The occurrence and origin of selenium minerals in Se-rich stone coals, spoils and their adjacent soils in Yutangba, China

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ABSTRACT

Several Se-bearing minerals have been identified in Se-rich stone coal, spoils, and their adjacent organic-rich soils in Yutangba of Enshi, China, where human Se toxicity occurred in the 1960s. These minerals mainly include native Se (Se^0), krutaite ($CuSe_2$), klockmannite ($CuSe$), mandarinoite ($Fe_2(SeO_3)_3 \cdot 6H_2O$), Se-bearing chalcopyrite ($CuFe(Se, S)_2$), and pyrite ($Fe(Se,S)_2$). The assemblage of native Se, krutaite, klockmannite, and Se-bearing pyrite and chalcopyrite is primarily present in the stone coal near a fault plane, while the assemblage of native Se and krutaite is found in the Se-rich carbonaceous mudstone and organic-rich soils which are 60 m away from the stone coal exposure. The assemblage of mandarinoite and native Se is present in abandoned stone coal spoils, where natural combustion occurred. Native Se is quite extensive in the stone coal spoils and nearby soils derived from them. The co-occurrence of Cu–Se minerals and native Se indicates that these minerals could have formed under a relatively acidic and reducing environment below 220 °C, and suggests that Cu could play a significant role in fixing reduced Se ions in the acidic, organic-rich surface environment. Furthermore, the occurrence of mandarinoite suggests that iron-oxides constrain the geochemical behavior of Se in oxidizing environments. Our observations provide new insights into the mechanisms of Se fixation and accumulation during weathering of Se-rich rocks.

1. Introduction

Selenium, an essential trace element for humans and animals, has attracted ongoing attention in the fields of geological, environmental, agricultural, life, and medical sciences in recent years (Rayman, 2000; Fordyce, 2007; Zhu et al., 2008; Lenz and Lens, 2009; Rosen and Liu, 2009; Williams et al., 2009; Zhu et al., 2009; Clark and Johnson, 2010; Sun et al., 2010; Floor et al., 2011; Wen and Carignan, 2011; Winkel et al., 2012). The range between selenium deficiency (<40 μg per day) and selenium toxicity (>400 μg per day) in humans is rather narrow (WHO, 1987; Rayman, 2000; Fordyce, 2005, 2007). This narrow tolerance has resulted in well-documented health problems caused by excessive Se intake (Se poisoning) and Se deficiency ("Keshan and Kashin-Beck disease") in humans and white muscle disease in grazing animals, all prevalent in China (Yang et al., 1983;

Zheng et al., 1999; Finkelman et al., 2002; Tan et al., 2002; Lenz and Lens, 2009).

Selenium in the natural environment occurs in relatively high abundance in organic-rich rocks such as coals and shales (Gao et al., 1998; Bouska and Pesek, 1999; Yudovich and Ketris, 2006; Stilling and Amacher, 2010; Dai et al., 2012). During coal weathering, mining, and combustion, selenium is released into the environment, increasing its concentration in the air, soils, water and plants, and, in some situations, posing human health concerns (Finkelman, 1999; Zheng et al., 1999; Finkelman et al., 2002; Liu et al., 2007; Floor et al., 2011; Dai et al., 2012; Winkel et al., 2012). The modes of occurrence of Se in coal have been extensively studied. In a subbituminous coal from the Powder River Basin in Wyoming, USA, Dreher and Finkelman (1992) found that about 80% of the Se was organically associated and about 10% was associated with pyrite. The remaining 10% of the Se was divided amongst five other forms. Finkelman (1994) concluded with a high level of confidence that Se in coal is predominantly present in organic association with lesser amounts in pyrite, accessory sulfides, and selenides. The results from Riley et al. (2007) suggested that selenoprotein structures in coal's precursors give Se a binding characteristic different from that of the other trace elements in coal. To date, there is a general

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consensus that Se is mainly associated with organic matter, may substitute for S in pyrite and accessory sulfides, and may occur as selenides such as clausthalite (PbSe) and di-selenide carbon compounds (Finkelman, 1994, 1995;Swaine and Goodarzi, 1995; Hower and Robertson, 2003; Yudovich and Ketris, 2006; Riley et al., 2007; Shah et al., 2007; Vesper et al., 2008; Dai et al., 2012). However, a recent review by Yudovich and Ketris (2006) suggests the studies of Se in coal are insufficient, and further detailed studies are needed, especially regarding Se modes of occurrence (Aurelio et al., 2010; Montes-Hernandez et al., 2011).

