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Geochemical Characteristics of Selenium and Its Correlation to Other Elements and Minerals in Selenium-Enriched Rocks in Ziyang County, Shaanxi Province, China

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ABSTRACT: Ziyang County, Shaanxi Province, China is a world known selenium (Se)-enriched area, and a severe selenosis incident was reported in Naore Village during the 1990s. This study investigated the geochemical characteristics of Se and its fractions in Se-enriched rocks from Ziyang. Se distribution is uneven, ranging from 0.23 to 57.00 μg/g (17.29±15.52 μg/g). Se content is higher in slate than chert, and even lower in carbonate rocks. Cd, As and V are enriched but Pb is depleted in Se-enriched strata. Se has different correlations both with TS (total sulfur) (R^2=0.59 for chert) and TC (total carbon) (R^2=0.77 for slate, R^2=0.87 for carbonate). Se has significant positive correlations with V (r=0.65), As (r=0.485), Cd (r=0.459) and Pb (r=0.405). The Se level correlates with mineral content, positively with pyrite, chlorite and illite, negatively with albite. Se associated with sulfide/selenide and elemental Se are the predominant fractions of total recovered Se, suggesting that a reducing environment and the formation of sulfides were significant to Se deposition during its geochemical cycle. Although low concentration of bio-available Se (average 5.62%±3.69%) may reduce the risk of Se poisoning in the target area, utilization of Se-rich rock as natural fertilizer should be restricted.

KEY WORDS: selenium, Ziyang County, statistical analysis, fractions.

0 INTRODUCTION

The selenium content of the dispersed element selenium in the Earth's crust is quite low (Huang et al., 2009). Selenosis or selenium poisoning in people and livestock was reported in two areas (Enshi District, Hubei Province and Ziyang County, Shaanxi Province), China in the 1960s. Between 1961 and 1963, morbidity due to selenosis reached almost 50% in a few villages in the Enshi District (Zheng et al., 1999; Yang et al., 1983). In Naore Village, Ziyang County there was a sudden increased incidence of selenosis occurred which led to designation as a second high selenosis area (Mei, 1986; Cheng and Mei, 1980). In contrast numerous studies have reported many endemic diseases caused by Se deficiency, such as Keshan disease and Kaschin-Beck disease (Fordyce et al., 2000; Ge and Yang, 1993). In the 1970s the World Health Organization declared Se to be an essential trace element for humans and animals with a narrow safety range (male: 40–400μg/d; female: 30–400 μg/d) (Tan et al., 2002; Luo et al., 2001; WHO, 1996). The international community paid significant attention to these discoveries by (Lenz and Lens, 2009; Sunde, 2006; Thomson, 2004; Tinggi, 2003; Koller and Exon, 1986). Studies have been conducted of the cultivation of Se-enriched potatoes and wheat, and also a few studies of the antagonism between Se and Cd during the growth of *Lepidium sativum* (Barrientos et al., 2012; Ježek et al., 2011; Lyons et al., 2005). There has also been research into internal causes of Se-related endemic diseases such as the Se levels of muscle and viscera *in vivo*, and the correlation between Se levels in adult blood and circumjacent soil (Kolawoleand Obueh, 2013; Mackay, 2006; Fordyce et al., 2000). Strachan and Wyncoll (2009) suggested that treatment with Se supplements can offer a valuable adjuvant therapy and reduce morbidity in critically ill patients.

There are numerous studies of the geochemistry of Se in rocks, soils, water and plants (Lei et al., 2011; Park et al., 2010; Zhu et al., 2008a; Kulp and Pratt, 2004; Luo et al., 2002b; Tan et al., 2002; Mao and Su, 1997; Chen and Luo, 1996). Depositional processes in sedimentary rock deposition are critical in controlling the degree of Se enrichment, and the Se content is controlled by lithology and organic carbon content. Ni et al. (2007) studied the Wanyuan area, Sichuan Province in the SW China and ranked Se contents collected from different strata of

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different ages as follows: Sinian, Cambrian, Permian, Triassic, Jurassic, Cretaceous and Silurian. They also found that the concentration of Se is higher in shale than in carbonate rocks.

Selenium behaves similarly to sulfur and occurs in a number of different oxidation states (VI, IV, 0, -II). This gives rise to different speciation states in different natural environments which influences the geochemical behavior and factors such as solubility, toxicity and bioavailability. The speciation of Se is affected by the concentration of carbon, sulfur and by Eh-pH values (Wen et al., 2006; Kulp and Pratt, 2004; Fordyce et al., 2000). The occurrence of elemental Se in organic matter is probably related to redox conditions, while the organic species present are related to high sulfur content of kerogen, possibly resulting from S-Se substitutions (Wen et al., 2006). Zhu (2004) and Zhu et al. (2008a, b) reported that elemental Se has been discovered in both carbonaceous-siliceous rocks and Se-enriched soils in Yutangba, Enshi City, China, and that the explanation of native Se crystals found in soils is the practice by local villagers of baking soil on coal fires for fertilizer.

A large number of people in the southwestern part of China suffer from such endemic diseases such fluorosis, arsenic poising and selenosis because of the use of high fluorine (2 000 μg/g), arsenic (35 000 μg/g) and selenium (>8 000 μg/g) coal in unvented ovens (Zheng et al., 1999). They also inferred that although the Se content in carbonaceous shalesis relatively high, the humid climate and acidic, Fe, Al-oxide-rich soils may resist accumulation of Se in soils or plants. The Se in soils and water ultimately comes from the geological surroundings including the parent materials and the types of outcrop rocks (Guo et al., 2012; Fordyce, 2007; Zhang et al., 2001). Understanding the geochemical properties of Se species, fractions and concentrations is crucial for the assessment of Se-related health risks and evaluation of pertinent environment issues and should guide the comprehensive management of Se by local authorities. Although much work has been done in the Ziyang study area, there is so far no comprehensive study of Se-enriched rocks. In the present study we have investigated the content and distribution of Se and its fractions along with other major elements and trace elements at four different sites. We have also measured correlations between Se and other elements or minerals in Se-enriched rocks to evaluate their influences on local residents.

1 GEOLOGIC SETTINGS

The research area Ziyang County, Shaanxi Province, has a subtropical climate and is located in the drainage basin of the Han River south of the Qinling Mountains. Se-enriched Lower Cambrian strata outcrop on Daba Mountain that extends over the whole county. The lowest Lujiaping Formation is a slightly metamorphosed marine sedimentary formation about 700–900 m thick, composed primarily of black siliceous and carbonaceous slate with coal, erite and pyrite layers. The overlying Jianzhuba Formation is mainly composed of black or dark grey argillaceous micrite especially concentrated in the upper part of the formation (Luo, 2006, 2003). Numerous studies have shown that selenium is concentrated in this formation and small scale sudden selenosis event occurred in the 1980s at Naore Village (Luo et al., 2004; Li, 1999; Luo and Jiang, 1995). Most of the samples collected for this study came from the Lower Cambrian Lujiaping Formation.

