn in the clastic rocks of LFm are more than 5.82, 4.88, 3.02, 2.97, 2.71, 2.35, 2.19, 2.06, 1.91, 1.27 and 1.21 times of those elements in the carbonate rocks.

Co, Cs, Rb, Be, Th and Li are depleted in clastic and carbonate rocks of the LFm. Contents of Co, Cs, Rb, Be, Th, Sc and Li in clastic rocks of the LFm are lower than 2.27, 3.75, 3.37, 3.02 and 2.47 times of those elements in the carbonate rocks.

Tl, Ni, Pb and Li are enriched in the clastic rocks and depleted in the carbonate rocks. Sr is enriched in the carbonate rocks, and depleted in the clastic rocks of the LFm.

Carbonate rocks

The highest average Se, Mo and Cd concentrations in the LFm carbonate rocks are located in Bed 5 (1st Member), with average values of 10 ppm (0.14-32 ppm), 19 ppm (0.00 -84 ppm) and 3.96 ppm (0.00-72 ppm), respectively. Both the highest S and As average contents of LFm carbonate rocks are located in Bed 11 (3rd Member), with values of 15435 ppm (618- 49790 ppm) and 38 ppm (11-156 ppm) (Table 3 and Fig. 10B).

Clastic rocks

Both the highest Se and Mo average contents of clastic rocks of the LFm are located in Bed 6 (1st Member), with averages of 49 ppm (1.45-154 ppm) and 137 ppm (0.97-562 ppm), and their corresponding average concentration coefficients (CC) are 947 (3.05-3090) and 91 (0.65-376). Both the highest average S and As contents are located in Bed 10 (2nd Member) and their average contents are 60512 ppm (3194-94300 ppm) and 48 (4.50-161 ppm), respectively, with corresponding average concentration coefficients of 172(9.13-269) and 32 (2.99-107). The highest Cd average content of clastic rocks are located on the Bed 4 (1st Member) with an average content of 13 ppm (0.41-144 ppm), and a corresponding average concentration coefficient of 131 (4.21-1473) (Table 3 and Fig. 10B).

Se is an important trace element in the environment. The excess and deficiency

of Se in the environment are closely related to human and animal health (Johnson et al. 2010; Rayman 2012). High levels of Se in the black shale suit of Ziyang County (Shaanxi Province, China) have implications for human and animal health due to soil composition and presence in edible plants (Fang et al., 2002). The Se contents of black shale parent rocks are important determinants of the concentration of Se in soils which satisfy the trace element needs of plants, humans, and livestock. Se concentrations in edible plants are influenced by Se concentrations in soils and waters (Fang et al., 2002; Yu et al., 2014). Thornton (1993) also suggested that trace element concentrations in soils and edible plants are controlled by anthropogenic metal input and natural geochemical sources. Negative environmental impacts can be caused by trace elements, such as Se, As, Cu, Cd, Cr, Co, Pb, Zn and Mo, from black shale (Yu et al., 2008). Black shale confers high levels of Se to ground waters through subsurface leaching (U.S. Department of Energy, (2011)), leaching of rock waste (Stillings and Amacher, 2010) and via overlying soils (Park et al., 2010; Tuttle et al., 2014). Bowland Shale (Central British Isles) is a black shale anomalously rich in trace elements, especially Se and As, which has the potential to release those elements into subsurface fluids (Parnell et al., 2016).

High Se, Cd, Mo, As, Cu and Zn concentrations in the carbonate and clastic rocks of the LFm of Ziyang County will result in high Se in soils through the process of weathering and leaching around the LFm rocks, which affect inhabitant and animal health through Se presence in soils and edible plants. This conclusion is also supported by Fang et al (2002). Therefore, we suggest that the potential threat for inhabitant and animal health persists.

5.2. Se-origin of the LFm anomalous Se-enrichment rocks

5.2.1 Source of the LFm anomalous Se-enrichment rocks.

5.2.1.1 Constraints from elements geochemistry

The concentrations of major, trace and rare earth elements of 40 anomalous Se-enrichment samples of the LFm are listed in Tables 5, 6 and 7, respectively. These samples include ten of siliceous rock, twenty-seven of black shale and three of dolomitic limestone, which are located in 1st Member (s2 and 3), 2nd Member (s4 and s5), 3rd Member (s6) and 4th Member (s7).

Major elements

Siliceous rocks of hydrothermal origin have relatively lower Mg and Al and higher Fe and Mn contents compared to siliceous rocks of non-hydrothermal origin (Yamamoto 1987). For example, MgO has been found to be depleted in mid-ocean ridge hydrothermal systems; in hydrothermal fluids (350°C) taken from the East Pacific Rise mid-ocean ridge, the MgO content is near zero (Edmond and Damm 1983). The MgO contents in ten siliceous rock samples are mostly less than 0.4 (Table 5), which is consistent with a hydrothermal origin (Yamamoto 1987).

In the Y-P₂O₅ plot (Fig. 11C), the 40 anomalous Se-enrichment samples in this study are located in modern hydrothermal sediments or within the area outlined for hydrothermal-type metalliferous sediments (HD) but are distant from the fields of diagenic-type metalliferous sediments.

In addition, detrital and authigenic components contribute to the trace element concentrations in bulk black shales (Tribovillard et al., 2006). An effective method to assess whether the content of a given element is dominantly controlled by the detrital flux is to plot this trace element versus aluminum (Al) or titanium (Ti), which can be considered as an indicator of the aluminosilicate fraction of the sediments, which is not mobile during diagenesis (Tribovillard et al., 2006; Schröder and Grotzinger,

2007). In table 8, Pearson correlation analysis shows the following: (1) no significant positive correlations between Se with Al of the 1st Member ($R_{\text{Se-Al}} = 0.13$, $n=22$), 2nd Member ($R_{\text{Se-Al}} = 0.51$, $n=4$), 3rd Member ($R_{\text{Se-Al}} = 0.45$, $n=9$) and 4th Member ($R_{\text{Se-Al}} = -0.75$, $n=4$); (2) no significant positive correlations between Se with Ti in both 2nd Member ($R_{\text{Se-Ti}} = 0.35$, $n=4$) and 4th Member ($R_{\text{Se-Ti}} = -0.75$, $n=5$) while significant positive correlations between Se with Ti in both 1st Member ($R_{\text{Se-Ti}} = 0.44^*$, $n=22$) and 3rd Member ($R_{\text{Se-Ti}} = 0.85^{**}$, $n=9$). Therefore, both the $R_{\text{Se-Al}}$ and $R_{\text{Se-Ti}}$ of Pearson correlation analysis suggest that anomalous Se-enrichment samples of 1st and 3rd Member of the LFm are influenced by detrital provenance, but 2nd and 4th Member are not controlled by terrigenous input.

Trace elements

High As, Mo, Ba, Cu, Ni, V and Zn concentrations in sediments should be influenced by hydrothermal activity (Yamamoto, 1987), because these elements could have been leached by hydrothermal fluids flowing through the dolomites and contributed to the above-mentioned acidic, high Cl-rich and high-temperature hydrothermal fluids (Barrett et al., 1988). As, Mo, Ba, Cu, Ni, V and Zn are anomalously enriched in the 40 anomalous Se-enrichment samples of the LFm (Table 6). The CC of As, Mo, Ba, Cu, Ni, V and Zn of ten siliceous rocks are 24.19, 42.66, 6.26, 5.15, 3.52, 17.92 and 12.67, respectively. The CC of As, Mo, Ba, Cu, Ni, V and Zn of twenty-seven black shale are 36.85, 126.56, 9.64, 7.12, 5.49, 29.68 and 9.62, respectively. The CC of As, Mo, Ba, Cu, Ni, V and Zn of three dolomitic limestone are 27.73, 6.16, 5.30, 3.54, 2.36, 9.94 and 11.73, respectively (Table 6).

Additionally, the Co to Zn ratio of 40 anomalous Se-enrichment samples ranges from 0.009 to 0.0913, with an average value of 0.017 (Table 6), which is less than that of BIF iron ore deposit ($\text{Co/Zn}=0.15$, hydrothermal origin) and iron-manganese ore deposit ($\text{Co/Zn}=2.5$, normal deposition) (Toth, 1980). In Figure 11A, the 40 samples are plotted into I area, which also indicates that these samples are influenced by hydrothermal fluids during their formation (Boström et al., 1973). In the $(\text{Cu}+\text{Co}+\text{Ni})\times 10\text{-Fe-Mn}$ diagram (Fig. 11C), all but four samples fall within the field for hydrothermal sedimentation from the Red Sea, which indicates that these 36 anomalous Se-enrichment samples are display characteristics that suggest they are of hydrothermal origin.

The U/Th ratio varies from 1.19 to 1011 (avg= 43) (Table 6), of 39 anomalous Se-enrichment samples, which is slightly high than that of hydrothermal sediments ($\text{U/Th} > 1$) (Girty et al., 1996; Rona, 1988), but the U/Th of black shale (HSBY318, Bed 4 of 1st Member) is 0.76. In Figure 11B, the 39 samples are plotted onto the FH (Fossil Hydrothermal Sedimentary) and ED (Eastern Pacific Ocean Hydrothermal Deposition) areas, which indicate hydrothermal-originated features. One sample (HSBY318, Bed 4 of 1st Member) is plotted into the deep sea area.

Therefore, 40 anomalous Se-enrichment samples of this study are further characterized by low Co/Zn ratios (averaging 0.017, high U/Th ratios (1.19- 1011), and high As, Mo, Ba, Cu, Ni, V and Zn contents (Table 6), which is typical of hydrothermal origin (Bostrom et al. 1979; Marchiget al. 1982), excluding four samples from the 1st and 3rd Member of the LFm.

Rare earth element (REE)

It is necessary to estimate the influence of terrigenous materials before interpreting the REE signatures of the studied 40 anomalous Se-enrichment samples. No systematic relationships of total REE ($\sum\text{REE}$, excluding yttrium), Y/Ho, Ce/Ce*

and Eu/Eu* with TiO₂ were observed (Table 11, $R_{\Sigma\text{REE-TiO}_2} = -0.039$, $R_{Y/\text{Ho-TiO}_2} = -0.282$, $R_{\text{Ce/Ce}^*-\text{TiO}_2} = 0.122$, $R_{\text{Eu/Eu}^*-\text{TiO}_2} = 0.22$; n=40), which suggested that the REE characteristics of these samples are not significantly contaminated by terrigenous materials (Sugahara et al., 2010).

REE composition is an important indicator used to distinguish hydrothermal sediments from those of a non-hydrothermal origin (Marchig et al., 1982; Wang et al., 1989). Generally, hydrothermal sedimentary are characterized by ΣREE and typical hydrothermal siliceous rock's ΣREE is below 200 ppm (Murray et al., 1991). In table 7 and figure 12, ΣREE contents vary from 8.11 to 312 ppm in 40 anomalous Se-enrichment samples of the Lfm. 1st Member ranges from 51 to 312 ppm (avg= 194 ppm), 2nd Member ranges from 8.11 to 177 ppm (avg= 90), 3rd Member ranges from 36 to 169 ppm (avg= 87 ppm) and 4th Member ranges from 16 to 101 ppm (avg= 50 ppm). ΣREE of 9 anomalous Se-enrichment black shales of 1st Member are 300 ppm (HSBY318), 312 ppm (HSBY370), 245 ppm (HSBY372), 285 ppm (HSBY375), 202 ppm (HSBY384), 213 ppm (HSBY386), 271 ppm (HSBY387), 263 ppm (HSBY388), 255 ppm (HSBY401), which indicate that they are influenced by terrigenous materials. ΣREE of 31 samples of anomalous Se-enrichment of the Lfm are below 200 ppm, which indicate that they are characterized by hydrothermal sediments.

In the sea floor hydrothermal system, REE patterns of vent fluids generally show an apparent enrichment in LREE (Light Rare Earth Element) relative to HREE (High Rare Earth Element) with pronounced positive Eu anomalies and weak or no negative Ce anomalies (Michard et al., 1983; German et al., 1991). This is a result of crysto-chemical exchange with plagioclase phenocrysts formed in the vent and speciation of vent fluids (Douville et al., 1999). Therefore, sediments deposited from vent fluids generally inherit the REE patterns of the parent vent fluids, i.e., with positive Eu anomalies (German et al., 1991), although REE patterns will vary as the influx of ambient sea water increases. From figure 11, REE patterns normalized by PAAS show a flat or moderate leftward inclination with slightly Ce negative anomaly and a significant positive Eu anomaly, of 40 samples of anomalous Se-enrichment of the Lfm, which is consistent with those of sediments of hydrothermal genesis (Fig. 12 A, B, C, D and F). The REE patterns of 40 anomalous Se-enrichment samples of the Lfm are similar to the patterns of the Yaolinghe group (underlain strata of the Lfm) (Fig. 12E), which may support the proposal that the Se and other elements tend to be associated with basic to acid volcanic rocks (especially Ni and V). All of the LREE/HREE vary from 1.7 to 20.6 (Table 7) and are to over 1, of 40 anomalous Se-enrichment samples of the Lfm, which indicate their hydrothermal origin.