Although Se minerals are relatively rare, more than 100 have been described (Zhu et al., 2003). Selenide minerals are predominantly found in four main types of ore deposits defined by Simon and Essene (1996) and Simon et al. (1997) as teletethermal selenide veins, unconformity-related uranium deposits, sandstone-hosted (roll-front type) uranium deposits, and epithermal Au–Ag deposits in subaerial volcanic environments. In addition, several selenide minerals have also been reported in recent years from other types of deposits. For example, at the Larma Se–Au deposit hosted in carbonaceous cherts and slates in western Qinling, China, Liu et al. (2000) distinguished several selenide minerals including tiemannite (HgSe), clausthalite (PbSe), antimonselite (Sb_2Se_3), kullerudite ($NiSe_2$), and an unnamed $Ni_3As_3S_3Se$ mineral. In Yutangba of Enshi Prefecture, Hubei Province, China, Se is present in Se-rich carbonaceous shales and carbonaceous cherts (locally know as stone coal) in the Lower Permian Maokou Formation. In fresh Se-rich stone coals, native Se and eskebornite ($CuFeSe_2$) have been reported by Song (1989) and Zhu et al. (2004). On the surface of burned coal waste piles, native Se, laphamite, and downeyite (SeO_2) were found (Finkelman and Mrose, 1977; Finkelman, 1985). However, there has been limited research on the Se minerals in stone coals that are widely used in rural China for domestic heating and cooking (Zheng et al., 1992, 1999; Finkelman et al., 1999, 2002; Zhu et al., 2008).

Yutangba village is one of the high-Se areas in Enshi, China. In the 1960s, 19 of the 23 local villagers manifested symptoms of Se toxicity and all livestock died of Se poisoning (Mao et al., 1990, 1997). Because of this problem, all villagers were forced to evacuate their homes. In Yutangba, stone coal samples containing more than 84,000 mg/kg Se, were collected by Yang et al. (1983), but few reports have described the modes of occurrence of Se in these samples. Zheng et al. (1992) and Song (1989) collected samples of Se-rich stone coals with Se concentrations up to 6470 and 8390 mg/kg, respectively, and conducted preliminary investigations into the modes of occurrence of Se. The results showed that a small amount of Se was incorporated in the pyrite due to isomorphous substitution and a part of the Se was found as eskebornite ($CuFeSe_2$), both forms accounting for 33.9% of the total Se based on electron microprobe analysis and extraction experiments. Consequently, Zheng et al. (1992) deduced that Se occurred mainly in the form of micro-particulates of elemental Se in association with organic matter. Song (1989) inferred that Se was present predominantly in the form of adsorbed Se on organic matter. Zhu et al. (2004) collected fresh Se-enriched stone coal samples with Se concentrations greater than 3%, and carried out a comprehensive investigation into the different mechanism of formations of native Se present in the stone coal. They suggested a probable relationship between Se-rich stone coal and Se poisoning in the local population. Meanwhile, several mandarinoite ($Fe_2Se_3O_9 \cdot 6(H_2O)$) crystals were also discovered in two stone coal samples from Yutangba Village (Belkin et al., 2003). However, relatively little is known about the modes of Se occurrence in Se-rich stone coals, spoils, and their adjacent soils.

Previous studies identified the Se minerals and their compositions. Nevertheless, not much information is available about the occurrence and origins of the Se minerals. In this paper, we have identified a copper-selenide series, a number of mandarinoite minerals and Se-bearing sulfides as well as native Se crystals, presenting a detailed discussion on the origin and occurrence of Se minerals in the Se-rich stone coals, spoils and soils in Yutangba, Enshi, China.