2 SAMPLES AND METHODS

2.1 Sample Locations and Preparation

A total of 35 fresh representative rock samples were collected from Ziyang County, Shaanxi Province, in July 2012. As shown in Fig. 1, the samples were from four different places including Gaoqiao Town (GQ, 5 samples), Wamiao Town (WM, 19 samples), Shuang'an Town (SA, 5 samples), Haoping Town (HP, 6 samples). Four samples from Gaoqiao Town are limestone and one (GQSC) is black carbonaceous shale (called 'stone coal' by local residents) characterized by high carbon content. All 19 samples from Wamiao Town are carbonaceous siliceous slate or siliceous slate. Samples from Shuang'an and Haoping towns are similar to those from Wamiao, except one of chlorite schist (SA-03), one of dolomite (SA-02) and one of phosphorite (SA-03).

The samples were cleaned with tap water to wipe off all contaminants, washed again with deionized water and stored in dry conditions. Then the samples were air-dried and powdered to 0.074mm using a Retsch RS200 grinding mill.

2.2 Analytical Methods

Major elements were determined by X-ray fluorescence spectrometry (XRF, PANalytical B.V AXIOS^{MAX}) in all the 35 samples. The sample was firstly divided into two parts. One part was used for loss on ignition (LOI) determination by placing ~0.5 g sample into a weighed porcelain crucible and combusting in a furnace at 1 000 °C for 2 h. The other part was used for simultaneous XRF analysis of 3 g powder samples and 10g boric acid (H_3BO_3) pressed into a disks. Compositions were calibrated using Chinese rock standards GSR-5, GSR-6 and GSR-13 with an average error less than 1%. Samples were also semi-quantitatively analyzed by X-ray diffract meter (XRD, Bruker AXS D8-Fcous) for the mineral identification and proportion determinations. The analytical work above was carried out the Ministry of Education Nano-Geomaterials Center of China University of Geosciences.

In addition to Se, trace elements including lead (Pb), cadmium (Cd), arsenic (As) and vanadium (V) were determined in the target samples. A digestion protocol was adapted from the methods of Liang et al. (2001) for total Se analysis, and the resultant solution was analyzed by hydride generation-atomic fluorescence spectrometry (HG-AFS) with a detection limit of 0.1 μg/L. 0.5 g powdered samples were treated with concentrated HNO_3, $HClO_4$ and HF in polytetrafluoroethylene (PTFE) lined bomb vessels, then the bombs were placed in an oven at 180 °C for 6 h. 2mL of 6 mol/L HCl solution were added and put on a heated plate (<100 °C) for 1 h to oxidize Se(VI) to Se(IV) before final analysis. Additionally, five Se species in 15 selected samples: water-soluble, phosphate exchangeable, base-extractable organic matter-bound, sulfide/selenide associated Se and elemental Se, and residual Se, were determined by methods modified from Fan et al. (2011) and Kulp and Pratt (2004). These samples included carbonate rocks, carbonaceous siliceous/calcareous slate, carbonaceous chert and stone coal. The analytical procedure was as follows: (1) extraction of water-soluble Se using Milli-Q water (18.2 MΩ cm); (2) extraction of exchangeable Se with 0.1 mol/L with a K_2HPO_4-KH_2PO_4 buffer (P-buffer); (3) extraction of base-soluble organic Se using 0.1 mol/L NaOH; (4) extraction of sulfide/selenide and elemental Se using a mixture of 0.5g $KClO_3$ solid powder and 10ml of concentrated HCl; (5) extraction of residual Se using the standard digestion protocol for total Se analysis.

Other trace elements were determined using inductively coupled plasma-mass spectrometry (ICP-MS) after sample digestion using four acids. The certified reference materials GSR-1, GSR-2, GSR-6 were analyzed along with the samples for quality assurance and quality control. Total carbon (TC) in all samples was measured using a high frequency infrared carbon and sulfur analyzer. Total sulfur (TS) was determined using a high temperature carbon testing furnace.

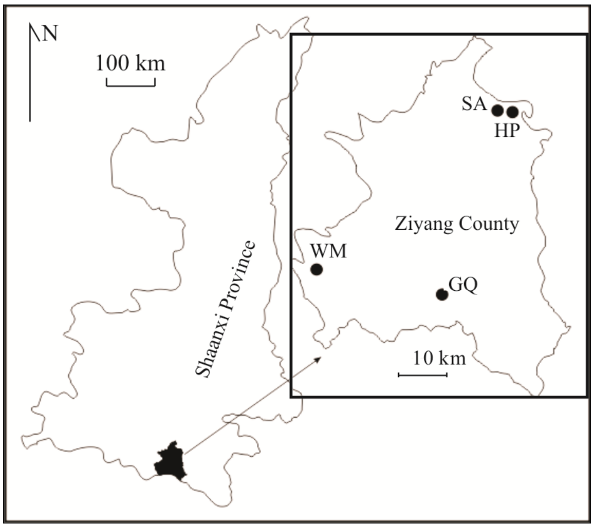

Figure 1. Map showing the four sampling locations in this study. WM. Wamiao Town; GQ. Gaoqiao Town; SA. Shuang’an Town; HP. Haoping Town.

2.3 Statistical Methodology

The normality of the distributions of the data from the 35 samples was analyzed using the Shapiro-Wilk test, and the results (not shown here) show that data of all 35 samples do not obey a normal distribution for $P<0.05$. (The significance of Pearson’s correlation coefficient between a pair of elements is based on the normality of the distribution of both elements (Bech et al., 2010).) Spearman Rank non-parameter correlation analysis which avoids distribution assumptions was conducted by SPSS v19 software in order to obtain correlation estimates, as was linear regression analysis.

3 RESULTS AND DISCUSSION

3.1 Concentration and Distribution of Total Se in Se-Enriched Rocks from Ziyang, China

The concentrations of Se in the whole samples range from 0.23 to 57.00 μg/g with an average of 17.29±15.52 μg/g (*n*=35). Enrichment coefficients of Se in all the samples are greater than 1, ranging from 2.77 to 686.75 with a mean value of 208.28, suggesting that the Se is widely abundant in this study area, and the high variation coefficient (89.76%) for Se in Se-enriched rock indicates that the distribution of Se is significantly uneven, like that in the soil (Zhu et al., 2008). The stone coal sample GQSC contains a relatively high Se concentration of 54.26 μg/g (Table 1). With this exception, the four sampled sites can be arranged from highest to lowest Se content as follows: Haoping, 37.15±16.54 μg/g (15.37–57.00 μg/g, *n*=6); Shuang’an, 14.45±16.19 μg/g (1.92–38.83 μg/g, *n*=5); Wamiao, 13.31±5.77 μg/g (4.39–25.43 μg/g, *n*=19); and Gaoqiao, 0.72±0.61 μg/g (0.23–1.59 μg/g, *n*=4). A significant positive correlation was found between soils and parent materials: $Y=1.27X-0.55$, $R^2=0.99$, $P < 0.01$, $n=8$, where Y (μg/g) is Se content in soil, X (μg/g) is Se content in parent material, because variations in Se contents of soils are due to Se variations of the bedrock from which the soil was derived. This leads to the conclusion that the incidence of selenosis is closely connected with the Se content of bedrock strata (Li et al., 2008; Luo et al., 2004; Luo, 2003).However, the Se content of samples from Shuang’an Town, where human selenosis occurred in the early 1980s, is not the highest among the four selected study areas (Cheng and Mei, 1980). There is also no report of selenium poisoning in Haoping Town which has the highest Se content. Thus there is not a simple relationship between potential health risk of selenosis and the Se content of bedrocks, which is probably controlled by multiple factors such as geologic structure, lithology of strata, daily diet, Se speciation in soil, Se levels in drinking water and irrigation water (Qin et al., 2013; Luo, 2003).