Eu is the only rare earth element that can be reduced from Eu³⁺ to Eu²⁺ (Brookins, 1989). Positive Eu anomalies in shallow seawater may not reflect the redox state of waters but are always associated with high temperature (>250°C) (Sverjensky, 1984) and reducing hydrothermal fluid (Michard and Albarède, 1986; Kamber and Webb, 2001). In table 7, Eu/Eu* of 38 anomalous Se-enrichment samples range from 1.07 to 4.83. Eu/Eu* show an increasing trend upward, with 1st Member range from 1.09 to 2.09 (avg = 1.40), 2nd Member range from 1.20 to 1.38 (avg= 1.29), 3rd Member range from 1.12 to 4.00 (avg = 2.38) and 4th Member range from 2.51 to 4.48 (avg= 3.56). However, Eu/Eu* of 2 samples are 0.90 (HSBY324, Bed 4 of 1st Member) and 0.95 (HSBY401, Bed 6 of 1st Member). These Eu/Eu*

features indicate that 38 anomalous Se-enrichment samples are characterized by hydrothermal fluid, except HSBY324 and HSBY401 of 1st Member of the LFm.

Furthermore, Douville (2005) suggested that high temperature water–rock interaction could not fractionate Y and Ho resulting in the chondritic values of hydrothermal fluids (Y/Ho as 26–27). Additionally, modern deep-sea hydrothermal fluids' Y/Ho varying from 25 to 50, and Y/Ho of the “black smokers” and “white smokers” hydrothermal fluids are 25-28 and 30-35, respectively (Bau and Dulski, 1999). In table 7 and figure 12, Y/Ho of 37 anomalous Se-enrichment samples range from 27.73 to 44.55, but HSBY403 (Bed 6 of 1st Member), HSBY573 (Bed 12 of 3rd Member) and HSBY574 (Bed 12 of 3rd Member) samples are 18.86, 23.22 and 21.42, respectively.

5.2.1.2 Constraints from the petrographic evidence.

Siliceous rock is characterized by typical micro-crystalline, meso-crystalline texture and bed structure. In Bed 3 (1st Member), Bed 8 (2nd Member), and Bed 13 (4th Member) (Fig. 5A), these features are similar to the structure of typical hydrothermal siliceous rock. These features, including metasomatic residual texture and recrystallization phenomena are not observed in all parts of the LFm, which indicate that these samples were influenced by contemporaneous hydrothermal activity rather than later activity (Knauth, 1994). Orbicular, nodular structure (Fig. 4E) and sharp-clast (Fig. 5C1) were observed within black shale of HSBY 382 sample (Bed 6 of 1st Member), which are similar to the feature of typical hydrothermal black shale (Yang et al., 2005). Graded-bedding structures are observed within dolomitic limestone (Bed 11 of 3rd Member) with fine grain, which are influenced by hydrothermal activity (Yang et al., 2005). Sporadic pyrite was also seen within black shale of HSBY601 (Fig. 4D), and fine-grains and undeformed pyrite were observed within the siliceous rock of HSBY307 (Fig. 4F) The pyrite texture suggests a contemporaneous hydrothermal origin (Knauth, 1994), and this conclusion was also supported by a few calcite veins of dolomitic limestone (Fig. 5D) and pseudo-parallel mega-crystalline quartz vein (Fig. 4C).

Anomalous concentrations of Se, together with S, Mo, Se, Cu, As, Cd and Zn in the Ediacaran-lower Cambrian strata, is not only distributed in the Ziyang County but also in many parts of the Yangtze and Tarim cratons of southern and western China. This anomalous elemental association and their concentration within a limited stratigraphic interval occurring over a wide area suggests that the enrichment processes may have been controlled by contemporaneous hydrothermal activity (rather than the latter).

Therefore, based on section 5.2.1.1 and 5.2.1.2, the 40 anomalous Se-enrichment samples of the LFm are consistent with sediments of hydrothermal genesis. However, some samples from the 1st and 3rd Member of the LFm are also influenced by terrigenous input.

5.2.2 Connection between the Se with hydrothermal activity

Forty anomalous Se-enrichment samples of the LFm are strongly influenced by contemporaneous hydrothermal activity. However, this study aims to understand whether there is a connection between Se content and hydrothermal activity.

Se is a typical dispersed element with a low crustal concentration (0.05 ppm) (Liu, 1984) and tends to enrich toward the core of the Earth (Xia et al., 1995). Se concentrations in modern seawater are approximately 0.08 ppb, but because of the low oxidation rate of Se, S/Se ratios are high (e.g., seawater shows ratios $> \times 10^8$) (Measures and Burton, 1980). Se contents in sulfides of most clastic

sedimentary rocks and evaporites are also low, and the S/Se ratios are more than 100,000 (Measures and Burton, 1980). Although Se may be enriched in organic-rich black shale formed in anoxic basins, Se concentrations range usually from several ppm to tens ppm (Stanton, 1972; Howard, 1977). However, in this study, Se contents of 40 anomalous Se-enrichment samples ranges from 47 ppm to 303 ppm, which cannot be entirely explained by anoxic basins. This is also supported by the Se contents (more than several hundreds and thousands ppm) of Zunyi Ni-Mo-Se deposit of Guizhou Province in China (Wen and Garignan 2011).

Some researchers suggested that Se tends to increase in high-temperature systems (Nough and Sun, 1995; Hamlyn et al., 1986). Se in hydrothermal sulfide minerals are highly variable but are universally higher. For example, at 13° N, high Se values up to 2500 ppm occur in high-temperature mineral assemblages in the middle of the deposit (Auclair et al., 2014). High Se contents are also found in pyrite (200 ppm) in volcanic-hosted Cu-rich massive sulfide deposits (Huston et al., 1995). The S/Se ratios are relatively lower in MOR hydrothermal fluxes (~ 4000) (And and Schultz, 1996), in the primitive mantle (~ 3300) (Nough and Sun, 1995) and in MOR basalts (3000-6000) (Hamlyn et al., 1986). As shown in Figure 13 and Table 6, in the 1st Member of the LFm, S/Se ranges from 17 to 875, with increasing-upward trend. In the 2nd Member, S/Se of siliceous rocks (Bed 8) are 11 (HSBY 446) and 20 (HSBY 456), with a slight decreasing upward trend in this Member. Then, S/Se increase to 834 (black shale of HSBY513 of Bed 10 of 2nd Member). In the 3rd and 4th Member, S/Se range from 21 to 893, with a decreasing-upward trend (Fig. 12). The S/Se of 40 anomalous Se-enrichment samples range from 11 to 893 (Table 6), which are below 3-5 orders of magnitude of clastic sedimentary rocks and evaporites of modern water origin ($S/Se > \times 10^5$), but closer to that of high-temperature hydrothermal fluids ($S/Se \sim 1000$) (Wignall, 1994). Among the 40 samples, HSBY 446 and HSBY 456 (2nd Member) siliceous S/Se are lowest, which indicates that the degrees of hydrothermal activity within 2nd Member are more extensive than the 1st, 3rd and 4th Member. The boiling point of Se is 682.9 °C, and its isomorphism could be expanded under high temperatures; therefore, Se is more easily enriched in high temperature sediment than in low temperature sediment (Lott et al., 1999; Liu, 1984). Therefore, the measurements mentioned above indicated that hydrothermal fluids (rather than seawater) provide a large amount of Se for 40 anomalous Se-enrichment samples of the LFm from the Ediacaran-early Cambrian time.

Enriched Ba in sediment is an indication of a hydrothermal contribution to sediments (Weaver and Tarney, 1984), because minerals of hydrothermal sediments consist of barite ($BaSO_4$), cymrite ($BaAlSi_3O_8(OH)$) and coronite ($NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_3(OH)$) (Qi, 1999). Barite mineral deposits account for 13% of hydrothermal sediments of oceanic spreading centers. Ba content is higher than 1% in 47% of hydrothermal sediments of oceanic spreading centers. The Ba content is approximately 6.3% in hydrothermal sediments of the East African rift (Rona, 1988). Weaver and Tarney (1984) report that Ba contents are 1079.3, 1079.3, 1375 and 1869 ppm in hydrothermal sediments, siliceous rock, metal-rich shale and black shale, respectively. Our data show that the average Ba content is 3828, 4505 and 2914 ppm (Table 6), for ten siliceous rock, twenty-seven black shale and three dolomitic limestone. There is a significant positive correlation between Se and Ba ($R_{Se-Ba} = 0.738^{**}$, $n = 40$, Table 10). Additionally, approximately 2.5 m thick witherite deposits were distributed on Bed 13 of 4th Member (Table 1). Ba contents of HSBY677B, 677C and 677E samples are 112100, 144200 and 138700 ppm, with corresponding Se concentrations of 24 ppm, 10 ppm and 24 ppm, respectively

(Appendix). Figure 14 illustrates that the nor.C of Ba (L Series) are 55.50 wt.%, 54.94 wt.% and 27.20 wt.%, respectively, in a three-point X-ray energy spectrometric analysis of black shale mineral anomalous Se-enrichment samples (HSBY601), with a corresponding Atom. C of 14.80, 14.50 and 5.72. Finally, more than forty witherite deposits or witherite-barite deposits (Ediacaran-early Cambrian) have been discovered in Ziyang county, which hosts some of the largest Ba deposits in China and is also among the world's largest witherite deposits (Lv et al., 2004).

5.2.2.2 Sedimentary environment

The Ziyang Se enrichment areas as studied in this article are located the Caledonian fold belt of the North Daba Mountains (Mei 1985; Luo et al. 2001, 2004). Hydrothermal siliceous rocks appear to be preferentially formed in extensional, rift-type environments or fault-controlled basins, and tend to be associated with large-scale syn-sedimentary faults. For example, the La'erma-Qiongmo Se deposit in western Qinling is located on the Bailongjiang Great Fault (Liu et al. 2000).

The Ediacaran-early Cambrian "black rock series" lithologies comprise carbonate, black shale, stone coal, siliceous shale, chert, carbonaceous siliceous rock, and carbonaceous slate (Fan 1983; Orberger et al. 2007; Feng et al. 2010), and is not only distributed in Ziyang area of the Southern Shaanxi province of S-SQM but also in many parts of the Yangtze cratons. On the one hand, the absence of coarse grained sediments within the sequence of Huoshibian section (this study) would appear to exclude a shallow marine environment. On the other hand, sporadic pyrite and deposition of organic matter were observed within black shale (Figure 4C). Fine grains and undeformed pyrite were also observed with the siliceous rock (Figure 4F). Almost no fossils of benthon and bioturbation were observed from field and section's photomicrographs. Those indicate that the LFM are considered to have formed in a deep to semi-deep sea sedimentary environment.

Molybdenum (Mo) is conservative under the oxic marine environment, with the oxides form of MoO_4^{2-} , but in the anoxic marine environment, S will replace O and form the thiomolybdate: $\text{MoO}_4^{2-} \rightarrow \text{MoO}_x\text{S}_{4-x}$ ($x=0-3$), and then form the MoS_4^{2-} under more sulfide environment, finally Mo is enriched into sediments (Algeo and Lyons, 2004). In this study, Mo are anomaly enriched in the 40 anomalous Se-enrichment samples of the LFM (Table 6). The average Mo contents of ten siliceous rocks, twenty-seven black shales and three dolomitic limestone are more than 42.66, 126.56 and 6.16 times of the upper continental crust (Table 6). Pearson correlation analysis showed that there is a significant positive correlations between Mo with V ($R_{\text{Mo-Al}}=0.516^{**}$, $n=40$, Table 10), which indicate that they formed under the anoxic marine environment (Yang et al., 2004).

Additionally, negative Ce anomalies have been found mostly within the ocean basins since seawater is typically depleted in Ce due to the preferential removal of Ce^{4+} from the water column (Elderfield and Greaves, 1982) and likely sinking in manganese nodules in view of their positive Ce anomalies (Fleet, 1983). The Ce/Ce^* values were proven fairly consistent during diagenesis (Murray et al., 1992), thus are valuable to identify the depositional environment (Murray et al., 1990, 1991; Ding and Zhong, 1995). Previous studies (Murray et al., 1990, 1991) show that sediments deposited near ocean spreading ridges have the lowest Ce/Ce^* values (avg. 0.29), while those deposited on the ocean basin floor have the intermediate Ce/Ce^* values (avg.=0.60), and those deposited on continental margins basin have the higher Ce/Ce^* values (0.79-1.78, avg.=1.03). In table 7 and figure 12, HSBY370 sample (Bed 6 of 1st Member) have a obvious negative Ce anomalies ($\text{Ce}/\text{Ce}^*=0.38$), suggesting a deep

sea environment. Ce/Ce* show an increasing trends upward (Fig. 12) and 2nd Member range from 0.58 to 0.83, 3rd Member range from 0.63 to 1.93 and 4th Member range from 0.69 to 0.83 (Table 7), suggesting a semi-deep sea environment, which indicate that the SQM sedimentary environment evolved from the ocean basin to continental margins basin during the Ediacaran-early Cambrian time. This scenario is further demonstrated by the (La/Ce)_N values that mainly cluster between 1.0 and 1.5, which are also in a good agreement with the values of continental margins basin (0.5-1.5) proposed by Murray(1994). HSBY370 sample (Bed 6 of 1st Member) also show the highest (La/Ce)_N values (2.35) (Table 7 and Fig. 12), which are in a good agreement with the values of open-ocean basins (1.5-2.5) proposed by Murray(1994).

Therefore, during the Ediacaran-early Cambrian time, the South Qingling Mountains were located in a rift basin (Tang et al., 2007). Based on this regional tectonics characteristic and these data mentioned above, we conclude that frequent magmatic activities carried a large amount of hydrothermal fluids the basin; thus, the circulation of hydrothermal fluids could have easily carried a large amount of Se. High temperatures enabled enriched Se in the LFm and then ultimately formed anomalous Se-enrichment sediments.