2. Materials and methods

2.1. Geological setting

The Se-rich carbonaceous shale and carbonaceous chert strata, locally known as Se-rich stone coal strata, are located in the northwestern wing of the Shuanghe syncline with a synclinal axis extending NEE (Song, 1989; Wang and Li, 1996), and geographically lies in an upland ridge 210 m north of Yutangba, approximately 81 km SE of Enshi City (Fig. 1). The strata strike NEE and dip SSE with a dipping angle of 55–70°. The Se-rich stone coal strata, with a thickness of 10–16 m, are generally a suite of black, thin-layered carbonaceous cherts interbedded with carbonaceous shale of the Lower Permian Maokou Formation (Song, 1989; Wang and Li, 1996). Several Se deposits were discovered within the Se-rich stone coal strata during geological exploration in 1987. These ore bodies were generally lenticular and were distributed along the lithological interfaces where normal faults dipping SSE were developed and extend several kilometers (Song, 1989; Wang and Li, 1996). The Se-rich stone coal in Yutangba and other sites in Enshi had been mined for fertilizer to improve crop yield and as fuel for local villagers for many years.

2.2. Sample collection and analysis

The Se-rich rock samples were mainly collected from the outcrops of Se-rich stone coal in a hillside quarry at Yutangba (No. 1 site in Fig. 1). Less-weathered carbonaceous chert, carbonaceous shale, and three carbonaceous mudstone samples were obtained from a recently dug trench. The other stone coal samples were taken from abandoned stone coal spoils (No. 2 site in Fig. 1). Five organic-rich soils with high Se content were taken from a site approximately 60 m away from the outcrop of Se-rich stone coal (No. 1 site in Fig. 1). Eleven "baked" soil samples were collected from the overburden soil of abandoned stone coal spoils and surrounding area (60 m radius), where natural combustion of stone coal occurred in 1995 (No. 2 site in Fig. 1). All soil samples were taken from the near-surface with the depth of less than 30 cm. The collected samples, generally 2 kg in weight, were sealed in polyester plastic bags packaged within cotton cloth bags. The wet samples were freeze-dried (Instrument model: FD-3-85-MP) as soon as they were taken back to the laboratory.

All dried samples, including 9 soil samples, were imbedded in epoxy (M-Bond 610 for soils) and prepared as polished sections. Some samples were also prepared as 30 μm thin sections for studying rock minerals, textures, and chemical analysis. After coating with carbon, the sections were mounted in a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometers and electron microprobe (EMPA) for observation and qualitative and quantitative compositional analysis. The SEM instruments were JEOL JSM-840A (Kevex 2003) and JEOL JSM-6060LV, respectively. A transmission electronic microscope (TEM) was also used for observing smaller Se-bearing particles. The electron microprobes used in this study were a JEOL JXA-50A with EDX (EDAX-PV 9400) and a fully-automated SHIMADZU EPMA-1600 equipped with EDX and five-wavelength dispersive spectrometers. Operating conditions were generally 20 keV and 25 keV potential using 10 nA, 1.0–3 μm spot size with counting times of 60 s on the peak and background. The standard minerals (USA SPI standards for microanalysis) include elemental Se (Se), metallic copper (Cu), sphalerite (ZnS), clausthalite (PbSe), guanajuatite (Bi_2Se_3), magnetite (Fe_3O_4), chalcopyrite ($CuFeS_2$), and marcasite (FeS_2). The data were reduced by a ZAF correction program as supplied with the electron microprobe.