The rock samples from different areas display a relatively large spread in Se contents, which may be partly attributed to sample locations and lithology (Table 2). The average concentration of Se in carbonaceous siliceous slate is 23.78±15.19 μg/g (*n*=18), higher than that in chert (10.02±4.21 μg/g, *n*=9). The mean content of Se in carbonate is 1.44±1.7 μg/g (*n*=5), similar to the Se content of schist (1.92 μg/g, *n*=1). The one phosphorite sample collected near Naore Village contains 23.41 g Se per kg, lower than the Se content of phosphorite from Zunyi City, Guizhou Province (Feng et al., 2010). The occurrence of phosphorite in Naore Village may suggest that there was volcanic activity in the Early Paleozoic (Luo et al., 2004). The results in the present study are in agreement with previous reports from the same area (Luo et al., 2001; Li, 1999). The concentrations of Se in rocks from Ziyang are lower

Table 1 Total Se (μg/g) and enrichment coefficients (EC)in rocks from four towns, Ziyang County

Area	Min	Max	Mean	SD	EC_{Mean}	N
GQ#	0.23	1.59	0.72	0.61	8.64	4
WM	4.39	25.43	13.31	5.77	160.3	19
SA	1.92	38.83	14.45	16.19	174.1	5
HP	15.37	57.00	37.15	16.54	447.53	6
GQSC	54.26	54.26	54.26	--	653.73	1
Total	0.23	57.00	17.29	15.52	208.28	35

#. Stone coal values omitted. Enrichment coefficients calculated as the ratio between element content in a sample and that in the upper continental crust (Wedepohl, 1995).

than those at Enshi, China, the World Selenium Capital (Zheng et al., 1992), but 115 times higher than those in Wanyuan, Sichuan Province, one of the lowest Se areas in China (Ni et al., 2007). The Se concentrations of shales from Wymoing, USA and South Korea are 2.3–52 and 0.1–41 μg/g, respectively, both higher than those of Ziyang, whereas Se contents in coals from America and Australia are 0.46–10.7, 0.21–2.5 μg/g, far below the level in Chinese stone coal. Compared with other countries, carbonate rocks of both high-Se and low-Se areas in China contain much more selenium (Plant et al., 2003; Mao and Su, 1997; Song, 1989). Feng et al. (2010) studied a Se-enriched area at Zunyi City, China and found that phosphorite, K-bentonite and Ni-Mo-rich strata accumulated Se contents as high as 1.2–118, 11.4–219 and 998–1 006 μg/g, respectively. The Se content of Se in Chinese phosphorite is consistent with the world level and the Se concentration in sedimentary rocks is higher compared with volcanic rocks (Feng et al., 2010; Fordyce, 2007). We conclude that the concentrations of Se in rocks generally vary according to the sampling site and lithology, although there may be uniform results in specific samples.

3.2 Major Element Correlation to Total Se

Major element contents determined by XRF are shown in Table 3. The mean SiO_2 content is 63.42 wt.%, followed by Al_2O_3 (7.66 wt.%), CaO (5.79wt.%), Fe_2O_3 (2.77wt.%), MgO (2.13wt.%) and K_2O (1.92wt.%). Weight percent loss on ignition (LOI) is 11.33% of precombustion weight, partly due to complex reactions taking place during the combustion at 1000°C. The rock samples can be separated into two categories, those with low silica content (GQ: 33.57 wt.%; SA: 39.76 wt.%) and those with high silica content (WM: 77.98 wt.%; HP: 61.90 wt.%). LOI, CaO, MgO show a negative correlation with SiO_2 in each category, implying that more labile components such as organic matter, pyrite and calcite appear to be retained in low-SiO_2 rocks. The mean SiO_2 content (91.87 wt.%) in carbonaceous chert determined in this work is slightly lower than that (93.67 wt.%) collected by Wen et al. (2003), while average SiO_2 in carbonaceous siliceous slate (61.78 wt.%) is consistent with Se-enriched back shale (61.59 wt.%) from Zunyi, China (Feng et al., 2010). CaO in carbonate rocks (23.79 wt.%) ranks only second to SiO_2 (29.42 wt.%), followed by MgO, Al_2O_3, Fe_2O_3, K_2O and NaO. Luo et al. (2002a) concluded that the mobility of selenium in rock has negative correlation to SiO_2 and a positive correlation to CaO, so that selenosis in Naore Village was related to the existence of Se-enriched pyritized carbonaceous slate and volcanic tuff (Luo, 2003), and in Shuang'an, Ziyang County to the high mobility of Se in low-SiO_2 and high-LOI rocks.

Fordyce et al. (2000) discovered that LOI has significant positive correlations to organic matter (OM) and total organic carbon (TOC) in soils, $LOI=5.519+1.72\times TOC$, $LOI=5.519+0.998\times OM$ (wt.%), $R^2=0.862$. A similar correltation was found in the present study between LOI and TC in Se-enriched rocks, where the $LOI=1.66+2.2\times TC$, $R^2=0.47$ (Fig. 3). The difference between LOI and TOC in soils is mainly due to the loss of water and structural water from clays and sesquioxides during ignition between 100 °C and 500 °C (Rowell, 1994), whereas during ignition under 1 000 °C, some minerals such as pyrite and calcite can be oxidized or decomposed, resulting in more loss and less correlation between LOI and TC compared with soils.

A few researchers have reported that not only particular strata, lithology and total carbon content but also the content of other major elements such as Si, Al, Ca, Mg, and P control the degree of Se-enrichment in rocks (Luo and Jiang, 1995; Zheng et al., 1992). Spearman rank correlation, a method for analyzing the degree of close contact between the two groups of variables, has been widely used for geochemical study (Bech et al., 2010; Li et al., 2008; Fordyce et al., 2000). The results of

Table 2 Se contents (μg/g) in samples of different lithology from different places and data, shown as average ranges

Types	Abroad	Enshi, China	Zunyi, China	Ziyang, China	Wanyuan, China	Present paper
Chert		0.29–127.4 (47.04)[c]	11.1[f]	>12[g,h]		4.39–15.99(10.02±4.21, *n*=9)
Shale	1–675[USA];2.3–52[Wyoming, a] 0.1–41[KOR, a]	2.36–280.6 (60.12)[c]	2.34–104 (40.41)[f]	0.1–3[h]	0.01–1.35 (0.36)[i]	
Slate				0.08–35[g,h]		3.76–57(23.78±15.19, *n*=18)
Mudstone	0.1–1500[a]	0.87[c]		0.02–2[g,h]		1.92
Carbonate	0.03–0.17[a]	0.01–15.58 (3.85)[c]		0.05–3[g,h]	0.02–0.58 (0.11)[i]	0.23–4.33(1.44±1.7, *n*=5)
Sandstone	<0.05[a]			0.05–3[g,h]	0.01–0.55 (0.09)[i]	
Coal	0.46–10.7[USA]; 0.21–2.5[AUS, a]	6–8390 (177.56)[d,e]		8–45[h]		54.26
Phosphorite	1–300[a]		1.2–118 (47.8)[f]			23.41
K-bentonite[#]			11.4–219 (72.08)[f]			
Ni-Mo layer	0.1–7[&, b]		998–1006 (1001.97)[f]			

[#]. Potassium-bentonite; &.volcanic; a. Plant et al.(2003); b. Floor and Román-Ross(2012); c. Zheng et al. (1992); d. Mao and Su (1997); e. Song (1989); f. Feng et al. (2010); g. Li (1999); h. Luo et al. (2001); i. Ni et al. (2007).