6. Conclusion

1) The only trace element with a concentration coefficient (CC) > 100 was Se (CC=324). Trace elements with a CC of 10 to 100 included Cd (CC=53), Mo (31), S (22) and As (13). Other elements were slightly enriched in the LFm, including V (8.07), Ba (7.65), Ga (7.24), Zn (7.22), U (5.43), Cu (4.02), Bi (2.55), Tl (2.16), Ni (1.75), P (1.03). However, Pb (0.97), Cr (0.97), Sr (0.81), Li (0.78), In (0.69), Sc (0.69), Be (0.38), Cs (0.35), Co (0.30), Rb (0.29) and Th (0.26) were depleted

2) Se concentrations in the LFm range from 0.03 (sample no. of HSBY607, dolomitic limestone) to 303 ppm (sample no. of HSBY601, black shale), with an average value of 16 ppm and CC of 324. The average Se content of Bed 6 (1st Member, ca. 63-meter-thick) was the highest, reaching 49.20 ppm (1.45-154 ppm), among the 14th Bed of the LFm, which may be utilized as a Se resource. Additionally, S, Mo, Se, Cu, As, Cd and Zn were enriched in clastic and carbonate rocks of the LFm. A potential threat for inhabitant and animal health still exists.

3) Anomalous Se-enrichment beds from the 1st, 2nd, 3rd and 4th Members of the LFm were consistent with those of sediments of hydrothermal genesis, and the degrees of hydrothermal activity within 2nd Member was more extensive than the 1st, 3rd and 4th Members. However, those samples from the 1st and 3rd Member of the LFm were also influenced by terrigenous input. Contemporaneous hydrothermal fluids provide a large amount of Se to those anomalous Se-enrichment bed of LFm of Ediacaran-early Cambrian in Southern of South Qingling Mountains.

Acknowledgements

The authors express their heartfelt thanks to Du Yanjun and Xiang Linhua for helping us collect the samples in the fieldwork. We gratefully acknowledge the editor and anonymous reviewers for their constructive comments and suggestions. This work was supported financially by the Chinese National Science Foundation Project (41172310,41472322), the Major State Basic Research Development Program (973) (2014CB238906), and the National High Technology Research and Development Program (863) of China (2004AA601080, 2006AA06Z380).

References

- And, H.E., Schultz, A., 1996. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annual Review of Earth & Planetary Sciences* 24, 191-224.
- Auclair, G., Fouquet, Y., Bohn, M., 2014. Distribution of selenium in high-temperature hydrothermal sulfide deposits at 13 degrees North, East Pacific Rise. *Canadian Mineral* 25, 577-587.
- Bader, T., Ratschbacher, L., Franz, L., Yang, Z., Hofmann, M., Linnemann, U., Yuan, H., 2013. The heart of China revisited, I. Proterozoic tectonics of the Qin mountains in the core of supercontinent Rodinia. *Tectonics* 32, 661-687.
- Barrett, T.J., Anderson, G.M., Lugowski, J., 1988. The solubility of hydrogen sulphide in 0–5 m NaCl solutions at 25°–95°C and one atmosphere. *Geochimica Et Cosmochimica Acta* 52, 807-811.
- Bau M, Dulski P. 1999. Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater. *Chemical Geology*, 1999, 155, 77-90.
- Boström, K., Kraemer, T., Gartner, S., 1973. Provenance and accumulation rates of opaline silica, Al, Ti, Fe, Mn, Cu, Ni and Co in Pacific pelagic sediments. *Chemical Geology* 11, 123-148.
- Bostrom, K., Rydell, H., and Joensuu, O., 1979, Langbank: An exhalative sedimentary deposit: *Economic Geology*, v. 74, p.1002-1011.
- Brookins, D., 1989. Aqueous geochemistry of rare earth elements. *Reviews in Mineralogy and Geochemistry*, 21: 201-225.
- Butterman, W.C., Brown, R.D., 2004. Mineral Commodity Profiles: Selenium. Open-File Report.
- Cai, Z.Y., Luo H., Xiong, X.L., Wu, D.K., 2006. A discussion on the age of the meta-sedimentary rocks in the upper part of the wudang group: constrained by the grain-zircon U-Pb dating. *Journal of Stratigraphy*, 30, 60-63.
- Cai, Z.Y., Xiong, X.L., Luo H., Wu, D.K., Sun, S.C., and Rao, B.L., 2007. Forming age of the volcanic rocks of the yaolinghe group from wudang block, southern qinling mountain: constraint from grain-zircon U-Pb dating. *Acta Geologica Sinica*, 81, 620-625.
- Chen, N.S., 1990, Lower Cambrian black shale series and associated stratiform deposits in southwest China: *Chinese Journal of Geochemistry*, 9, 244-255.
- Dong, Y.P., Zhou, M.F., Zhang, G.W., Zhou, D.W., Liang, L., Qi, Z., 2008. The Grenvillian Songshugou ophiolite in the Qinling Mountains, Central China: implications for the tectonic evolution of the Qinling orogenic belt. *J Asian Earth Sci. Journal of Asian Earth Sciences* 32, 325-335.
- Dong, Y.P., Zhang, G.W., Neubauer, F., Liu, X.M., Genser, J., and Hauzenberger, C. 2011. Tectonic evolution of the qinling orogen, china: review and synthesis. *Journal of Asian Earth Sciences*, 41, 213-237.
- Douville E, Bienvenu P, Charlou J. L., 1999. Yttrium and rare earth elements in fluids from various deep-sea hydrothermal systems. *Geochimica et Cosmochimica Acta*, 63 , 627-643.
- Elderfield, H., Greaves, M.J., 1982. The rare earth elements in seawater. *Nature* 296, 214 - 219.
- Ellis, D.R., and Salt, D.E., 2003. Plants, selenium and human health. *Curr. Opin. Plant Biol*, 6, 273-279.
- Foth, H.D., 1978, *Fundamentals of Soil Science*, 4th edn, Wiley, New York.
- Fan, D.L., 1983, Polyelements in the Lower Cambrian black shale series in southern China, in Augustithis, S.S., ed., *The significance of trace metals in solving petrogenetic problems and controversies*: Athens, The Ophrastus Publication, p. 447-474.
- Fan, D.L., Yang, R.D., and Huang, Z.X., 1984, The Lower Cambrian black shale series and iridium anomaly in South China, in *Development in Geoscience, Contributions to the 27th International Geological Congress*, Moscow: Beijing, Science Press, 215-224.
- Fang, W.X., Hu, R.Z., and Wu, P.W., 2002. Influence of black shales on soils and edible plants in the ankang area, shaanxi province, P. R. of china. *Environmental Geochemistry and*

Health, 24, 35-46.

Feng, C.X., Liu, J.J., Hu, R.Z., and Liu, S., 2004, Geochemistry of the Yutangba Se Deposit in Western Hubei, China: Chinese Journal of Geochemistry, 23, 255-264.

Feng, C.X., Liu, S., Hu, R.Z., Liu, J.J., Luo, T.Y., Chi, G.X., and Qi, Y.Q., 2010, Geochemistry of Lower Cambrian Se-rich black rock series in Guizhou Province, southwest of China: The petrogenesis and enrichment mechanism of selenium: Earth Science- Journal of China University of Geosciences, 35, 947-958 (in Chinese with English abstract).

Feng, C.X., Chi, G.X., and Liu, J.J., 2012, Geochemical constraints on the origin and environment of Lower Cambrian, selenium-rich siliceous sedimentary rocks in the Ziyang area, Daba region, central China. International Geology Review, 54, 765-778.

Fike, D.A.G., J. P; Pratt, L. M; Summons, R.E, 2006. Oxidation of the Ediacaran Ocean. Nature 444, 744-747.

Fleet, A.J., 1983. Hydrothermal and hydrogenous ferro-manganese deposits: Do they form a continuum? The rare earth element evidence. In: Rona, P.A., Boström, K., Laubier, L., Smith, K.L. (Eds.), Hydrothermal Process at Seafloor Spreading Centers. Plenum Press, New York, 535 -555.

Förster, H. J., Tischendorf, G., 2001. Se-rich tennantite and constraints on p-T-X conditions of selenide mineral formation in the Schlema-Alberoda uranium ore district (western Erzgebirge, Germany). Neues Jahrbuch für Mineralogie - Abhandlungen 176, 109-126.

German C. R., Holliday B. P., 1991. Elderfield H. Redox cycling of rare earth elements in the suboxic zone of the Black Sea. Geochimica et Cosmochimica Acta, 55. 3535-3558.

Hamlyn, P.R., Keays, R.R., Hamlyn, P.R., 1986. Sulfur saturation and second-stage melts; application to the Bushveld platinum metal deposits. Economic Geology 81, 1431-1445.

Howard J. H. 1977. Geochemistry of selenium: formation of ferroselite and selenium behavior in the vicinity of oxidizing sulfide and uranium deposits. Geochim. Cosmochim. Acta 41, 1167-1196.

Huston, D.L., Cooke, D.R., Sie, S.H., Suter, G.F., Both, R.A., 1995. Trace elements in sulfide minerals from eastern Australian volcanic-hosted massive sulfide deposits; Part I, Proton microprobe analyses of pyrite, chalcopyrite, and sphalerite, and Part II, Selenium levels in pyrite; comparison with delta 34 S values and implications for the source of sulfur in volcanogenic hydrothermal systems. Economic Geology 90, 1167-1196.

Johnson C.C., Fordyce F.M., Rayman M.P., 2010. Symposium on "Geographical and geological influences on nutrition": factors controlling the distribution of selenium in the environment and their impact on health and nutrition. Proc Nutr Soc, 69: 119-132. doi:10.1017/S0029665109991807.

Knoll, A.H., Walter, M.R., Narbonne, G.M., N., C.-B., 2006. The Ediacaran Period: a new addition to the geologic time scale. Lethaia 39, 13-30.

Knauth, L.P., 1994. Petrogenesis of chert. Silica Physical Behavior Geochemistry & Materials Applications 29, 233-258.

Large, R.R., Halpin, J.A., Danyushevsky, L.V., Maslennikov, V.V., Bull, S.W., Long, J.A., Gregory, D.D., Lounejeva, E., Lyons, T.W., Sack, P.J., McGoldrick, P.J., Calver, C.R., 2014. Trace element content of sedimentary pyrite as a new proxy for deep time ocean-atmosphere evolution. Earth Planet. Sci. Lett. 389, 209-220.

Lin, Z.W., 2013. Zircon U-Pb dating and geochemistry of the volcanic rocks at Huachanggou area, Mian-Lue suture, South Qinling. Acta Petrologica Sinica 29, 83-94.

Ling, W.L., Duan, R.C., Liu, X.M., Cheng, J.P., Mao, X.W., Peng, L.H., Liu, Z.X., 2010. U-Pb dating of detrital zircons from the Wudangshan Group in the South Qinling and its geological significance. Chinese Science Bulletin 22, 2440-2448.

Liu, Y. J., 1984. Element geochemistry (in Chinese). Science Press, Beijing.

Liu, J. J., 1993. Geochemistry of hydrothermal sedimentary silicalite. Acta geologica Sichuan, 13. 110-118.

Liu, J.J., Zheng, M.H., Liu, J.M., and Su, W.C., 2000, Geochemistry of the La'erma and Qiongmou Au-Se deposits in western Qinling Mountains, China: Ore Geology Review, 17, 91-111.

Liu, J.J., Feng, C.X., and Zhang, M.H., 2001. The studying situation on selenium resource and