3. Results

We found native Se (Se^0), krutaite ($CuSe_2$), klockmannite (CuSe), naumannite (Ag_2Se), mandarinoite ($Fe_2(SeO_3)_3 \cdot 6H_2O$), Se-bearing pyrite ($Fe(Se,S)_2$) and an unnamed Cu–Se mineral (Cu_3Se_4) in the
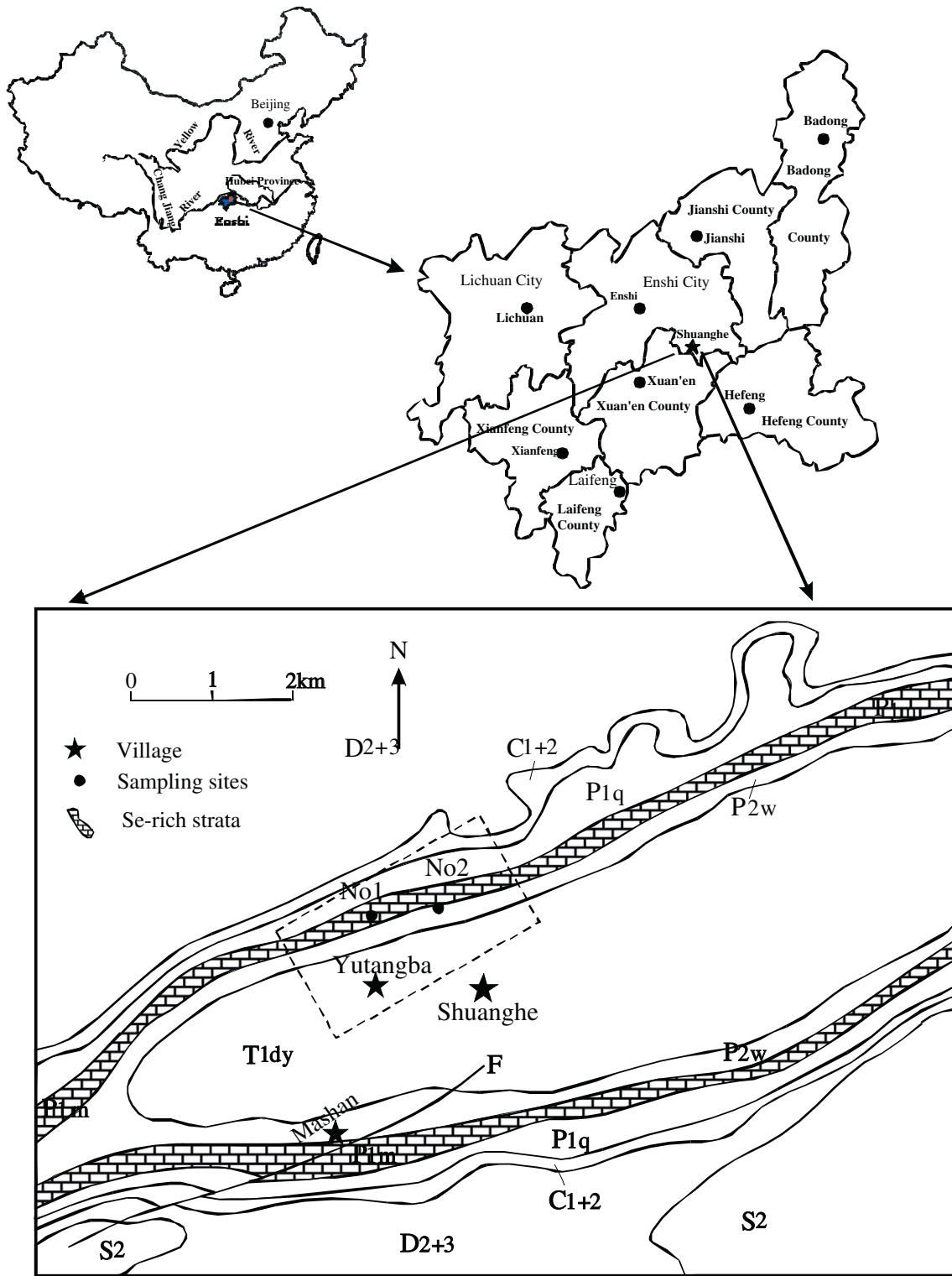
Fig. 1. Geological map of Yutangba showing sampling locations. T_1dy: Limestone; P_2w: Muddy siltstone, carbonaceous shale and chert; P_1m: Carbonaceous chert, carbonaceous shale and mudstone; P_1q: Limestone and dolostone; C_{1+2}: Dolostone, dolomitic limestone and limestone; D_{2+3}: Limestone, shale and sandstone; S_2: Fine sandstone, bioclastic limestone and shale; F: Dip–Slip Faults.

samples from Yutangba using the SEM-EDX and TEM-EDX. These minerals are mainly found in three types of environments as described in the following sections. The mineral composition was quantitatively determined by electron microprobe. Table 1 gives the results of representative electron microprobe analysis (EMPA) for several selenide minerals.

3.1. Selenium minerals in Se-rich stone coals

Se-rich stone coals generally contain native Se, krutaite, klockmannite, naumannite, Se-bearing pyrite, Se-bearing chalcopyrite and an unnamed Cu–Se mineral. These minerals are described in detail as follows.

Table 1
Electron microprobe analyses (%) of Se-bearing minerals in Se-rich stone coals in Yutangba.