Spearman Rank correlation analysis in Table 4 show that the Se contents have a significant negative correlation with SiO_2 contents in both carbonate (-0.9) and chert (-0.72) and the correlation coefficient is 0.06 in slate. There are however a significant positive correlation between Se and P_2O_5 (0.48), and negative between Se and NaO (-0.58). The correlations between Se and TiO_2, Al_2O_3 are 0.84, 0.67 respectively, but no significant correlations can be found in the rest of the sample dataset (*n*=35). We interpret this distinction as related to different lithologies.

3.3 Mineral Content Correlations to Total Se

There are no comprehensive studies of the relationships between Se and minerals in Se-enriched rocks, although numerous researchers have investigated Se-enriched areas and got a mass of data from Se-enriched rocks. Therefore, we have investigated correlations between mineral contents and Se by analyzing XRD results (Table 5). The minerals present in the studied rocks include quartz, illite, albite, pyrite, calcite, dolomite and chlorite, whilst barytocalcite, gypsum or hydroxy phosphate may also occur in a few samples.

The differences of mineral contents in rocks indicate that the mineral composition was related to sampling location and lithology. Samples collected from Gaoqiao Town contain an average of 30.7% illite, followed by calcite (16.84%), quartz (15.55%), dolomite (14.72%), chlorite (13.29%), albite (11.28%), and pyrite (2.07%). Quartz content is highest in stone coal (GQSC) mean 40.03%, and the contents of illite and albite are slightly lower than other samples from the same town. Concentrations of albite, chlorite, and calcite are 40.78%, 15.95% and 7.48% as in others samples (GQ-01–GQ-04). These results suggest that a clear distinction exists between Se-enriched stone coal and argillaceous limestone. Samples from Wamiao Town where the rocks WM-01–WM-13 are of the Lower Cambrian Lujiaping Formation extending from northeast (NE) to southwest (SW) are mainly comprised of quartz (mean 72.41%) and illite (mean 20.63%). In samples collected from NE to SW, quartz content increases from 46.28% to 93.37%, while illite, albite and pyrite show an opposite trend. Rocks collected from Shuang'an Town show diverse mineral composition because of their different lithologies. The chlorite content in sample SA-01 is 84.14% is the highest in all samples. Dolomite content in SA-02 is 78.54%, while mineral composition in SA-03 is relatively uniform. Illite predominates in SA-04 and SA-05 at 80.32% and 67.88%, respectively. The above results imply that Shuang'an Town is located in a relatively active layer which may be undergoing slow geological movements (Luo, 2003). The minerals in rocks from Haoping Town are relatively simple containing illite (mean 50.55%), quartz (mean 44.08%) and albite (mean 5.37%).

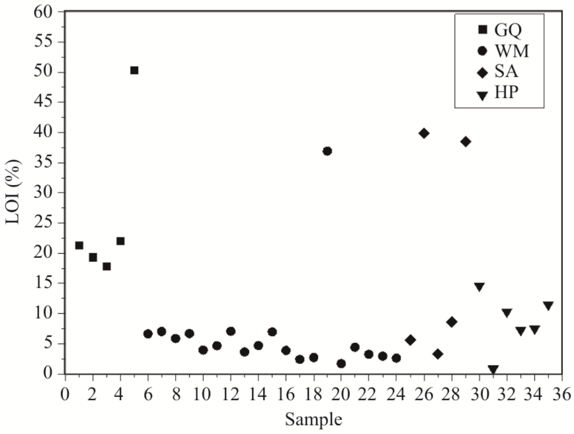

Figure 2. Values of LOI (%) in all rock samples from Ziyang County.

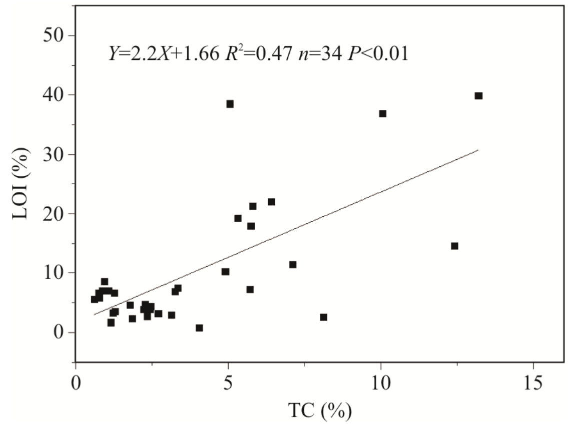

Figure 3. Correlation between LOI and TC in rocks from Ziyang County, China (result of GQSC was removed for its too high TC as a outlier).

Spearman rank correlation analyses show that the Se content has a significant positive correlation to pyrite with *r*=0.56, *P*=0.046 (*n*=13) and positive correlations to chlorite (*r*=0.667, *P*=0.071, *n*=8) and illite (*r*=0.316, *P*=0.074, *n*=33), but a negative correlation to albite with *r*=-0.377, *P*=0.084 (*n*=22). In order to find out whether there are any significant effects of mineral content on Se-enrichment, we suggest such a correlation would be acceptable if the confidence coefficient (*P*) is <0.1. The significant positive correlation between Se and pyrite indicates that Se should easily be concentrated in pyrite during diagenesis (Yang and Yi, 2012; Zhu et al., 2007b; Luo et al., 2005). We discover from the relationships between Se and the clay minerals chlorite and illite that clay minerals absorb selenium in Se-enriched rocks. On the contrary, the occurrence of albite has an opposite effect on Se-enrichment compared to clay minerals. Although better understanding of Se enrichment characteristics might be achieved from the above results, further research on Se concentrations and single mineral species such as pyrite, chlorite, illite or albite is still required to understand the enrichment mechanisms of Se.

3.4 Correlation between TC, TS and Total Se

The average concentrations of total carbon and total sulfur in Se-enriched rocks from Ziyang County, China are 5.09% and 1.37% (Table 3). The highest TC concentration (46.32%) is found in Se-enriched stone coal, carbonate contains much more carbon (7.29%) than slate (3.72%), followed by chert (2.94%), phosphorite (1.23%) and chlorite schist (0.61%). The highest sulfur content is 3.04% in stone coal, followed by 1.99% in slate and only 0.25% in chert, while it is less than 0.1% in phosphorite and chlorite schist (Table 3). The ratios of Se/S from all samples ($0.03–110.42\times10^{-3}$, mean 7.14×10^{-3}) from Ziyang County are close to the range of Lower Cambrian

Table 3 Concentrations (wt.%) of major oxides, TC , TS and Se/S ($\times10^{-3}$) in Se-enriched rocks from Ziyang, China