780 its exploiting and utilizing prospect (in Chinese). World Sci-tech R & D.
 781 Lott, D.A., Coveney, R.M.J., Murowchick, J.B., Grauch, R.I., 1999. Sedimentary exhalative
 782 nickel-molybdenum ores in south China. *Economic Geology* 94, 1051-1066.
 783 Luo, K.L., Chen, D.M., Ge, L.M., 1994. Accompanied and associated ores of the Paleozoic
 784 black shale and coal, Shaanxi Province, China. Northwest University Press, Xi'an pp
 785 36-46.
 786 Luo, K.L., Jiang, J.S., 1995a. Enrichment of Selenium in stone coal in South Qinling Mountain
 787 and its significance (in Chinese). *Journal of Chang Chun U Earth Sci* 25, 125-130.
 788 Luo, K.L., Su, W.Z., Du, M.L., Lei, F.Y., 1995b. Some microelements of lower Paleozoic stone
 789 coal in South Qinling. *Journal of Xi'an Mining Institute*.
 790 Luo, K. L., Pan, Y. T., Wang, W. Y. & Tan, J. A. 2001 Selenium content and distribution pattern
 791 in the Palaeozoic strata in the southern Qinling Mountains. *Geological Review*, 47(2),
 792 211-217.
 793 Luo, K.L., Xu, L.R., Tan, J.A., 2004. Selenium source in the selenosis area of the Daba region,
 794 South Qinling Mountain, China. *Environmental Geology* 45, 426-432.
 795 Luo, K.L., 2006. The Lujiaping formation of Northern Daba Mountain. *Journal of Stratigraphy*
 796 30, 149-156.
 797 Luo, K. L., 2011, Arsenic and Fluorine Contents and Distribution Patterns of Early Paleozoic
 798 Stone like Coal in the Daba Fold Zone and Yangtze Plate, China: *Energy Fuels*, v. 25, p.
 799 4479-4487.
 800 Lv, Z.C., Liu, C.Q., Liu, J.J., 2004. The bio-barite in witherite deposits from Southern Qinling
 801 and its significance. *Progress in Natural Science Materials* 10, 889-895.
 802 Mac Farquhar, J.K., Broussard, D.L., Melstrom, P., Hutchinson, R., Wolkin, A., Martin, C.,
 803 Burk, R.F., Dunn, J.R., Green, A.L., Hammond, R., Schaffner, W., Jones, T.F., 2010.
 804 Acute selenium toxicity associated with a dietary supplement. *Archives Intern. Med.* 170,
 805 256-261.
 806 Marchig, V., Gundlach, H., and Moller, P., 1982, Some geochemical indication for
 807 determination between diagenetic and hydrothermal metalliferous sediments: *Marine*
 808 *Geology*, 50, 241-256.
 809 Measures, C.I., Burton, J.D., 1980. The vertical distribution and oxidation states of dissolved
 810 selenium in the northeast Atlantic Ocean and their relationship to biological processes.
 811 *Earth & Planetary Science Letters* 46, 385–396.
 812 Mei, Z.Q., 1985. Summary on two selenium-rich areas of China (in Chinese). *Journal of*
 813 *Chinese Endemic* 12, 379-385.
 814 Michard, A., and Albarède, F., 1986. The REE content of some hydrothermal fluids. *Chemical*
 815 *Geology*, 55: 51–60.
 816 Morel, F.M.M., 2008. The co-evolution of phytoplankton and trace element cycles in the
 817 oceans. *Geobiology* 6, 318–324
 818 Murray, R.W., Buchholtz ten Brink, M.R., Jones, D.L., Gerlach, D.C., Russ III, G.P., 1990. Rare
 819 earth elements as indicators of different marine depositional environments in chert and
 820 shale. *Geology* 18, 268 - 271.
 821 Murray, R.W., Gerlach, D.C., Iii, G.P.R., Jones, D.L., 1991. Rare earth, major, and trace
 822 elements in chert from the Franciscan complex and Monterey group, California:
 823 Assessing REE sources to fine-grained marine sediments. *Geochimica Et Cosmochimica*
 824 *Acta* 55, 1875–1895.
 825 Murray, R.W., Buchholtz ten Brink, M.R., Gerlach, D.C., Russ III, G.P., Jones, D.L., 1992. Rare
 826 earth, major, and trace element composition of Monterey and DSDP chert and associated
 827 host sediment: assessing the influence of chemical fractionation during diagenesis.
 828 *Geochim. Cosmochim. Acta*, 56, 2657- 2671.
 829 Murray, R.W., 1994. Chemical criteria to identify the depositional environment of chert:
 830 general principles and applications. *Sediment. Geol.* 90, 213 - 232.
 831 Ni, R. X., 2015. Distribution and enrichment mechanism of selenium and arsenic in
 832 Ediacaran-Early Cambrian strata of southern Hunan and southern Shanxi Province and
 833 its environmental effects (In Chinese) [Ph.D. dissertation]: Beijing, China, the Institute of

Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences (in Chinese with English abstract)

Nough, W. F., Sun, S.S., 1995. The composition of the Earth. *Chemical Geology* 120, 223-253.

Park, M., Chon, H.T., Marton, L., 2010. Mobility and accumulation of selenium and its relationship with other heavy metals in the system rocks/soils-crops in areas covered by black shale in Korea. *J. Geochem. Explor.* 107, 161-168.

Parnell, J., Brolly, C., Spinks, S., and Bowden, S. 2016. Selenium enrichment in carboniferous shales, britain and ireland: problem or opportunity for shale gas extraction?. *Applied Geochemistry*, 66, 82-87.

Peng, D. M., 1997, Selenium resources of China: an outline. *Geology of Chemical Minerals* (in Chinese with English abstract). 19, 37-42.

Qi, S.J., 1999. The upper Paleozoic submarine exhalative sedimentary metallogenic system in South Qinling. *Earthence Frontiers* 6, 171-178.

Rona, P.A., 1988. Hydrothermal mineralization at oceanic ridges. *Canadian Mineralogist* 26, 431-465.

Rosenfeld, I., Beath, O.A., 1964. Selenium : geobotany, biochemistry, toxicity, and nutrition. Academic Press.

Schröder, S., and Grotzinger, J.P., 2007. Evidence for anoxia at the Ediacaran–Cambrian boundary: the record of redox-sensitive trace elements and rare earth elements in Oman. *Journal of the Geological Society*, 164: 175-187.

Shields-Zhou, G., Och, L., 2011. The case for a neoproterozoic oxygenation event: Geochemical evidence and biological consequences. *GSA Today* 21, 4-11.

Simon, G., Kesler, S.E., Essene, E.J., 1997. Phase relations among selenides, tellurides, and oxides; II, Applications to selenide-bearing ore deposits. *Economic Geology* 92, 468-484.

Slack J.F., Grenne T, Bekker A. 2007. Suboxic deep seawater in the late Paleoproterozoic : Evidence from hematitic chert and iron formation related to seafloor-hydrothermal sulfide deposits, central Arizona, USA. *Earth and Planetary Science Letters*, 2007, 255, 243-256.

Song, C.Z., 1989, A brief description of the Yutangba sedimentary-type selenium mineralized area in southwestern Hubei: *Mineral Deposits*, 8, 83–89. (in Chinese with English abstract).

Stanton R. L. 1972. *Ore Petrology*. Mc Graw-Hill Book Company, New York.

Stillings, L.L., Amacher, M.C., 2010. Kinetics of selenium release in mine waste from the Meade peak phosphatic shale, Phosphoria Formation, Wooley Valley, Idaho, USA. *Chem. Geol.* 269, 113-123.

Sverjensky, D.A., 1984. Europium redox equilibria in aqueous solution. *Earth and Planetary Science Letters*, 67: 70-78.

Sugahara, H., Sugitani, K., Mimura, K., Yamashita, F., Yamamoto, K., 2010. A systematic rare-earth elements and yttrium study of Archean cherts at the Mount Goldsworthy greenstone belt in the Pilbara Craton: Implications for the origin of microfossil-bearing black cherts. *Precambrian Research* 177, 73-87.

Sun, H.J., Rathinasabapathi, B., Wu, B., Luo, J., Pu, L.P., Ma, L.Q., 2014. Arsenic and selenium toxicity and their interactive effects in humans. *Environ. Int.* 69, 148-158.

Tang, Y.Z., Qi, W., Liu, S.W., Hou, M.T., 2007. Paleozoic hydrothermal sedimentary basin and hydrothermal sedimentary mineralization in the Southern Qinling. *Geology in China* 34, 1091.

Taylor, S.R., 1964. Trace element abundances and the chondritic Earth model. *Geochim. Cosmochim. Acta* 28, 1989-1998.

Taylor, S.R., McLennan, S.M., 1985. The continental crust: Its composition and evolution. *Journal of Geology* 94.

Terry, N.; Zayed, A.M.; de Souza, M.P.; Tarun, A.S., 2000. Selenium in higher plants. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* 51, 401-432.

Thornton, I., 1993, *Geochemistry applied to agriculture*, in: I. Thornton (ed.) *Applied Environmental Geochemistry*, Academic Press, London, pp. 231-266.

Toth, J.R., 1980. Deposition of submarine crusts rich in manganese and iron. *Geological*

888 Society of America Bulletin, 91: 44-54.

889 Tribovillard, N., Algeo, T.J., Lyons, T., and Riboulleau, A., 2006. Trace metals as paleoredox
890 and paleoproductivity proxies: An update. *Chemical Geology*, 232: 12–32.

891 Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the Elements in Some Major Units of
892 the Earth's Crust. *Geological Society of America Bulletin* 72, 175.

893 Tuttle, M.L.W., Fahy, J.W., Elliott, J.G., Grauch, R.I., Stillings, L.L., 2014. Contaminants from
894 Cretaceous black shale: I. Natural weathering processes controlling contaminant cycling
895 in Mancos Shale, southwestern United States, with emphasis on salinity and selenium.
896 *Appl. Geochem.* 46, 57-71.

897 U.S. Department of Energy, 2011. Natural Contamination from the Mancos Shale.
898 Experimental Sciences Laboratory Report ESL-rpt-2011-01

899 Vinceti, M., Mandrioli, J., Borella, P., Michalke, B., Tsatsakis, A., Finkelstein, Y.,
900 2014. Selenium neurotoxicity in humans: Bridging laboratory and epidemiological studies.
901 *Toxicol. Lett.* 230, 295-303.

902 Wang, J., 2015. The Geochemistry of the coals at P/Tboundary in Xuanwei, Yunnan and its
903 Paleoenvironmental significance (In Chinese) [Ph.D. dissertation]: Beijing, China, China
904 University of Mining & Technology, Beijing (in Chinese with English abstract)

905 Wang, Z.G., Yu, X.Y., and Zhao, Z.H., 1989, The geochemistry of REE: Beijing, Science Press
906 (in Chinese).

907 Weaver, B.L., Tarney, J., 1984. Empirical approach to estimating the composition of the
908 continental crust. *Nature* 310, 575-577.

909 Wen, H.J., and Qiu, Y.Z., 1999, Organic and inorganic occurrence of selenium in La'erma
910 Se-Au deposit: Science in China (Series D), 29, 426-432.

911 Wen, H. J., Qiu, Y.Z., Yao, L.B., Lu, J.L., Peng, P.A., Lin, Q. 2000. Organic geochemistry and
912 biomarkers of some lower Cambrian high-selenium formations in China. *Geochimica*, 29,
913 28-35.

914 Wen, H. J., Qiu Y.Z., and Lin H.W., 2003. Geochemistry and genesis of bedded cherts in some
915 typical Paleozoic high selenium black shales, China. *Acta Sedimentologica Sinica* 21,
916 619-626.

917 Wen, H. J., Garignan J., 2011. Selenium isotopes trace the source and redox processes in the
918 black shale-hosted Se-rich deposits in China. *Geochimica et Cosmochimica Acta* 75,
919 1411-1427.

920 Wignall, P.B., 1994. *Black Shales* [M]. Oxford, Clarendon Press, 127.

921 Xia, B.D., Zhong, L.R., Fang, Z., Lu, H., 1995. The origin of cherts of the Early Precambrian
922 Gufeng formation in the lower Yangtze area, Eastern China. *Acta Geologica Sinica* 4,
923 325-331.

924 Xia, L.Q., Xia, Z.C., 2008. Petrogenesis of the Yaolinghe Group, Yunxi Group, Wudangshan
925 Group Volcanic Rocks and Basic Dyke Swarms from Eastern Part of the South Qinling
926 Mountains. *Northwestern Geology* 41, 1-29.

927 Xiang, L.W., Zhu, Z.L., 1999. *China stratigraphy*. Beijing: Geological Publishing House.

928 Xu, L.G., Lehmann, B., Mao, J.W., Nägler, T.F., Neubert, N., Böttcher, M.E., Escher, P., 2012.
929 Mo isotope and trace element patterns of Lower Cambrian black shales in South China:
930 Multi-proxy constraints on the paleoenvironment. *Chemical Geology* 318, 45–59.

931 Yamamoto, K., 1987. Geochemical characteristics and depositional environments of cherts
932 and associated rocks in the Franciscan and Shimanto Terranes. *Sedimentary Geology* 52,
933 65-108.

934 Yang, J. H., Jiang, S. Y., 2004. Paleoenvironmental significance of redox-sensitive metals of black
935 shale in the basal Lower Cambrian Niutitang Formation in Guizhou Province, South
936 China. *Progress in Natural Science*, 14, 152-157.

937 Yang, R.D., Zhu, L.J., Gao, H., Zhang, W.H., Jiang, L.J., Wang, Q., 2005. A Study on
938 Characteristics of the Hydrothermal Vent and Relating Biota at the Cambrian Bottom in
939 Songlin, Zunyi County, Guizhou Province. *Geological Review* 12, 214-223.

940 Yao, L.B., Gao, Z.M., Yang, Z.S., and Long, H.B., 2002, Origin of seleniferous cherts in
941 Yutangba Se deposit, Southwest Enshi, Hubei Province: Science in China (Series D), 45,

741-854.

Yu, B.S., and Qiu, Y.Z., 1998, The geochemistry of sedimentary rocks and its relation to crustal evolution in the southwest Yangtze Massif: *Chinese Journal of Geochemistry*, 17, 265-274.

Yu, B.S., Dong, H.L., Widom, E., Chen, J.Q., and Lin, C.S., 2009, Geochemistry of basal Cambrian black shales and cherts from the Northern Tarim Basin, Northwest China: Implications for depositional setting and tectonic history: *Journal of Asian Earth Sciences*, 34, 418-436.

Yu, C.X., Peng, B. Tang, X.Y., 2008. The black shale and relative heavy metal contamination of soils derived from the black shale. *Bulletin of Mineralogy Petrology & Geochemistry*, 27, 137-145.

Yu T, Yang Z.F., Lv Y.Y., 2014. The origin and geochemical cycle of soil selenium in a Se-rich area of China. *Journal of Geochemical Exploration*, 139, 97-108.

Zhang, G.W., Yu, Z.P., 2000. On Precambrian framework and evolution of the Qinling belt. *Acta Petrologica Sinica*.

Zhao C.Y, Ren J.H, Xue C.Z (1993) Selenium in soils of selenium-rich areas in Ziyang County (in Chinese). *Acta Pedolog Sin* 30, 253-259

Zhou, Y.Z., 1990. On sedimentary geochemistry of siliceous rocks originated from thermal water in Nandan-Hechi basin. *Acta Sedimentologica Sinica*.

Zhou, Y.Z., Edward, H., Huangzhang, L.U., 1994. Hydrothermal Origin of Top Sinian Chert Formation at Gusui, Western Guangdong, China: Petrologic and Geochemical Evidence. *Acta Sedimentologica Sinica*.