Minerals	Se(%)	S(%)	Cu(%)	Fe(%)	Total	Chemical formula	Figs.
Native selenium	95.92	0.90	0.96	2.23	100.00	Se	2b(1)
Native selenium	86.04	1.00	10.59	2.37	100.00	Se	2b(2)
Krutaite or Cu_3Se_4	63.84	0.75	33.44	1.97	100.00	$(Cu_{1.2652}Fe_{0.0748})_{1.340}(S_{0.0562}Se_{1.9438})_2$ $(Cu_{2.5304}Fe_{0.1596})_{2.690}(S_{0.1124}Se_{3.8876})_4$	2b (3)
Krutaite or Cu_3Se_4	64.21	0.10	34.92	0.77	100.00	$(Cu_{1.3463}Fe_{0.0335})_{1.3798}(S_{0.0076}Se_{1.9924})_2$ $(Cu_{2.6926}Fe_{0.0670})_{2.7596}(S_{0.0152}Se_{3.9848})_4$	2b (4)
Native selenium	88.12	0.00	11.55	0.33	100.00	Se	2c(1)
Native selenium	78.96	0.00	20.63	0.41	100.00	Se	2c (2)
Native selenium	83.75	0.00	15.88	0.37	100.00	Se	2c (3)
Native selenium	78.00	0.00	21.61	0.39	100.00	Se	2c (4)
Native selenium	89.54	0.00	9.97	0.49	100.00	Se	2c(5)
Native selenium	82.44	0.00	17.05	0.51	100.00	Se	2c (6)
Krutaite	71.04	0.00	28.57	0.39	100.00	$(Cu_{0.9994}Fe_{0.0155})_{1.0149}Se_2$	2c (7)
Krutaite	66.46	0.00	31.49	2.05	100.00	$(Cu_{1.1772}Fe_{0.0872})_{1.2644}Se_2$	2c (8)
Native selenium	98.15	0.00	1.50	0.35	100.00	Se	2d (1)
Native selenium	83.21	0.00	16.45	0.34	100.00	Se (?)	2d (2)
Krutaite or Cu_3Se_4	59.26	2.31	37.97	0.45	99.99	$(Cu_{1.4527}Fe_{0.0196})_{1.4723}(S_{0.1752}Se_{1.8248})_2$ $(Cu_{2.9055}Fe_{0.0392})_{2.9447}(S_{0.3504}Se_{3.6496})_4$	2d (3)
Krutaite or Cu_3Se_4	60.76	1.79	36.93	0.53	100.01	$(Cu_{1.4082}Fe_{0.0115})_{1.4197}(S_{0.1353}Se_{1.8647})_2$ $(Cu_{2.8194}Fe_{0.0460})_{2.8654}(S_{0.2706}Se_{3.7294})_4$	2d (4)
Krutaite	65.64	2.17	31.65	0.53	99.99	$(Cu_{1.1080}Fe_{0.0106})_{1.1186}(S_{0.1506}Se_{1.8494})_2$	2d (5)
Krutaite or Cu_3Se_4	56.40	3.16	40.06	0.39	100.01	$(Cu_{1.5510}Fe_{0.0172})_{1.5682}(S_{0.2425}Se_{1.7575})_2$ $(Cu_{3.1020}Fe_{0.0344})_{3.1364}(S_{0.4850}Se_{3.5150})_4$	2d (6)
Native selenium	91.83	3.44	4.12	0.61	100.00	Se	2d (7)
Krutaite or Cu_3Se_4	58.82	2.25	38.44	0.5	100.01	$(Cu_{1.4842}Fe_{0.0220})_{1.5061}(S_{0.1722}Se_{1.8278})_2$ $(Cu_{2.9683}Fe_{0.0439})_{3.0122}(S_{0.3444}Se_{3.6556})_4$	2d (8)
Krutaite	64.44	2.42	32.49	0.65	100.00	$(Cu_{1.1468}Fe_{0.0261})_{1.1729}(S_{0.1693}Se_{1.8307})_2$	2d (9)
Krutaite	70.20	0.00	29.80	0.00	100.00	$Cu_{1.0549}Se_2$	3a
Krutaite	69.57	0.35	29.55	0.54	100.00	$(Cu_{1.0426}Fe_{0.0217})_{1.0643}(S_{0.0245}Se_{1.9755})_2$	3b
Krutaite	69.19	0.31	29.90	0.60	100.00	$(Cu_{1.0623}Fe_{0.0243})_{1.0866}(S_{0.0218}Se_{1.9782})_2$	3b
Klockmannite	55.65	2.06	41.87	0.42	100.00	$(Cu_{0.8567}Fe_{0.0098})_{0.8665}(S_{0.0836}Se_{0.9164})_1$	5a
Klockmannite	52.29	1.75	45.49	0.47	100.00	$(Cu_{0.9986}Fe_{0.0117})_{1.0103}(S_{0.0761}Se_{0.9239})_1$	5a
Klockmannite	54.75	1.91	42.85	0.49	100.00	$(Cu_{0.8955}Fe_{0.0117})_{0.9072}(S_{0.0791}Se_{0.9209})_1$	5a
Klockmannite	54.01	2.36	43.02	0.6	100.00	$(Cu_{0.8935}Fe_{0.0142})_{0.9077}(S_{0.0972}Se_{0.9028})_1$	5b(1)
Klockmannite	52.63	2.31	44.38	0.69	100.00	$(Cu_{0.9455}Fe_{0.0167})_{0.9622}(S_{0.0976}Se_{0.9024})_1$	5b(2)
Klockmannite	51.24	2.93	45.18	0.66	100.00	$(Cu_{0.9607}Fe_{0.0160})_{0.9767}(S_{0.1231}Se_{0.8769})_1$	5b(3)
Se-bearing pyrite	3.48	51.03	0.78	44.80	100.00	$(Fe_{0.9849}Cu_{0.0151})_1(Se_{0.05411}S_{1.9539})_{2.008}$	
Se-bearing pyrite	4.26	49.59	1.71	44.44	100.00	$(Fe_{0.9673}Cu_{0.0327})_1(Se_{0.0656}S_{1.8800.})_{1.9456}$	
Krutaite	71.31		28.69			$CuSe_2$ (theoretical value)	
Cu_3Se_4 (unnamed)	62.36		37.64			Similar to $(Cu, Ni, Co)_3Se_4$ (?)	
Klockmannite	55.41		44.59			CuSe (theoretical value)	