Sample number	Lithology	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	TiO_2	P_2O_5	LOI	TC	TS	Se/S
GQ-01	I_1	36.85	7.87	2.81	5.89	21.45	0.54	1.56	0.04	0.44	0.06	21.31	5.81	0.17	0.13
GQ-02	I_1	36.31	8.74	3.79	4.42	22.45	0.49	1.86	0.02	0.53	0.61	19.32	5.31	0.44	0.15
GQ-03	I_1	32.70	7.21	10.45	5.90	18.39	0.56	1.41	0.04	0.41	0.08	17.89	5.74	6.05	0.03
GQ-04	I_1	33.89	8.25	3.30	5.18	22.60	0.41	2.20	0.05	0.57	0.08	22.00	6.41	0.34	0.11
GQSC	II	28.10	5.79	2.74	1.96	2.78	0.20	1.48	0.02	0.46	0.57	50.33	46.32	3.04	1.79
WM-01	III	63.60	13.64	4.02	0.69	0.10	0.94	3.62	0.00	0.75	0.07	6.63	0.77	3.58	0.41
WM-02	III	64.39	14.73	2.71	0.81	0.05	0.81	2.91	0.00	0.59	0.03	7.01	0.87	3.81	0.45
WM-03	III	64.06	13.43	4.48	0.76	0.14	1.20	3.51	0.02	0.68	0.07	5.85	0.77	3.70	0.33
WM-04	III	65.39	12.66	3.84	0.64	0.08	1.08	3.45	0.02	0.67	0.02	6.65	1.28	2.88	0.31
WM-05	IV	83.95	6.15	0.93	0.44	0.14	0.47	1.55	0.01	0.37	0.04	3.94	2.45	0.56	2.64
WM-06	III	76.94	10.09	1.22	0.77	0.10	0.56	2.68	0.00	0.50	0.05	4.65	1.79	0.78	1.98
WM-07	III	64.18	13.34	3.99	0.75	0.15	1.18	3.48	0.00	0.65	0.05	7.05	1.09	3.29	0.28
WM-08	III	83.95	7.80	0.33	0.58	0.02	0.47	1.39	0.00	0.25	0.04	3.62	1.29	0.45	3.54
WM-09	III	83.05	7.62	0.36	0.64	0.03	0.33	1.35	0.00	0.26	0.03	4.69	2.28	0.50	5.12
WM-10	III	78.98	8.13	0.68	0.70	0.05	0.34	1.36	0.00	0.24	0.04	6.96	3.25	0.91	2.56
WM-11	IV	90.64	2.46	0.32	0.30	0.07	0.01	0.55	0.00	0.08	0.03	3.89	2.23	0.37	4.30
WM-12	IV	94.64	1.26	0.46	0.15	0.06	0.00	0.33	0.00	0.03	0.01	2.39	1.85	0.09	6.64
WM-13	IV	95.32	0.42	0.53	0.10	0.15	0.02	0.09	0.00	0.02	0.08	2.71	2.35	0.10	6.96
WM-14	III	10.36	0.95	0.60	11.73	30.87	0.01	0.15	0.02	0.00	0.46	36.90	10.06	0.35	5.70
WM-15	IV	92.52	0.96	1.03	0.22	1.00	0.01	0.13	0.00	0.04	0.04	1.70	1.15	0.39	3.37
WM-16	IV	88.10	0.36	0.61	0.18	2.89	0.01	0.05	0.01	0.04	0.04	4.42	2.46	0.28	3.22
WM-17	IV	94.77	0.31	0.59	0.14	0.15	0.00	0.05	0.00	0.02	0.08	3.24	2.71	0.12	3.54
WM-18	IV	93.37	0.77	0.99	0.33	0.19	0.02	0.15	0.02	0.04	0.07	2.94	3.14	0.18	3.66
WM-19	IV	93.50	0.90	0.76	0.26	0.32	0.03	0.16	0.00	0.04	0.39	2.60	8.12	0.14	9.39
SA-01	V	72.32	8.60	2.58	0.71	0.19	0.07	3.41	0.00	0.60	0.08	5.61	0.61	0.01	23.70
SA-02	I_2	7.36	1.65	1.19	13.75	34.07	0.05	0.20	0.04	0.12	0.97	39.85	13.19	0.03	15.03
SA-03	VI	33.35	4.08	1.11	1.52	25.55	0.04	0.58	0.02	0.20	26.80	3.32	1.23	0.02	110.42
SA-04	III	55.63	16.99	5.56	2.14	0.20	0.29	4.13	0.04	1.24	0.08	8.60	0.95	0.03	13.93
SA-05	III	30.17	9.18	3.51	1.98	11.99	0.05	1.69	0.04	0.49	1.01	38.50	5.05	5.57	0.70
HP-01	III	38.78	13.80	17.91	4.93	5.20	1.19	0.16	0.21	2.14	0.38	14.60	12.41	0.96	2.92
HP-02	III	68.61	15.74	1.08	1.34	0.11	0.08	6.53	0.00	0.94	0.07	0.83	4.06	0.87	2.87
HP-03	III	58.52	13.41	4.11	1.37	0.36	0.07	4.90	0.00	0.82	0.32	10.30	4.9	2.93	1.95
HP-04	III	68.33	11.51	3.41	0.76	0.19	0.05	4.43	0.00	0.68	0.29	7.28	5.7	0.56	8.97
HP-05	III	71.76	8.64	2.61	0.95	0.20	0.04	2.09	0.00	0.28	0.30	7.52	3.35	3.65	1.31
HP-06	III	65.40	10.70	2.49	1.74	0.28	0.08	3.68	0.00	0.64	0.05	11.47	7.1	0.97	1.58
M.GQ		33.57	7.57	4.62	4.67	17.53	0.44	1.70	0.03	0.48	0.28	26.17	5.82	1.75	0.44
M.WM		77.98	6.10	1.50	1.06	1.92	0.39	1.42	0.01	0.28	0.09	6.20	2.63	1.18	3.39
M.SA		39.76	8.10	2.79	4.02	14.40	0.10	2.00	0.03	0.53	5.79	19.18	4.21	1.13	32.76
M.HP		61.90	12.30	5.27	1.85	1.06	0.25	3.63	0.04	0.92	0.24	8.67	6.25	1.66	3.26
M.carbonate	I	29.42	6.74	4.31	7.03	23.79	0.41	1.45	0.04	0.41	0.36	24.07	7.29	1.41	3.09
M.slate	III	61.78	11.24	3.49	1.85	2.78	0.49	2.86	0.02	0.66	0.19	10.51	3.72	1.99	3.05
M.chert	IV	91.87	1.51	0.69	0.23	0.55	0.06	0.34	0.00	0.08	0.09	3.09	2.94	0.25	4.86
M.total		63.42	7.66	2.77	2.13	5.79	0.33	1.92	0.02	0.45	0.95	11.33	5.09	1.37	7.14

I. Carbonate; I_1. argillaceous limestone; I_2. dolomite; II. stone coal; III. carbonaceous silicious/calcareous slate; IV. carbonaceous chert; V. chlorite schist; VI. phosphorite.