Zhu, J.M., 2000. Modes of occurrence of Se in the black Se-rich rocks of Yutangba and its impact on the local environment (in Chinese) [Ph.D. dissertation]: Guiyang, Guizhou Province, China, Institute of geochemistry, Chinese Academy of Sciences (in Chinese with English abstract).

Zhu, X.Y., Chen, F.K., Nie, H., Siebel, W., Yang, Y.Z., Xue, Y.Y., Zhai, M.G., 2014. Neoproterozoic tectonic evolution of South Qinling, China: Evidence from zircon ages and geochemistry of the Yaolinghe volcanic rocks. *Precambrian Research* 245, 115-130.

1 Figure

2
3 **Figure 1.** **A** The location of Qinling Mountains within China. (modified form Dong et al., 2009). **B** Simplified geologic map of South Qinling Mountains
4 (modified after Dong et. al., 2011). **C** The Sketch map of Lujiaping formation in South Qinling Mountains and location of sample collection, modified from
5 (Luo, 2006).

6

7 **Figure 2.** **A** Route map. **B** Columnar map of Huoshibian section.

8

9 **Figure 3** The overview of Huoshibian section

Figure 4. Photomicrographs of siliceous and black shale samples of the LFM:
A Geopetal structure containing micro-crystalline quartz, meso-crystalline quartz and mega-crystalline quartz. Crossed polars; bar scale -500 μm . **B** Close-up of mesocrystalline quartz, showing the characteristic irregular crystal boundaries. Crossed polars; bar scale -500 μm . **C** Pseudo-parallel mega-crystalline quartz veins. Crossed polars; bar scale -2 μm . **D** Sporadic pyrite and deposition of organic matter within black shale of HSBY601. Crossed polars; bar scale -1 μm . **E** Drill hole with fine-grains pyrite aggregates in dark matrix of quartz, adularia and chlorite of black shale. Orbicular and nodular structure of black shale, Sharp-clast within the black shale: Crossed polars; bar scale -1. **F** Fine-grains and undeformed pyrite with the siliceous rock of HSBY307.

Figure 5. Field photographs of the LFm of Huoshibian section. **A** Dark gray to black siliceous rock of Series 6. **A1** Bedding siliceous rock. **B** and **B1** black colored stone like coal. **C** Laminated black shale of Series 3, steep schistosity showing strong N-S compression. **C1** Sharp clast within black shale of HSBY 382 sample. **D** and **D1** Horizontal bedding dolomitic limestone with a few calcite veins.

Figure 6 Enrichment patterns of elements of 14th Bed of the LFM.

Figure 7. A Distribution and enrichment patterns of Se, Cd, Mo, As and S (CC>10) of of 14th Bed of the LFm.

Figure 7. B Distribution and enrichment patterns of Se, Cd, Mo, As and S (CC > 10) of 14th Bed of the LFM.

Figure 8. A Distribution and enrichment patterns of elements ($10 > CC > 1$) of 14th Bed of the LFM.

Figure 8. B Distribution and enrichment patterns of elements ($10 > CC > 1$) of 14th Bed of the LFM.

Figure 9. A Distribution and enrichment patterns of elements (CC<1) of 14th Bed of the LFm.

Figure 9. B Distribution and enrichment patterns of elements (CC<1) of 14th Bed of the LFm.

Figure 10. Enrichment patterns of elements of carbonate and clastic rocks of 7th series of the LFm.

Figure 11. **A** Scheme of Co/Zn vs. (Co+Ni+Cu) from (Boström et al., 1973). **I**=Hydrothermal crust; **II**=Hydrogenous sediment. **B** LgU vs. LgTh diagram (from Rona, 1978) of 40 anomalous Se-enrichment samples of the LFM. **ED**=Eastern Pacific Ocean Hydrothermal Deposition. **RH**=Red Ocean Hot Brine Hydrothermal Sedimentary. **FH**=Fossil Hydrothermal Sedimentary. **P**=Pain Ocean. **M**=Manganese area. **C** P_2O_5 (wt.%) versus Y (ppm) diagram for different types of sediments (after Marchig et al. 1982). a, trend line for modern hydatogen sediments; b, trend line for modern hydrothermal sediments. **DS**, field of deep-sea sediments. **WR**, field for diagenetic-type metalliferous sediments. and **HD**, field for hydrothermal-type metalliferous sediments. **D** $(\text{Cu+Co+Ni}) \times 10$ -Fe-Mn diagram for sediment rocks of different origin(s) (modified from Rona 1978). **ED**, East Pacific hydrothermal metalliferous sediment. **CR**, hydrothermal ferromanganese crust sediment. **HD**, hydrothermal sedimentation area. **RH**, Red Sea hydrothermal sedimentation area. **HN**, hydrous sediment. **ND**, hydrous nodule.

Figure 12. Shale-normalized (PAAS) REE distribution of 40 anomalous Se-enrichment samples of the LfM.

63

64 **Figure 13** Distribution of REE of 40 anomalous Se-enrichment samples of the LFM..

65

66 **Figure 14** X-ray energy spectrometric analysis for black shale (HSBY 601) minerals of
 67 Bed 12 of the LFM.

Table 1 The detailed description of five Member of the LFm of Ziyang County of southern Shaanxi Province, China.

Abbreviation: LFm=Lujiaping Formation, M.=Member, s.=series, T.= Thickness, B.=Bed, Lith.=Lithology. CLR=Clastic rock, CAR=Carbonate rock.

M.	s.	T.	B.	Sample	Lith.	Description
V(5 th M)	s 7	ca.300m	B 14	HSBY682-728	CLR	Gray or gray-black shale interbedded with gray calcareous shale, limestone and stone like coal.
IV(4 th M)		77.1 m	B 13	HSBY632-681	CLR	Black or light-green siliceous rock (Fig. 5A) interbedded with gray or black-gray dolomitic limestone, limestone and witherite ore (ca.2 m-thick).
III(3 rd M)	s 6	95.5 m	B 12	HSBY573-631	CLR	Black or light-green siliceous rock interbedded with gray or black-gray dolomitic limestone and black shale.
			B 11	HSBY551-571	CAR	Gray or black-gray dolomitic limestone (Fig. 5D).
II(2 nd M)	s 5	70.4 m	B 10	HSBY513-548	CLR	Black shale interbedded with siliceous rock (ca.0.3 m-thick) and limestone (ca. 1-m-thick).
			B 9	HSBY497-512	CAR	Gray or gray-black dolomitic limestone.
	s 4	106.8m	B 8	HSBY431-495	CLR	Black or gray-black siliceous rock interbedded with dolomitic limestone and limestone (ca. 0.9m-thick).
			B 7	HSBY416-430	CAR	Black or gray-black dolomitic limestone interbedded with siliceous rock, and limestone (ca. 0.9m-thick) and black shale (ca. 0.2m-thick).
I(1 st M)	s 3	107.2m	B 6	HSBY367-415	CLR	Black shale (Fig. 5B and C) interbedded with black siliceous rock, stone-like coal and dolomitic limestone.
			B 5	HSBY331-366	CAR	Dolomitic limestone interbedded with black siliceous rock (ca.1.1-m-thick) and Black shale (ca. 0.7-m-thick).Those black shale and siliceous rock overlying the black or gray dolomitic limestone which intercalated with black-gray mud siliceous rock (ca. 0.1 m-thick) and gray limestone (ca. 0.2m-thick).
	s 2	46.6 m	B 4	HSBY315-329	CLR	Laminated black shale.
			B 3	HSBY287-315	CAR	Light green dolomitic limestone interbedded with siliceous rock and yellow or light gray mud limestone.
	s 1	7.9 m	B 2	HSBY279-286	CLR	Black shale.

B 1 HSBY266-278 CAR Light gray dolomitic limestone interbedded with black-gray siliceous rock.

1 **Table 2 The average and range contents of Carbonates and Clastics' major elements from the LFm of southern Shaanxi Province (unit: wt%)**

2 **Abbreviations :** LFm=Lujiaping Formation, UCC=Upper Continental Crust, Avg.=average, Std.=Stdevp.

The LFm	Sample No.	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI
Carbonates	<i>Min</i>	0.11	0.07	8.90	0.04	nd.	0.65	0.02	nd.	nd.	0.01	8.30
	<i>Max</i>	44.85	8.89	47.43	4.32	2.75	21.39	3.20	0.42	0.32	3.41	46.43
	<i>Std.</i>	9.07	1.58	6.93	0.75	0.51	4.24	0.88	0.08	0.06	0.43	6.16
	<i>Avg.</i>	14.44	1.73	27.49	0.72	0.51	14.71	1.30	0.08	0.05	0.20	39.18
Clastics	<i>Min</i>	44.68	0.13	0.02	0.47	nd.	0.05	0.01	nd.	0.01	nd.	0.22
	<i>Max</i>	98.04	20.13	8.94	11.17	5.71	27.27	6.81	1.53	0.20	6.94	31.69
	<i>Std.</i>	12.09	5.76	1.42	1.44	1.53	0.85	0.90	0.33	0.04	0.67	3.94
	<i>Avg.</i>	78.92	6.26	0.83	2.77	1.82	1.14	1.40	0.31	0.07	0.12	6.21
UCC^a		30.80	8.04	3.00	3.50	2.80	1.33	2.89	0.41	0.08	0.16	-
Shale^b		7.30	8.00	2.21	4.70	2.66	1.50	0.96	0.46	0.09	0.07	-
Carbonate^b		2.40	0.42	30.23	0.38	0.27	4.70	0.04	0.04	0.11	0.04	-
Franciscan siliceous rock^c		92.30	1.31	0.11	2.63	0.35	0.28	0.11	0.09	0.53	0.03	-

3 a Taylor and McLennan, 1985;

4 b Turekian et al., 1961

5 c Yamamoto et al, 1987

6 “nd”=Below the detection limit.

7 **Table 3 The variation of the Se, Cd, Mo, S and As contents of 14th Bed of the LFm of southern Shaanxi Province(unit: ppm)**

8 **Abbreviations :** M.=Member; B.=Bed; UCC=Upper Continental Crust, Avg.=average, Std.=Stdevp. nd.=Below the detection limit.

M.	Bed.	Se				Cd				Mo				S				As			
		<i>Min</i>	<i>Max</i>	<i>Avg.</i>	<i>Std.</i>	<i>Min</i>	<i>Max</i>	<i>Avg.</i>	<i>Std.</i>	<i>Min</i>	<i>Max</i>	<i>Avg.</i>	<i>Std.</i>	<i>Min</i>	<i>Max</i>	<i>Avg.</i>	<i>Std.</i>	<i>Min</i>	<i>Max</i>	<i>Avg.</i>	<i>Std.</i>
V	B 14	0.81	18	2.29	2.81	0.12	12	1.23	2.48	0.37	57	14.29	13.69	105	24140	2807	4081	0.12	52	7.14	12.84
IV	B 13	0.36	104	19.82	22.06	0.36	59	6.62	12.01	1.20	352	36.65	61.20	96	30380	5966	7491	1.62	53	12.84	10.41
III	B 12	0.03	303	21.72	43.26	<i>nd.</i>	129	8.52	18.12	<i>nd.</i>	60	10.16	13.11	303	60780	5800	13458	1.45	81	14.58	16.70
	B 11	0.14	44	9.25	11.18	0.43	8	1.56	1.65	0.35	17	4.01	4.16	618	49790	15435	14108	11.43	156	37.87	37.00
	B 10	0.14	71	17.88	13.76	0.31	3	0.76	0.50	2.80	251	24.43	39.30	3194	94300	60512	21285	4.50	161	48.14	28.10
II	B 9	0.38	46	6.24	10.99	0.12	7	1.53	1.62	0.56	74	10.63	18.28	433	7314	1482	1681	0.95	70	8.45	17.05
	B 8	0.04	65	9.90	15.92	0.25	65	8.70	15.09	0.85	235	18.96	32.44	146	18850	1771	3747	<i>nd.</i>	53	6.61	8.63
	B 7	0.42	8	2.75	2.27	0.18	7	2.43	1.94	1.12	40	12.10	12.34	148	2822	840	730	<i>nd.</i>	12	5.62	3.60
	B 6	1.45	154	49.20	43.78	0.08	55	7.06	9.60	0.98	562	136.66	149.03	1210	70010	22045	23323	3.80	144	42.81	32.86
I	B 5	0.14	32	10.07	10.21	<i>nd.</i>	72	3.96	11.65	<i>nd.</i>	84	19.39	25.03	287	45440	5458	10936	1.51	45	7.82	10.40
	B 4	0.83	58	33.57	13.35	0.41	144	12.86	36.53	52.08	145	97.35	24.84	4028	41170	19459	12281	13.25	100	43.41	27.76
	B 3	0.34	42	5.34	8.51	0.58	20	3.05	3.79	0.82	332	17.34	59.78	165	28360	2636	5520	3.19	207	33.95	45.42
	B 2	2.60	14	6.90	3.70	0.08	1.56	0.30	0.48	2.80	23	8.68	6.42	156	19810	7952	5986	<i>nd.</i>	16	7.87	5.57
	B 1	0.06	1	0.30	0.26	0.09	1.11	0.32	0.28	0.55	3	1.34	0.66	929	16330	4155	4479	<i>nd.</i>	4	2.11	0.86
The LFm.		0.03	303	16.40	27.41	<i>nd.</i>	144	4.34	12.94	<i>nd.</i>	562	29.53	69.81	96	94300	11546	19760	<i>nd.</i>	207	20.12	26.78
UCC ^a		0.05				0.098				1.5				420				1.5			
Shale ^b		0.60				0.3				2.60				2400				13			