Note: Last column gives identifiers for analysis locations shown in figures (e.g. 2b(1) represents measuring point 1 in Fig. 2b).

3.1.1. Native selenium

Isolated grains of native Se occurred extensively in the Se-rich stone coals near fractures and in the combusted stone coal spoils (Zhu et al., 2004). However, the native Se found in this study was different from the previous studies in which it coexisted with pyrite, was present independently, or was associated with iron selenides (Howard, 1977; Kruglova and Ryabeva, 1983; Menshikov and Zvezdiskaya, 1990; Herring, 1991; Yakovleva et al., 2003; Zhu et al., 2004). The native Se in the stone coal is physically associated with several selenide minerals and Se-bearing minerals such as krutaite, mandarinoite, and chalcopyrite. Fig. 2a illustrates a Se-bearing chalcopyrite aggregate in which native Se encased the contiguous boundary of Se-bearing chalcopyrite grains, occurring as fine veins. Fig. 2b–d shows that native Se is associated with either krutaite or an unnamed Cu-selenide, whose mineral formula is Cu_3Se_4 based on EMPA. As observed from the characteristics of native Se grains in Fig. 2b, they seem to have formed during $CuSe_2$ decomposition or catagenisis (Supplementary Fig. A1). In the upper part, there is a gradient in Cu–Se concentration, while it is a sharp contact between Cu-selenide and native Se in lower end, where the finer native Se particles are concentrated on the rims of larger Cu-selenide grains. In addition, native Se