Table 4 Spearman rank correlation coefficients (*r*) for Se and major elements in rocks from Ziyang, China

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	NaO	K_2O	TiO_2	P_2O_5	LOI
r-All (*n*=35)	-0.07	0.25	-0.05	0.03	-0.19	-0.04	0.16	0.18	0.12	0.04
r-Carbonate (*n*=5)	-0.90*	-0.60	0.00	0.60	0.30	-0.30	-0.70	-0.70	0.82	0.10
r-Slate (*n*=18)	0.06	-0.28	-0.19	0.25	0.29	-0.58*	-0.14	-0.12	0.48*	0.28
r-Chert (*n*=9)	-0.72*	0.67*	0.13	0.62	0.04	0.50	0.55	0.84**	-0.26	0.22

**. *P*-value≤0.01; *. *P*-value≤0.05.

Table 5 Mineral compositions of Se-enriched rocks from Ziyang County, China (%)

Sample number	Quartz	Dolomite	Pyrite	Illite	Chlorite	Albite	Calcite	Remark
GQ-01	18.11	13.57		23.57	16.31	13.27	16.17	
GQ-02	15.12		2.17	36.42	14.32	10.22	21.75	
GQ-03	13.90	15.71	3.68	30.00	14.43	10.41	11.86	
GQ-04	15.08	14.89	0.37	32.81	8.09	11.20	17.56	
GQSC	40.03	10.33	16.92	24.75	2.12	4.60	1.26	
WM-01	46.28		11.58	24.77		12.24	5.14	
WM-02	44.39		11.30	32.48		11.83		
WM-03	48.10		13.26	19.47		19.17		
WM-04	39.96		9.63	38.06		12.36		
WM-05	86.17			13.21		0.62		
WM-06	75.96			22.83		1.21		
WM-07	39.64	0.03	9.77	34.94		15.62		
WM-08	70.68			25.46		3.86		
WM-09	66.44			30.71		2.85		
WM-10	66.32			30.85		2.83		
WM-11	92.83			7.17				
WM-12	88.89			11.11				
WM-13	93.67			6.33				
WM-14	43.85			27.58			22.04	6.52^{a}
WM-15	98.78							1.22^{b}
WM-16	99.65							0.35^{a}
WM-17	88.27			11.73				
WM-18	98.73			1.27				
WM-19	87.21			12.79				
SA-01	4.11			0.20	84.14	10.59	0.96	
SA-02	3.16	78.54		10.09	5.77		2.43	
SA-03	31.18	5.52	26.65	12.63				23.35^{c}
SA-04	16.45		2.97	80.32		0.26		
SA-05	17.30	0.93	0.52	67.88	3.05		10.31	
HP-01	65.90			17.75		16.35		
HP-02	28.66			65.63		5.71		
HP-03	25.45			72.84		1.71		
HP-04	59.48			37.87		2.65		
HP-05	54.71		5.42	39.43		0.44		
HP-06	30.25			69.75				

a. Barytocalcite; b. gypsum; c. hydroxy phosphate.

Se-enriched strata generally ($0.6–46.5\times10^{-3}$ with mean 14.9×10^{-3}) (Fan et al., 2011).

A few studies have reported that the concentration of organic matter (OM), pyrite and sulfur can affect the Se content in Cambrian strata (Wen et al., 2000; Wen and Qiu, 1999; Luo and Jiang, 1995). We therefore compared Se in sediments and Se-enriched rocks to speciation of Se associated with OM, Se adsorbed by iron or manganese oxide, and Se incorporated into sulfide by substitution (Zhu et al., 2007a; Kulp and Pratt, 2004; Martens and Suarez, 1997; Qu et al., 1997). Luo et al. (2002a) discovered that the leaching losses of Se from different varieties of rock of different ages from Daba Mountain, China, have positive correlations to those of carbon and sulfur. A similar phenomenon was also discovered between Se and OC and TS in chalk (R^2=0.62 and 0.8, respectively) and shale (R^2=0.85, 0.54, respectively) collected from Upper Cretaceous rocks (Kulp and Pratt, 2004). Meseck and Cutter (2011) studied the geochemical behavior of Se in sediments from San Francisco Bay and obtained a strong correlation line between total selenium and organic carbon: $\text{Se (mol/g)}=1.46\times10^{-6}\times C_{org}\text{(mol/g)}+1.87\times10^{-9}$, R^2=0.83, P<0.05. In the present work the R^2 value when Se (μg/g) is plotted against TC (%) in a scatter plot is 0.77 for slate and 0.87 for carbonate (Fig. 4). The fact that no significant correlation between Se and TS was found in slate illustrates that the Se content in Se-enriched rocks from Ziyang was largely influenced by TC compared to TS, in agreement with that of Cretaceous shale (Kulp and Pratt, 2004). The positive correlation between Se and TS in carbonaceous chert (R^2=0.59, P<0.05) may reveal that the Se was mostly enriched by the substitution of S by Se (Fig. 5). Therefore the relationships between Se content and TC, TS in Se-enriched rocks vary from the lithology.

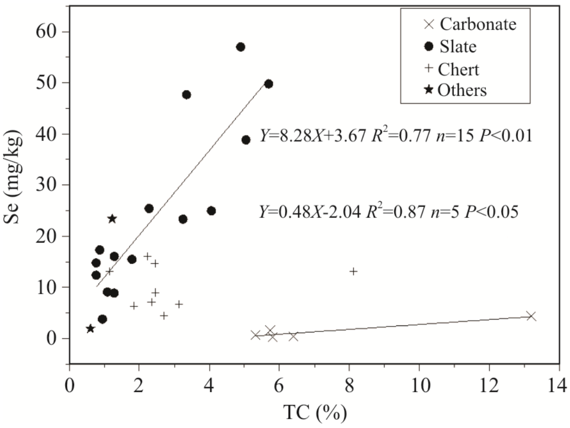

Figure 4. Scatter diagram between Se and TC contents of Se-enriched rocks from Ziyang county, China.

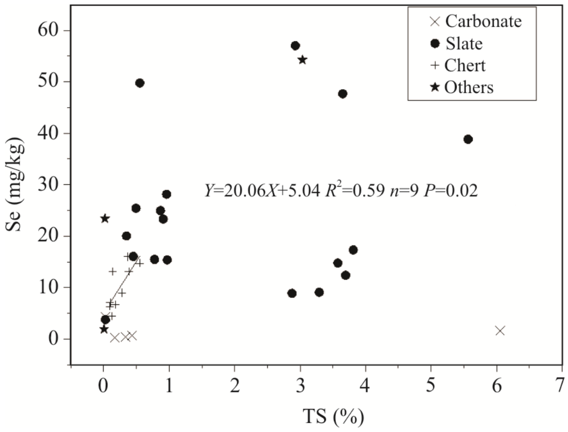

Figure 5. Scatter diagram between Se and TS contents of Se-enriched rocks from Ziyang County.

3.5 Correlations of Trace Elements As, Cd, Pb, V to Total Se

A large number of trace elements are enriched in black shales, for instance selenium, arsenic, cadmium and vanadium (Feng et al., 2010; Park et al., 2010). The ranges, mean concentrations and enrichment coefficients (Tables 6a, 6b) of trace elements in the study area were calculated by using the elemental abundance in upper continental crust (Wedepohl, 1995). Cd, V, As and Pb were all highly enriched in Se-enriched stone coal as compared to other samples. The other samples from the four towns are depleted in Pb, and enriched in As, Cd and V.