9 a Taylor and McLennan, 1985;

10 b Turekian et al., 1961

11

12
13 **Table 4 Se contents of Se-ore deposits of the world (Peng, 1997) and the LFm (this study)**

Country	Location	Se-Ore Industry Type	Geologic Feature			
			Ore-containing Rock	Mineral Species	Se Grade (ppm)	Scale
Bolivia	Puhakka	Altered Rock Type	Altered Rock	Se	>10	Small
Canada	Noranda	Volcanic Hydrothermal Type	Volcanics	Se, Cu, Ni	64	Supper-Large
	Fiynn Furlong	Volcanic Hydrothermal Type	Volcanics	Se, Cu, Ni	64	Supper-Large
Philippines	Atlas	Magma Type	Granodioritic	Se, Cu	>10	Large
Chile	La Escondida	Magma Type	Graniteporphyry	Se, Cu	>10	Large
	Chuquicamata	Magma Type	Graniteporphyry	Se, Cu	>10	Large
America	Bingham	Magma Type	Graniteporphyry	Se, Cu	21.5	Large
	Twin Buttes	Magma Type	Graniteporphyry	Se, Cu	21.5	Large
Zaire	Kolwezi	Clastic Type	Carbonic Sandstone. Carbonic Shale	Se	>10	Large
Zambia	Shuifu In La	Clastic Type	Carbonic Sandstone and Shale	Se	>10	Large
	Nchanga	Clastic Type	Carbonic and Carbonic Shale	Se	>10	Large

China	Jinshan,Dexing, Jiangxi Province	Porphyry Type	Graniteporphyry	Se、Cu、Au	15.4	Supper-Large
	Baijiazuizi,Jinchuan, Gansu Province	Magma Type	Gabbro	Se、Au、Ni	>10	Supper-Large
	Chengmenshan,JIUJIAN g,Jiangxi Province	Skarn Type	Skarn	Polymetallic		Supper-Large
	Dabaoshan,Qujiang, Guangdong Province	Hydrothermal	Carbonatite			Large
	Qingyunshan,Fogang, Guangdong Province	Hydrothermal	Carbonatite		>30	Large
	Laerma,Luqu ,Gansu Province	Hydrothermal	Carbon Siliceous Rock 、Carbonaceous Slate	U、Hg、Se、Au	29.4	Large
	Ongguanshan,Tongling, Anhui Province		Skarn	Se、Au、Cu		Large
	Qibaoshan, Liuyang, Hunan Province		Skarn	Au、Fe、Se、S	>10	Large
	Magushan, Jinxi, Jiangxi, Province		Skarn	Au、Se、Cu、Mo		Large
	Deerni, Maqing, Qinghai Province	Hydrothermal	Carbonation-Hui Olive Breccia	Cu、Co、Au、Se、 S		Large
	Baiguoyuan,Xingsha, Hubei Province		Dolomitite、Carbon Siliceous Slate	Pd、Se、V	67-79	Large
	Jinduncheng,Huaxian, Shanxi	Porphyry Type	Graniteporphyry	Au、Se、Mo		Middle
	Dashigou, Luonan, Shanxi Province	Magma Type	Monzogranite、Lode Rock	Se、Mo	>10	Middle
	Huayangchuan,Huay, Shanxi Province	Magma Type	Granite Pegmatite、 Graniteporphyry	Sr、Pb、Nb、Pd、 Se And REE	>10	Middle

	Yutangba, Enshi, Hubei Province	Clastic Type	Carbon Siliceous Rock, Carbonic Shale	Se	84.12	Middle
	Shuanghe, Enshi, Hubei Province	Clastic Type	Carbon Siliceous Rock, Carbonic Shale	Se	84.12	Middle
The LFm (this study)						
	Bed 14 (ca. 82.2 meter)	Clastic Type	Siliceous rock and shale	Se	2.29	-
	Bed 13 (ca. 77.1 meter)	Clastic Type	Siliceous rock	Se	19.82	-
	Bed 12 (ca. 62.2 meter)	Clastic Type	Siliceous rock	Se	21.72	-
	Bed 11 (ca. 40.2 meter)	Carbonate Type	Carbonate rock	Se	9.25	-
	Bed 10 (ca. 33.9 meter)	Clastic Type	Black shale	Se	17.88	-
	Bed 9 (ca. 37.1 meter)	Carbonate Type	Carbonate rock	Se	6.24	-
Ziyang, Shanxi Province (China)	Bed 8 (ca. 64.7 meter)	Clastic Type	Siliceous rock	Se	9.90	-
	Bed 7 (ca. 42.1 meter)	Carbonate Type	Carbonate rock	Se	2.75	-
	Bed 6 (ca. 63.7 meter)	Clastic Type	Black shale and siliceous rock	Se	49.20	-
	Bed 5 (ca. 43.6 meter)	Carbonate Type	Carbonate rock	Se	10.07	-
	Bed 4 (ca. 6.3 meter)	Clastic Type	Black shale	Se	33.57	-
	Bed 3 (ca. 39 meter)	Carbonate Type	Carbonate rock	Se	5.34	-
	Bed 2 (ca. 2.2 meter)	Clastic Type	Black shale and siliceous rock	Se	6.90	-
	Bed 1 (ca. 5.7 meter)	Carbonate Type	Carbonate rock	Se	0.30	-

Table 5 Major elements of anomalous Se-enrichment samples of the LFm from Ziyang county, southern Shaanxi Province (China)(unit:%).**Abbreviations :** SR=Siliceous rock, DL=Dolomitic Limestone, BS=Black Shale, No.=Sample number.

Depth(m)	Member	Series	Bed	Lithology	No.	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI
474.1	IV(4 th M)	S 7	B 13	SR	HSBY-662	93.68	1.21	0.13	1.63	0.34	0.15	0.66	0.07	0.13	0.01	1.91
459.2	IV(4 th M)	S 7	B 13	SR	HSBY-648	89.86	3	0.14	1.26	0.91	0.16	1.01	0.17	0.07	0.03	3.32
458.1	IV(4 th M)	S 7	B 13	SR	HSBY-647	94.03	1.29	0.11	1.13	0.38	0.12	1.03	0.09	0.07	0.01	1.71
450.3	IV(4 th M)	S 7	B 13	SR	HSBY-640	83.96	5.01	0.19	1.94	1.66	0.68	0.85	0.27	0.06	0.05	4.62
449.4	IV(4 th M)	S 7	B 13	SR	HSBY-639	91.15	2.61	0.08	1.09	0.79	0.39	1.03	0.16	0.06	0.02	2.35
408.2	III(3 rd M)	S 6	B 12	DL	HSBY-606	13.74	1.49	25.29	0.34	0.38	16.22	2.16	0.07	0.02	0.45	39.83
403.4	III(3 rd M)	S 6	B 12	BS	HSBY-601	56.45	12.21	0.44	4.87	3.41	0.82	2.42	1.3	0.03	0.09	17.95
401.4	III(3 rd M)	S 6	B 12	SR	HSBY-598	85.13	4.79	0.17	1.65	1.52	0.56	1.63	0.28	0.07	0.04	3.81
399.8	III(3 rd M)	S 6	B 12	SR	HSBY-596	91.46	2.08	0.11	1.77	0.61	0.25	1.3	0.09	0.11	0.03	2.05
377.4	III(3 rd M)	S 6	B 12	BS	HSBY-576	53.69	12.69	0.48	5.91	4.29	1.48	2	0.62	0.03	0.18	18.63

376.6	III(3 rd M)	S 6	B 12	BS	HSBY-575	56.1	11.35	0.44	5.17	4.09	1.36	2.93	0.61	0.04	0.13	17.8
376.1	III(3 rd M)	S 6	B 12	BS	HSBY-574	61.84	11.61	0.26	4.97	4.89	2.49	2.48	0.69	0.02	0.02	10.73
375.4	III(3 rd M)	S 6	B 12	BS	HSBY-573	67.07	8.07	0.18	6.3	4.46	0.74	1.73	0.69	0.02	0.15	10.57
349.6	III(3 rd M)	S 6	B 11	DL	HSBY-559	44.85	7.03	8.9	2.61	2.17	7.23	1.6	0.36	0.03	0.07	25.16
331.5	II(2 nd M)	S 5	B 10	BS	HSBY-547	70.04	10.07	0.38	4	3.13	1.61	2.19	1.13	0.02	0.22	7.21
299.2	II(2 nd M)	S 5	B 10	BS	HSBY-513	46.08	13.04	0.25	6.57	3.62	1.67	1.69	1.06	0.05	0.1	25.88
216.2	II(2 nd M)	S 4	B 8	SR	HSBY-456	95.98	0.19	0.53	0.71	0	0.35	0.18	0.06	0.08	0.01	1.82
210.1	II(2 nd M)	S 4	B 8	SR	HSBY-446	96.6	0.26	0.15	1.01	0.01	0.14	0.13	0.06	0.1	0.02	1.48
149.5	I(1 st M)	S 3	B 6	BS	HSBY-403	54.1	8.53	0.74	6.61	4.32	0.22	3.23	0.13	0.05	0.15	21.91
145.2	I(1 st M)	S 3	B 6	BS	HSBY-401	55.4	12.5	0.22	1.73	3.77	3.02	1.52	0.15	0.03	0.13	21.55
134.3	I(1 st M)	S 3	B 6	BS	HSBY-393	50.84	9.8	3.99	6.72	2.83	4.32	0.17	0.1	0.04	0.37	20.82
Depth(m)	Member	Series	Bed	Lithology	No.	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI
133.1	I(1 st M)	S 3	B 6	BS	HSBY-392	56.41	4.51	3.98	6.93	2.48	2.65	0.76	0.09	0.06	0.37	21.75

127.8	I(1 st M)	S 3	B 6	BS	HSBY-389	52.13	10.44	1.58	8.23	3.15	2.01	0.34	0.1	0.03	0.45	21.55
126.9	I(1 st M)	S 3	B 6	BS	HSBY-388	57.34	11	0.33	5.73	3.27	1.92	0.16	0.12	0.04	0.31	19.77
125.6	I(1 st M)	S 3	B 6	BS	HSBY-387	47.05	10.98	0.84	3.21	3.19	2.48	0.22	0.12	0.02	0.2	31.69
124.3	I(1 st M)	S 3	B 6	BS	HSBY-386	57.35	11.07	0.18	6.1	3.24	1.81	0.11	0.12	0.04	0.15	19.84
122.5	I(1 st M)	S 3	B 6	BS	HSBY-385	64.11	8.53	0.35	4.56	1.03	1.32	0.21	0.09	0.03	0.25	19.53
120.6	I(1 st M)	S 3	B 6	BS	HSBY-384	42.83	8.54	12.17	6.44	2.57	3.28	0.21	0.09	0.07	0.41	23.4
119.5	I(1 st M)	S 3	B 6	BS	HSBY-383	50.97	8.87	6.42	6.54	2.68	4.76	0.36	0.09	0.04	0.4	18.88
118.2	I(1 st M)	S 3	B 6	BS	HSBY-382	44.68	9.19	7.91	7.78	2.76	6.37	0.12	0.12	0.05	0.48	20.55
117	I(1 st M)	S 3	B 6	BS	HSBY-381	53.69	8.32	5.81	6.56	2.55	4.56	0.27	0.09	0.04	0.41	17.71
115.1	I(1 st M)	S 3	B 6	BS	HSBY-380	51.42	9.21	5.94	7.01	2.76	4.05	0.14	0.09	0.05	0.41	18.92
112.4	I(1 st M)	S 3	B 6	BS	HSBY-379	53.71	7.87	6.4	5.96	2.37	4.01	0.13	0.08	0.03	0.34	19.11
107.5	I(1 st M)	S 3	B 6	BS	HSBY-375	49.15	14.51	1.13	1.89	4.22	2.29	0.58	0.18	0.04	0.5	25.51

103.7	I(1 st M)	S 3	B 6	BS	HSBY-372	50.19	11.68	3.87	7.93	3.76	3.27	0.61	0.12	0.02	0.54	18.01
102.4	I(1 st M)	S 3	B 6	DL	HSBY-371	25.19	3.33	18.56	2.35	0.99	14.07	0.18	0.03	0.03	0.29	34.98
101.3	I(1 st M)	S 3	B 6	BS	HSBY-370	67.31	6.62	0.25	1.09	2.08	1.28	1.67	0.04	0.06	0.04	19.56
51.1	I(1 st M)	S 2	B 4	BS	HSBY-324	62.8	15.06	1.31	3.18	4.69	1.78	1.73	0.07	0.03	0.16	9.19
48.6	I(1 st M)	S 2	B 4	BS	HSBY-318	68.55	14.54	0.6	1.27	4.65	1.65	1.52	0.07	0.01	0.03	7.11
23.4	I(1 st M)	S 2	B 3	SR	HSBY-307	80.86	5.54	0.45	6.15	1.72	0.64	1.6	0.03	0.03	0.11	2.67
Average value of anomalous Se-enrichment SR (n=10)						90.27	2.6	0.21	1.88	0.79	0.35	0.95	0.13	0.08	0.03	2.71
Average value of anomalous Se-enrichment BS (n=27)						54.52	10.15	3.04	5.2	3.26	2.9	1.06	0.29	0.04	0.26	19.29
Average value of anomalous Se-enrichment DL (n=3)						29.29	4.26	17.09	1.47	1.28	11.72	1.88	0.21	0.03	0.26	32.5
Franciscan SR (Yomatou et al 1987)						93. 10	1. 31	0. 11	2. 63	0. 35	0. 28	0. 11	0. 09	0. 53	0. 03	-

Table 6 Trace elements of anomalous Se-enrichment samples of the LFm from Ziyang county, southern Shaanxi Province (China) (unit: ppm)**Abbreviations :** D.=Depth, m=meter, s.=Series, SR=Siliceous rock, DL=Dolomitic Limestone, BS=Black Shale, No.=Sample number.