Phosphorite, with mean concentrations of trace elements 22.77 (As), 2.54 (Cd), 9.75 (Pb) and 857.68 μg/g (V), has similar enrichment characteristics to stone coal. The enrichment coefficients are 11.38 for As and 16.18 for V, similar to the results reported by other researchers (Feng et al., 2010; Wen et al., 2003). It is worth pointing out that EC of Cd (24.89) in our samples is four times higher than that of black shale (5.71) from Korea (Park et al., 2010). Although enriched in a few samples, Pb is depleted in the majority of samples (EC=0.57), an opposite characteristic compared to samples from Zunyi City, Guizhou Province, China (Feng et al., 2010). Potential high-As/Cd in crops in Ziyang grown on the soils derived from black shales with abundant As and Cd may have a bad influence on human health. Further investigations of concentrations of toxic trace elements are required in this area.

The cycling of trace element from rocks into soils and plants means that the latter is inevitably affected by the former; therefore rocks should be regarded as the initial source of trace elements in the whole cycle (Yu et al., 2013; Park et al., 2010; Li et al., 2008). Spearman rank non-parametric correlation analysis was conducted to understand the geochemical characteristics of Se-enriched rocks in Ziyang (Table 7). Se concentrations correlated strongly (P<0.01) with V concentrations (r=0.65), As (r=0.485), S (r=0.476), Cd (r=0.459), and Pb (r=0.405, P<0.05). Similar correlations were found in soils from southern Shaanxi Province, China (Li et al., 2008). Zheng et al. (1993) supposed that the abundance of V in Se-enriched rocks from western Hubei Province, China was related to hot groundwater sources by biogenic processes, which illustrates that the genetic mechanism of Se-enriched rocks from both Shaanxi and Hubei provinces may be similar.

In addition, as shown in Table 7, the As concentrations are correlated with Pb (r=0.653) and S (r=0.55), which shows that a close relationship exists between Se, As and S. The explanation for this is the similar positions of Se, As and S in the Periodic Table, which lead Se and As to more easily enter into sulfide minerals such as pyrite, galena, sphalerite, and chalcopyrite. Se-bearing minerals might have formed because there was

Table 6a Concentrations (μg/g) and ECs of trace elements of different areas from Ziyang County, China

Area	GQ (*n*=4)[a]	WM (*n*=19)	SA (*n*=5)	HP (*n*=6)	GQSC (*n*=1)	Total (*n*=35)	Crust*
As	3.33–11.75[b]	1.17–32.29	2.8–109.4	4.52–52.13	166.1	1.17–166.1	2
	6.42(3.21)[c]	11.29(5.65)	50.00(25.00)	23.43(11.72)	(83.05)	22.77(11.38)	
Cd	0.11–0.57	0.09–11.32	0.08–10.8	0.33–8.36	14.32	0.08–14.32	0.102
	0.27(2.63)	1.82(17.81)	5.36(52.53)	2.03(19.88)	(140.39)	2.54(24.89)	
Pb	6.3–12.84	1.29–17.48	1.45–26.04	6.38–17.33	25.87	1.29–26.04	17
	9.85(0.58)	6.98(0.41)	14.47(0.85)	11.83(0.70)	(1.52)	9.75(0.57)	
V	67.24–76.26	92.31–1580.13	115.6–4764.6	194.4–1260	4689	67.24–4764.6	53
	71.48(1.35)	665.35(12.55)	1609.82(30.37)	725.52(13.69)	(88.47)	857.68(16.18)	

[a]. Sample number; [b].range of concentrations; [c]. mean value (EC); *.data from Wedepohl, 1995.

Table 6b Concentrations (μg/g) and ECs of trace elements (ppm) from different lithologies from Ziyang County, China

Type	Carbonate (*n*=5)[a]	Slate (*n*=18)	Chert (*n*=9)	Chlorite schist (*n*=1)	Phosphorite (*n*=1)	Crust*
As	3.33–20.74[b]	4.46–87.49	1.17–7.74	2.8	109.4	2
	9.28(4.64)[c]	24.16(12.08)	4.15(2.08)	(1.4)	(54.7)	
Cd	0.11–5.72	0.08–11.32	0.1–7.79	0.18	10.01	0.102
	1.36(13.32)	2.07(20.29)	2.26(22.11)	(1.8)	(98.14)	
Pb	6.3–12.84	4.64–24.52	1.29–10.34	1.45	26.04	17
	9.02(0.53)	10.7(0.63)	5.59(0.33)	(0.09)	(1.53)	
V	67.24–1054.4	92.31–4764.6	259.9–1383.22	402.4	1712.1	53
	268.06(5.06)	877.76(16.56)	675.01(12.74)	(7.59)	(32.3)	

Table 7 Spearman rank correlation coefficients between selected elements in Se-enriched rocks from Ziyang County, China (*n*=35)

	As	Cd	Pb	V	TC	TS
Se	0.485**	0.459**	0.405*	0.650**	0.132	0.476**
As		0.187	0.653**	0.138	-0.005	0.550**
Cd			0.159	0.670**	0.489**	-0.008
Pb				0.112	0.095	0.434**
V					0.235	-0.067
C						0.027

**. When sig. is less than 0.01(two-tailed), the correlation is significant. *. When sig. is less than 0.05(two-tailed), the correlation is significant.

a deficiency of S during preliminary stages of diagenesis (Yang and Yi, 2012; Zhu et al., 2012; Lehmann et al., 2007; Kulp and Pratt, 2004). There is a need for further study and interpretation of the correlations between Cd-V (0.67), Cd-TC (0.489), Pb-TS (0.434).

3.6 Se Fractions in Se-Enriched Rocks in the Study Area

In this study a total of fifteen samples of rocks including carbonate, carbonaceous silicious/calcareous slate, carbonaceous chert and stone coal were selected for sequential extraction of Se in five operationally defined fractions characterized by properties of environmental relevance (Kulp and Pratt, 2004). The total Se recovery of all five fractions for sequential extraction ranged from 75.66%–115.78% (91.03% on average). Low Se recovery values (<85%) may be attributed to dissolved humic compounds and suspended solids in earlier extractions, because a Se signal could be retained without oxidative digestion. The distributions of Se species among the studied fractions are shown in tables 8 and 9.

Water-soluble Se and exchangeable Se were not detected in limestone. The average percentage of water-soluble Se in dolomite and slate are 1.44% and 1.79%, respectively. A higher percentage of water-soluble Se was found in chert (2.07%–3.89%, average 3.01%) and stone coal (4.39% average). The percentage of water-soluble fraction is regarded as an index of degree of weathering (Fan et al., 2011). In our study, the low proportion of water-soluble Se (0–4.39%) is similar to results from shales and cherts obtained by Fanet al. (2011) and from chalks and shales obtained by Kulp and Pratt (2004), suggesting that the Se-enriched rocks are not highly weathered or relatively fresh.

Se mobilized by P-buffer extraction accounted for 0–7.71% of the Se budget for slates, 2.72%–5.77% for cherts, 6.97% for stone coal and 4.36% for dolomite. Se fraction extracted by water and P-buffer represent the most bio-available forms of Se (Wang et al., 2012). The bio-available forms of Se in our samples account for less than 6.5% of total recovered Se, except for the stone coal with 9.9% and two slates HP-03, 8.7% and HP-05, 8.26%. These results may indicate that our high Se areas have the possibility of causing Se deficiency in plants or humans.

The percentages of base-soluble Se extracted by NaOH solution in carbonate (average 6.07% for limestone, none for dolomite) were lower than those in slates, cherts and stone coal, with averages of 28.93%, 34.39% and 47.2%, respectively. The high proportion of base-soluble Se demonstrates that organic-Se is quite stable in the slates and cherts under the redox conditions of Lower Cambrian strata, which was is confirmed by other studies (e.g., Qinet al., 2012; Fan et al., 2011).

In comparison with other rock types in the study area,

Table 8 Se concentration (μg/g) among extracts of water soluble (A), P-buffer solution (B), NaOH (C), mixture of 0.5 g $KClO_3$ solid powder and 10 mL concentrated HCl (D) and mixture of HNO_3, $HClO_4$ and HF solution (E)

Sample number	Lithology	A	B	C	D	E	ΣSe (μg/g)	Total Se (μg/g)	Recovery (%)
GQ-02	Argillaceous limestone	ND	ND	0.09	0.48	0.16	0.73	0.67	109.03
GQ-03	Argillaceous limestone	ND	ND	ND	0.75	1.09	1.84	1.59	115.78
SHA-02	Dolomite	0.06	0.18	ND	2.65	1.14	4.02	4.33	92.85
WM-04	Carbonaceous silicious slate	ND	0.07	1.61	4.63	1.43	7.74	8.88	87.19
WM-06	Carbonaceous silicious slate	0.41	0.36	5.66	3.93	2.34	12.69	15.44	82.21
WM-07	Carbonaceous silicious slate	ND	ND	2.28	6.56	1.31	10.14	9.09	111.55
HP-01	Carbonaceous silicious slate	0.61	1.22	11.89	8.48	3.05	25.25	28.11	89.83
HP-03	Carbonaceous silicious slate	1.04	3.92	20.19	18.54	10.21	53.9	57	94.57
HP-05	Carbonaceous silicious slate	0.76	3.18	11.97	13.94	11.39	41.24	47.67	86.5
WM-14	Carbonaceous calcareous slate	0.52	0.58	0.18	7.66	7.29	16.23	20.01	81.11
WM-05	Carbonaceous chert	0.32	0.49	5.21	3.81	2.05	11.89	14.66	81.09
WM-11	Carbonaceous chert	0.25	0.7	5.93	2.37	2.85	12.1	15.99	75.66
WM-12	Carbonaceous chert	0.19	0.14	1.38	1.25	2.04	5	6.3	79.43
WM-18	Carbonaceous chert	0.21	0.17	1.05	1.86	2.84	6.13	6.69	91.59
GQ-05	Stone coal	2.08	3.3	22.36	9.97	9.58	47.28	54.26	87.13

Recovery percentages represent the sum of sequentially extracted values (ΣSe) compared to total Se values obtained by whole rock digestion (total Se). ND.Not detected.

Table 9 Proportion of total Se mobilized in each step of the sequential extraction method (%)

		Water soluble	Ligand exchangeable	Base soluble	Sulfide/selenide and elemental associated	Residual
Limestone	Average (μg/g)	0	0	0.05	0.61	0.63
	Mean percent (%)	0	0	6.07	53.03	40.89
	Percent range (%)	0	0	0–12.14	40.72–63.35	22.5–59.28
Dolomite	Average (μg/g)	0.06	0.18	0	2.65	1.14
	Mean percent (%)	1.44	4.36	0	65.89	28.31
Slate	Average (μg/g)	0.47	1.33	7.68	9.11	5.29
	Mean percent (%)	1.79	3.88	28.93	43.48	21.92
	Percent range (%)	0–3.22	0–7.71	1.1–44.57	30.94–64.66	12.07–44.94
Chert	Average (μg/g)	0.24	0.37	3.39	2.32	2.45
	Mean percent (%)	3.01	3.86	34.39	26.75	31.99
	Percent range (%)	2.07–3.89	2.72–5.77	17.08–49.01	19.62–32.08	17.28–46.34
Stone coal	Average (μg/g)	2.08	3.3	22.36	9.97	9.58
	Mean percent (%)	4.39	6.97	47.29	21.08	20.26

dolomite and limestone contain a greater proportion of Se as sulfide/selenide and elemental Se (65.89% and 53.03%, average). Slates contain average 43.48% (varying from 30.94%–64.66%) of the recovered Se in sulfide/selenide and elemental fraction, cherts contain 19.62%–32.08% with average value 26.75% and stone coal contains 21.08% of Se extracted by a mixture of $KClO_3$ and HCl. Herbel et al. (2003) have reported the ability of certain anaerobic bacteria in pure culture and sediment slurries to reduce Se (0) to Se (-II) during the metabolism of organic matter and diagenetic process. Therefore, a dissimilatory reduction of anaerobic bacteria could be inferred by the data on sulfide/selenide and elemental Se. Unextractable Se associated with residual material accounted for 22.5%–59.28% of the limestone, 17.28%–46.34% of the cherts, 12.07%–44.94% of slates and 28.31% of dolomite and a lower fraction of stone coal (20.26%). The residual Se probably represents kerogen-bound organic Se complexes (Kulp and Pratt, 2004).

4 CONCLUSIONS

(1) The concentrations of Se in the whole rocks from Ziyang County, China range from 0.23 to 57.00μg/g with an average of 17.29±15.52μg/g (n=35), and that of stone coal (GQSC) is 54.26μg/g. The mean enrichment coefficient of Se is 208.28, suggesting that Ziyang County is an extremely Se-enriched area. The distribution of Se is significantly uneven, with a decreasing order of Se concentrations across the four towns studied: Haoping>Shuang'an>Wamiao>Gaoqiao; and across lithologies: slate>chert>carbonate>schist.

(2) The mean content of SiO_2 is 63.42 wt.%, followed by Al_2O_3 (7.66 wt.%), CaO (5.79 wt.%), Fe_2O_3 (2.77 wt.%), MgO (2.13 wt.%) and K_2O (1.92 wt.%). The LOI comprises 11.33% of precombustion weight including loss by complex reactions taking place during combustion up to 1 000 °C, LOI=1.66+2.2×TC, R^2=0.47, P<0.01. There is a negative correlation between LOI content and SiO_2 content, which suggests that the mobility of Se in low-SiO_2 high-LOI rocks is higher than that in high-SiO_2 rocks. The minerals in the studied rocks include quartz, illite, albite, pyrite, calcite, dolomite and chlorite, whilst barytocalcite, gypsum or hydroxy phosphate occurs in a few samples. Se contents in samples have a significant positive correlation to pyrite with r=0.56, positive correlations to chlorite (r=0.667) and illite (r=0.316), and a negative correlation to albite (r=-0.377).

(3) Se has different correlations with both TS (R^2=0.59 for chert) and TC (R^2=0.77 for slate, R^2=0.87 for carbonate rocks) due to different lithologies of rocks. Cd and As, as well as V are enriched, and may have a negative influence on the environment and human health but Pb is depleted in the Se-enriched rocks of the research area. Se is significantly correlated to V (r=0.65), As (r=0.485), Cd (r=0.459) and Pb (r=0.405) at P<0.05.

(4) Se associated with sulfide/selenide and elemental Se is the predominant fraction of total recovered Se, suggesting a reducing environment enhanced by dissimilatory reduction by anaerobic bacteria and the formation of sulfides is significant to Se concentration during the geochemical cycle. The low bio-available Se fraction (average 5.62%±3.69%) in the samples reduces the risk of Se poisoning in the target area, however, utilization of Se-rich rock as natural fertilizer should be restricted.

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