D.(m)	Member	s.	Bed	Lithology	No.	Se	As	Cd	Co	Tl	Cs	Ga	In	Rb	U	Bi	Mo	Be	Th	Cr	Cu	Li	Ni	P	Pb	S	Sc	Sr	V	Zn	Ba	S/Se	U/Th	Co/Zn
474.1	IV(4 th M)	S 7	B 13	SR	HSBY-662	81	26	31.85	10.43	7.81	3.04	45	0.06	40	69	0.58	210	1.71	3.16	271	172	24	620	462	18	20370	39.15	42	5085	5362	377	252	22	0.0019
459.2	IV(4 th M)	S 7	B 13	SR	HSBY-648	57	10	1.58	2.84	3.09	0.8	280	0.02	21	24	0.37	7	0.68	1.08	137	167	7	104	124	19	5378	3.94	37	1586	353	6564	94	22	0.0080
458.1	IV(4 th M)	S 7	B 13	SR	HSBY-647	104	33	9.02	11.04	14.64	2.92	554	0.04	55	82	0.98	13	2.12	5.47	208	211	32	472	406	74	23500	64.47	37	5425	1478	14330	227	15	0.0075
450.3	IV(4 th M)	S 7	B 13	SR	HSBY-640	53	27	2.32	2.44	6.93	1.77	314	0.06	29	43	0.63	17	0.98	3.82	197	58	20	355	223	33	8011	34.82	32	3886	487	8082	150	11	0.0050
449.4	IV(4 th M)	S 7	B 13	SR	HSBY-639	52	8	3.21	1.25	1.69	0.91	230	0.03	16	50	0.52	7	0.54	2	149	73	11	96	91	29	2293	13.97	36	1895	332	5815	44	25	0.0038
408.2	III(3 rd M)	S 6	B 12	DL	HSBY-606	41	11	13.96	0.96	1.42	0.4	54	0.03	9	62	0.36	2	0.42	0.88	29	129	10	117	1963	14	2091	12.95	388	1018	1093	3047	51	70	0.0009
403.4	III(3 rd M)	S 6	B 12	BS	HSBY-601	303	81	1.39	1.12	7.39	1.87	470	0.04	43	69	0.65	37	2.11	5.51	190	108	28	210	380	47	6216	27.37	122	4173	1131	28590	21	12	0.0010
401.4	III(3 rd M)	S 6	B 12	SR	HSBY-598	68	31	0.42	0.79	2.19	1.11	119	0.04	31	41	0.37	10	1.14	2.97	113	59	17	92	177	25	2039	16.69	55	2857	714	6313	30	14	0.0011
399.8	III(3 rd M)	S 6	B 12	SR	HSBY-596	51	15	1.86	1.12	1.46	0.45	54	0.03	12	35	0.28	23	0.33	1.16	91	174	6	72	136	19	1954	8.81	40	1412	565	2691	39	30	0.0020
377.4	III(3 rd M)	S 6	B 12	BS	HSBY-576	80	62	0.92	11.38	3.52	3.29	16	0.05	80	30	0.56	60	2.14	7.5	92	73	31	56	782	11	54670	15.3	109	239	686	448	685	4	0.0166
376.6	III(3 rd M)	S 6	B 12	BS	HSBY-575	60	53	0.51	8.27	3.05	3.53	142	0.05	78	21	0.92	56	2.58	7.69	97	63	32	52	548	48	47700	14.08	122	223	1636	8291	801	3	0.0051
376.1	III(3 rd M)	S 6	B 12	BS	HSBY-574	89	38	0.45	8.05	2.69	3.29	48	0.05	84	21	0.58	47	3.79	3.6	107	37	59	52	107	17	48930	15.19	57	256	915	2146	551	6	0.0088
375.4	III(3 rd M)	S 6	B 12	BS	HSBY-573	68	73	0.8	12	3.8	1.44	47	0.06	65	17	0.71	31	2.88	2.99	100	76	38	75	672	35	60780	10.92	28	248	866	2193	893	6	0.0139
349.6	III(3 rd M)	S 6	B 11	DL	HSBY-559	42	72	1.19	5.25	1.74	1.92	48	0.04	42	19	0.44	17	1.51	4.47	90	48	41	91	321	17	23360	8.22	155	1110	573	2781	560	4	0.0092
331.5	II(2 nd M)	S 5	B 10	BS	HSBY-547	47	33	0.52	1.68	1.7	2.62	28	0.05	52	40	0.57	43	1.77	3.32	97	53	27	72	967	13	34810	13.4	133	4421	1200	1057	748	12	0.0014
299.2	II(2 nd M)	S 5	B 10	BS	HSBY-513	71	20	0.43	12.52	2.75	3.48	14	0.04	62	8	0.33	21	2.22	4.32	100	85	20	58	448	7	59040	25.89	99	299	531	170	834	2	0.0236
216.2	II(2 nd M)	S 4	B 8	SR	HSBY-456	38	3	3.91	1.53	0.59	0.08	8	0	4	6	0.04	17	0.09	0.24	26	301	3	24	65	14	768	2.68	12	233	17	120	20	24	0.0913
210.1	II(2 nd M)	S 4	B 8	SR	HSBY-446	60	4	0.61	1.65	0.68	0.13	8	0	4	5	0.03	13	0.11	0.77	44	80	4	30	84	14	680	1.17	0	219	31	467	11	7	0.0540
149.5	I(1 st M)	S 3	B 6	BS	HSBY-403	62	41	0.85	1.41	5.09	1.4	35	0.11	59	29	0.6	405	2.91	2.11	209	69	43	31	674	51	31530	16.29	23	3938	567	1025	508	14	0.0025
145.2	I(1 st M)	S 3	B 6	BS	HSBY-401	87	36	2.45	1.09	6.36	4.03	23	0.04	66	88	0.42	256	2.84	4.49	136	74	55	44	582	39	11010	36.47	78	6834	615	1185	126	20	0.0018

134.3	I(1 st M)	S 3	B 6	BS	HSBY-393	92	45	16.63	15.99	8.13	3.84	16	0.05	52	67	0.14	351	2.39	4.46	124	167	27	614	1594	24	69930	24	84	3714	1149	4239	757	15	0.0139
D.(m)	Member	s.	Bed	Lithology	No.:	Se	As	Cd	Co	Tl	Cs	Ga	In	Rb	U	Bi	Mo	Be	Th	Cr	Cu	Li	Ni	P	Pb	S	Sc	Sr	V	Zn	Ba	S/Se	U/Th	Co/Zn
133.1	I(1 st M)	S 3	B 6	BS	HSBY-392	90	68	11.85	15.49	8.59	1.82	58	0.05	17	73	0.36	376	2.41	0.07	124	300	21	481	1635	42	64370	8.34	72	3412	649	3658	713	1038	0.0239
127.8	I(1 st M)	S 3	B 6	BS	HSBY-389	105	79	5.13	13.35	8.32	3.13	94	0.05	53	65	0.37	226	2.16	3.65	203	381	22	486	1949	46	70010	24.81	59	4073	525	7867	664	18	0.0254
126.9	I(1 st M)	S 3	B 6	BS	HSBY-388	143	73	3.55	6.21	5.62	3.62	192	0.07	71	82	0.43	321	4.56	5.75	138	174	25	321	1367	53	10490	27.65	92	4585	470	11760	73	14	0.0132
125.6	I(1 st M)	S 3	B 6	BS	HSBY-387	94	40	2.64	10.2	4.89	3.91	162	0.05	66	105	0.49	369	3.38	5.98	97	92	27	146	864	64	11850	28.78	123	5500	418	10820	125	18	0.0244
124.3	I(1 st M)	S 3	B 6	BS	HSBY-386	154	71	1.9	5.55	6.64	3.45	168	0.05	65	68	0.43	562	4.16	5	214	231	24	192	639	45	8164	25.14	85	4358	472	11200	53	14	0.0118
122.5	I(1 st M)	S 3	B 6	BS	HSBY-385	152	110	2.63	5.52	4.12	2.37	27	0.04	24	60	0.18	200	2.06	3.33	80	362	18	219	1102	8	4829	21.1	44	3356	462	2528	32	18	0.0120
120.6	I(1 st M)	S 3	B 6	BS	HSBY-384	114	66	55.06	19.86	8.06	3.06	102	0.05	52	42	0.32	352	3.06	4.26	182	343	22	863	1790	39	2937	19.5	184	3486	1918	7020	26	10	0.0104
119.5	I(1 st M)	S 3	B 6	BS	HSBY-383	69	76	11.19	14.59	10.27	2.73	15	0.05	49	60	0.19	177	1.95	2.79	87	296	21	424	1745	2	52350	20.09	117	3257	395	421	755	21	0.0369
118.2	I(1 st M)	S 3	B 6	BS	HSBY-382	77	77	10.94	17.42	9.62	3.11	16	0.05	54	62	0.25	306	2.29	3.28	197	328	22	420	2116	17	67670	22.1	133	3530	526	1222	875	19	0.0331
117	I(1 st M)	S 3	B 6	BS	HSBY-381	67	80	25.29	14.16	8.19	2.69	36	0.04	44	51	0.27	208	1.77	2.81	173	399	19	389	1786	23	48200	19	106	2994	424	2774	720	18	0.0334
115.1	I(1 st M)	S 3	B 6	BS	HSBY-380	67	100	14.08	16.97	9.68	3.25	23	0.05	58	60	0.31	257	2.61	1.12	294	445	22	386	1785	15	52950	18.9	101	3593	309	1071	789	54	0.0550
112.4	I(1 st M)	S 3	B 6	BS	HSBY-379	70	87	28.3	13.94	7.3	2.87	97	0.06	49	63	0.32	310	2.4	3.99	207	327	20	432	1470	39	28120	18.42	106	3194	440	5926	400	16	0.0317
107.5	I(1 st M)	S 3	B 6	BS	HSBY-375	102	20	0.42	0.91	6.51	4.29	173	0.02	92	29	0.65	99	5.07	4.88	123	22	22	25	2182	67	25700	34.23	308	3967	43	9787	251	6	0.0214
103.7	I(1 st M)	S 3	B 6	BS	HSBY-372	86	62	3.17	18.23	8.53	4.71	148	0.05	74	53	0.5	86	3.86	5.67	119	145	32	401	2373	50	63630	27.32	82	2846	497	10410	741	9	0.0367
102.4	I(1 st M)	S 3	B 6	DL	HSBY-371	85	15	8.4	5.47	3.04	1.36	29	0.03	20	35	0.12	28	1.47	2.01	53	78	16	245	1262	12	20130	6.3	210	1860	315	2107	237	17	0.0174
101.3	I(1 st M)	S 3	B 6	BS	HSBY-370	46	14	0.94	1.56	3.71	3.57	91	0.06	49	48	0.46	94	5	3.84	306	234	27	107	194	54	8244	29.39	62	9147	622	5843	178	12	0.0025
51.1	I(1 st M)	S 2	B 4	BS	HSBY-324	58	31	1.8	5.8	2.54	6.1	32	0.07	151	12	0.81	104	4.79	8.02	71	54	34	43	719	13	31480	20.3	75	1569	610	928	542	2	0.0095
48.6	I(1 st M)	S 2	B 4	BS	HSBY-318	52	14	0.41	1.33	2.03	6.35	121	0.05	165	8	1.39	57	4.31	10.94	50	16	34	13	112	42	10430	17.98	68	1099	508	5648	201	1	0.0026
23.4	I(1 st M)	S 2	B 3	SR	HSBY-307	42	207	2.03	7.4	0.9	2.22	61	0.1	48	12	0.46	332	1.52	3.61	94	167	15	105	478	42	705	4.9	55	1723	737	3582	17	3	0.0100

Table 7 Race earth elements of anomalous Se-enrichment samples of the LFm from Ziyang county, southern Shaanxi Province (China) (unit: ppm)**Abbreviations** : SR=Siliceous rock. DL=Dolomitic Limestone, BS=Black Shale, L/H=LREE/HREE,

Depth(m)	Member	Series	Bed	Lithology	No.	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	L/H	Eu*/Eu*	Ce/Ce*	Y/Ho	(La/Ce) _N
474.1	IV(4 th M)	S 7	B 13	SR	HSBY-662	11.90	4.27	6.29	1.05	3.21	1.45	0.85	0.86	0.17	0.75	0.28	0.67	0.19	1.07	0.33	21.44	3.96	3.69	0.69	42.64	1.41
459.2	IV(4 th M)	S 7	B 13	SR	HSBY-648	25.92	7.33	10.64	1.68	5.05	3.13	2.15	1.36	0.32	1.59	0.64	1.54	0.41	1.95	0.57	38.35	3.58	4.84	0.70	40.80	1.44
458.1	IV(4 th M)	S 7	B 13	SR	HSBY-647	10.92	2.57	5.43	0.86	2.47	0.78	0.36	0.66	0.15	0.71	0.27	0.61	0.15	0.72	0.19	15.92	3.61	2.51	0.83	29.55	0.99
450.3	IV(4 th M)	S 7	B 13	SR	HSBY-640	60.59	18.25	28.10	4.66	15.10	5.81	3.29	4.29	1.02	4.98	1.99	4.70	1.20	5.81	1.64	100.83	2.94	3.25	0.70	30.40	1.35
449.4	IV(4 th M)	S 7	B 13	SR	HSBY-639	32.51	13.62	21.56	3.28	10.06	3.75	2.17	2.40	0.58	2.74	1.08	2.55	0.66	3.20	0.92	68.57	3.85	3.53	0.74	30.14	1.32
408.2	III(3 rd M)	S 6	B 12	DL	HSBY-606	43.74	5.51	7.37	1.22	4.62	2.42	1.28	2.55	0.54	2.82	1.01	2.42	0.53	2.60	0.64	35.53	1.71	2.56	0.66	43.31	1.56
403.4	III(3 rd M)	S 6	B 12	BS	HSBY-601	40.58	40.86	50.05	8.31	30.21	11.97	6.91	5.41	1.03	4.72	1.49	3.36	0.69	3.04	0.89	168.95	7.19	4.00	0.63	27.19	1.70
401.4	III(3 rd M)	S 6	B 12	SR	HSBY-598	44.68	16.93	28.63	4.18	13.95	4.41	2.04	3.50	0.75	3.94	1.40	3.68	0.87	4.72	1.21	90.21	3.50	2.57	0.78	31.85	1.23
399.8	III(3 rd M)	S 6	B 12	SR	HSBY-596	38.41	7.32	11.04	2.02	7.73	3.43	1.47	3.62	0.72	3.56	1.22	2.94	0.65	3.35	0.82	49.88	1.96	2.07	0.66	31.60	1.38
377.4	III(3 rd M)	S 6	B 12	BS	HSBY-576	23.15	26.81	48.82	6.74	23.79	4.09	0.85	3.46	0.63	2.73	0.77	1.63	0.32	1.45	0.31	122.39	9.84	1.12	0.84	30.19	1.14
376.6	III(3 rd M)	S 6	B 12	BS	HSBY-575	16.10	29.63	49.05	6.52	22.46	5.17	2.17	2.73	0.48	1.99	0.56	1.25	0.26	1.24	0.34	123.87	12.98	2.76	0.81	28.87	1.26
376.1	III(3 rd M)	S 6	B 12	BS	HSBY-574	7.81	12.77	29.67	3.58	11.14	2.45	0.73	1.55	0.28	1.22	0.36	0.88	0.20	1.00	0.23	66.06	10.54	1.84	1.01	21.42	0.90
375.4	III(3 rd M)	S 6	B 12	BS	HSBY-573	4.35	6.25	26.13	1.56	4.69	1.53	0.63	0.92	0.15	0.65	0.19	0.44	0.10	0.49	0.11	43.85	13.40	2.59	1.93	23.22	0.50
349.6	III(3 rd M)	S 6	B 11	DL	HSBY-559	17.65	19.32	30.19	3.92	12.39	3.30	1.16	2.61	0.47	1.94	0.58	1.28	0.25	1.14	0.26	78.81	8.23	1.95	0.80	30.41	1.33
331.5	II(2 nd M)	S 5	B 10	BS	HSBY-547	28.42	34.36	48.82	10.59	45.42	8.29	1.98	6.01	0.82	2.80	0.77	1.68	0.31	1.34	0.28	163.47	10.67	1.38	0.58	37.11	1.47
299.2	II(2 nd M)	S 5	B 10	BS	HSBY-513	31.79	38.31	61.70	10.86	40.04	6.97	1.49	5.46	0.91	3.68	1.05	2.44	0.51	2.52	0.56	176.51	9.31	1.20	0.69	30.26	1.29
216.2	II(2 nd M)	S 4	B 8	SR	HSBY-456	6.32	1.46	2.13	0.31	1.45	0.41	0.12	0.48	0.07	0.48	0.11	0.42	0.07	0.53	0.08	8.12	2.63	1.30	0.73	55.00	1.43
210.1	II(2 nd M)	S 4	B 8	SR	HSBY-446	7.05	2.25	4.01	0.55	2.78	0.72	0.19	0.73	0.10	0.67	0.16	0.47	0.07	0.45	0.07	13.21	3.87	1.29	0.83	44.55	1.17
149.5	I(1 st M)	S 3	B 6	BS	HSBY-403	6.20	17.40	61.82	4.53	20.70	3.55	0.76	2.58	0.29	1.59	0.33	0.94	0.15	0.76	0.11	115.50	16.12	1.23	1.60	18.86	0.59
145.2	I(1 st M)	S 3	B 6	BS	HSBY-401	62.01	57.65	77.64	12.59	59.72	10.74	1.99	10.07	1.34	8.61	1.96	6.15	0.82	5.07	0.73	255.07	6.34	0.95	0.66	31.68	1.55

134.3	I(1 st M)	S 3	B 6	BS	HSBY-393	58.18	25.39	51.11	7.85	38.95	8.92	2.01	9.38	1.26	7.88	1.70	5.31	0.69	4.15	0.60	165.19	4.34	1.09	0.83	34.30	1.04
Depth(m)	Member	Series	Bed	Lithology	No.	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE	L/H	Eu*/Eu*	Ce/Ce*	Y/Ho	(La/Ce) _N
133.1	I(1 st M)	S 3	B 6	BS	HSBY-392	46.33	35.91	54.06	8.13	39.06	8.56	2.05	8.51	1.11	6.91	1.50	4.59	0.60	3.63	0.54	175.17	5.39	1.19	0.73	30.94	1.38
127.8	I(1 st M)	S 3	B 6	BS	HSBY-389	56.78	39.90	56.53	8.20	40.06	10.20	3.07	9.18	1.22	7.68	1.69	5.16	0.68	4.04	0.61	188.22	5.22	1.58	0.72	33.66	1.47
126.9	I(1 st M)	S 3	B 6	BS	HSBY-388	70.66	58.97	80.84	11.54	54.41	13.76	4.27	10.91	1.50	10.01	2.27	6.91	0.91	5.42	0.84	262.57	5.77	1.73	0.71	31.08	1.52
125.6	I(1 st M)	S 3	B 6	BS	HSBY-387	69.39	64.48	85.25	12.35	56.54	12.56	3.73	9.93	1.35	9.05	2.13	6.80	0.90	5.41	0.78	271.26	6.46	1.66	0.69	32.64	1.58
124.3	I(1 st M)	S 3	B 6	BS	HSBY-386	49.88	49.32	68.23	9.62	43.23	10.82	3.53	7.98	1.09	7.18	1.60	5.17	0.69	4.23	0.64	213.33	6.47	1.88	0.72	31.20	1.51
122.5	I(1 st M)	S 3	B 6	BS	HSBY-385	38.59	35.00	50.53	7.59	36.39	7.36	1.71	7.02	0.96	6.10	1.36	4.13	0.56	3.47	0.50	162.69	5.75	1.18	0.71	28.37	1.44
120.6	I(1 st M)	S 3	B 6	BS	HSBY-384	65.78	43.21	59.37	8.92	42.74	11.21	3.49	10.38	1.35	8.38	1.83	5.60	0.72	4.33	0.65	202.18	5.08	1.61	0.70	35.93	1.52
119.5	I(1 st M)	S 3	B 6	BS	HSBY-383	54.21	26.90	43.32	7.06	34.86	7.67	1.77	8.04	1.11	6.53	1.41	4.36	0.57	3.52	0.51	147.64	4.66	1.12	0.72	38.35	1.29
118.2	I(1 st M)	S 3	B 6	BS	HSBY-382	65.92	25.74	47.88	7.39	38.04	8.39	1.95	8.85	1.20	7.51	1.63	5.03	0.65	4.00	0.57	158.82	4.40	1.12	0.80	40.41	1.12
117	I(1 st M)	S 3	B 6	BS	HSBY-381	50.23	25.06	39.71	6.18	30.95	7.59	2.08	7.67	1.02	6.32	1.37	4.24	0.56	3.30	0.49	136.51	4.47	1.35	0.74	36.69	1.32
115.1	I(1 st M)	S 3	B 6	BS	HSBY-380	52.92	32.98	50.72	7.78	38.06	8.31	1.99	8.34	1.11	6.98	1.53	4.65	0.61	3.84	0.54	167.44	5.07	1.19	0.73	34.51	1.35
112.4	I(1 st M)	S 3	B 6	BS	HSBY-379	46.32	39.42	54.76	7.94	37.74	9.67	2.89	8.55	1.15	7.04	1.54	4.75	0.61	3.72	0.54	180.30	5.46	1.58	0.71	30.01	1.50
107.5	I(1 st M)	S 3	B 6	BS	HSBY-375	38.57	71.30	112.04	12.77	52.17	10.54	3.05	5.97	0.65	4.11	1.00	3.74	0.54	3.60	0.61	282.11	12.95	1.85	0.85	38.41	1.33
103.7	I(1 st M)	S 3	B 6	BS	HSBY-372	61.97	52.88	80.13	10.66	48.93	13.05	4.04	11.19	1.46	8.99	2.02	5.76	0.75	4.49	0.67	245.01	5.94	1.66	0.78	30.75	1.38
102.4	I(1 st M)	S 3	B 6	DL	HSBY-371	34.76	20.38	27.16	4.14	20.58	4.80	1.34	4.92	0.66	4.36	0.97	2.94	0.38	2.25	0.33	95.21	4.66	1.37	0.68	36.00	1.56
101.3	I(1 st M)	S 3	B 6	BS	HSBY-370	122.61	58.49	51.88	16.02	81.22	20.22	4.31	19.77	2.81	19.09	4.42	14.76	2.11	14.40	2.19	311.69	2.92	1.07	0.39	27.73	2.35
51.1	I(1 st M)	S 2	B 4	BS	HSBY-324	21.61	39.90	74.18	10.20	42.14	6.80	1.05	4.86	0.62	3.68	0.77	2.53	0.37	2.67	0.41	190.17	10.96	0.90	0.85	28.24	1.12
48.6	I(1 st M)	S 2	B 4	BS	HSBY-318	13.87	75.21	125.31	14.98	58.65	10.01	2.26	5.35	0.56	2.86	0.56	1.84	0.27	2.10	0.34	300.28	20.66	1.48	0.86	24.92	1.25
23.4	I(1 st M)	S 2	B 3	SR	HSBY-307	13.59	11.81	16.82	2.09	9.06	2.96	1.06	2.11	0.30	1.90	0.41	1.28	0.19	1.18	0.18	51.35	5.80	2.09	0.77	33.19	1.46

Table 8 The correlation between of Se, Al, Ti and Th of anomalous Se-enrichment samples of the LFM , southern Shaanxi Province, China.

Member	n.		Se	Al	Ti	Th
IV(4 th M)	n=5	Se	1	-0.751	-0.75	0.753
		Al		1	.995**	-0.217
		Ti			1	-0.21
		Th				1
III(3 rd M)	n=9	Se	1	0.492	.845**	0.286
		Al		1	.835**	.858**
		Ti			1	0.591
		Th				1
II(2 nd M)	n=4	Se	1	0.506	0.352	0.584
		Al		1	.973*	.994**
		Ti			1	.961*
		Th				1
I(1 st M)	n=22	Se	1	0.125	.435*	-0.024
		Al		1	.574**	.762**
		Ti			1	0.063
		Th				1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 9 The correlation between of Se, Cd, Mo, As and S of all the LFm rocks. , southern Shaanxi Province, China.

	Se	As	Cd	Mo	S
Se	1				
As	.461**	1			
Cd	0.087	0.043	1		
Mo	.632**	.491**	.133**	1	
S	.320**	.595**	-0.037	.290**	1

n= 464 ; ** Correlation is significant at the 0.01 level (2-tailed).

Table 10 The correlation between trace element of anomalous Se-enrichment samples of the LFm, southern Shaanxi Province, China.

	Se	As	Tl	Ga	Mo	Sr	Ba	Zn	V	Pb	Ni	Cu	S
Se	1												
As	0.244	1											
Tl	.376*	.334*	1										
Ga	.522**	-0.042	0.128	1									
Mo	0.255	.506**	.596**	-0.099	1								
Sr	0.011	-0.049	0.054	-0.011	-0.065	1							
Ba	.738**	0.136	0.258	.878**	0.102	0.124	1						
Zn	0.061	-0.02	0.16	-0.03	0.084	0.015	-0.029	1					
V	0.266	0.087	.542**	0.202	.516**	-0.003	.306*	0.163	1				
Pb	0.279	0.146	0.276	.492**	.423**	0.041	.630**	-0.053	.506**	1			
Ni	0.223	.302*	.773**	0.011	.509**	0.058	0.117	.405**	.359*	0.062	1		
Cu	0.128	.445**	.585**	-0.184	.497**	-0.07	-0.055	-0.023	0.292	-0.061	.638**	1	
S	-0.054	0.223	.529**	-.325*	0.194	0.014	-0.183	0.009	-0.044	-0.039	.326*	0.24	1

n=40 ; * Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 11 The correlation of ΣREE , Ce/Ce^* , Eu^*/Eu^* and Y/Ho with TiO_2 of anomalous Se-enrichment samples of the LFM, southern Shaanxi Province, China.

	ΣREE	Ce/Ce^*	Eu^*/Eu^*	Y/Ho	TiO_2
ΣREE	1				
Ce/Ce^*	-0.252	1			
Eu^*/Eu^*	-.436**	0.005	1		
Y/Ho	-0.3	-.414**	0.035	1	
TiO_2	-0.039	0.122	0.22	-0.282	1

n=40 ; * Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).