is also present in solid solution with Cu-selenide (Fig. 2d), in which the Se content ranges from 78.0% to 89.5% while Cu is 9.97% to 21.6% (Table 1). These native Se grains, unlike those previously reported by Zhu et al. (2004), usually occur as irregular forms (Supplementary Fig. A1 to A3). In most cases, their grain size is less than 20 μm in diameter and is greater than 100 μm in length.
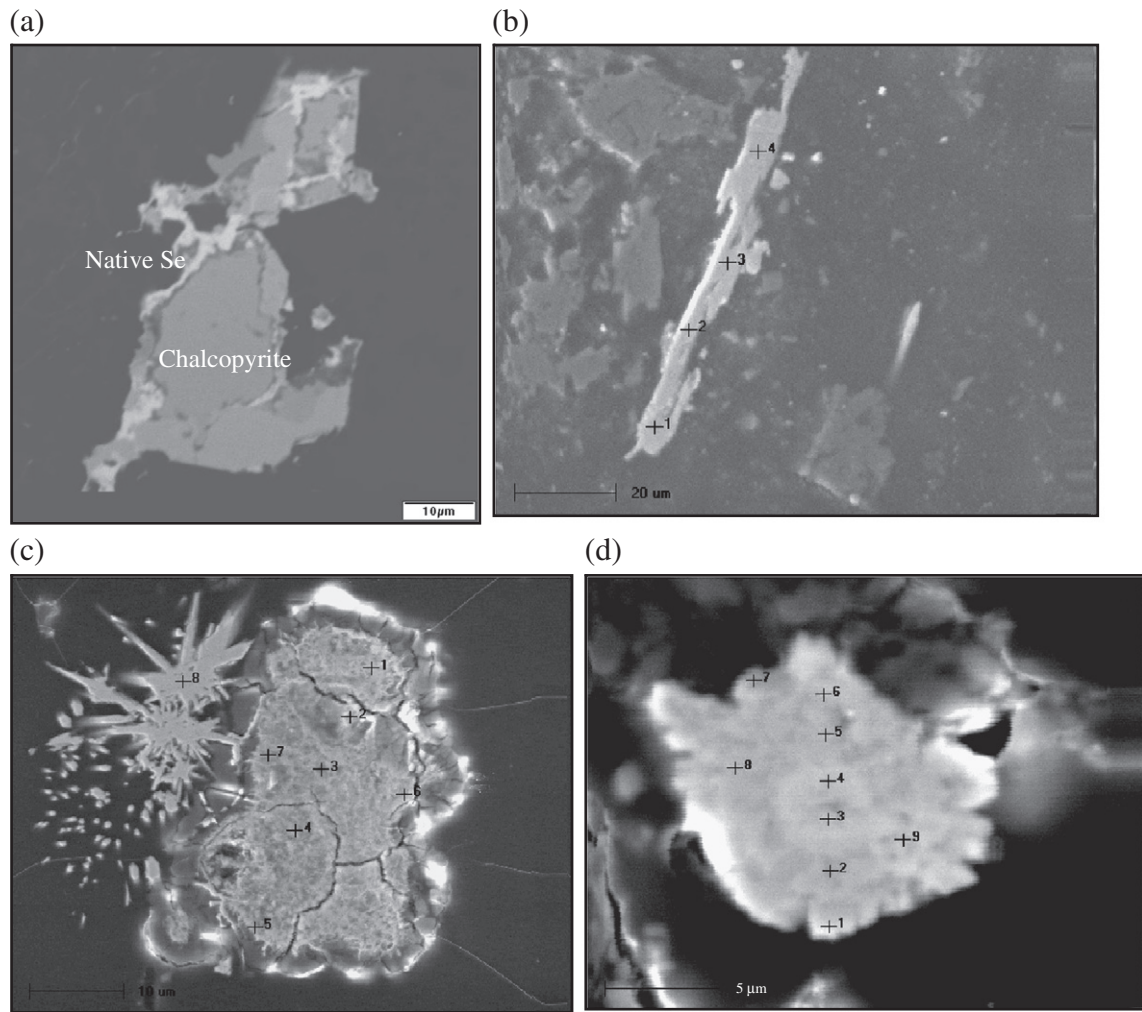
3.1.2. Krutaite

Krutaite occurs mainly in the stone coal near fracture planes and in weathered carbonaceous mudstone. There are three modes of occurrence of krutaite in our samples: (1) independent, isolated anhedral particles distributed in carbonaceous mudstone (Fig. 3a); (2) finely crystalline krutaite aggregates with radial forms (Figs. 2c, 3b) in stone coal; and (3) the Se–Cu solid solution in which krutaite is associated with native Se and an unnamed Cu_3Se_4 mineral phase (Fig. 2b and d).

The grain size of krutaite is generally in the range of 2 μm to 200 μm. In the krutaite grain in Fig. 2d, the elements are unevenly distributed in the minerals: There is no distinct boundary between mineral grains, although they show such a distribution tendency that klockmannite occurs in the interior whereas native Se is distributed at the rim. Electron microprobe analysis of representative krutaite grains shows that the average chemical composition is 69.3 ± 1.7% Se and 29.9 ± 1.1% Cu by weight, with a trace of Fe and S (Table 1). The calculated chemical formula is Cu_3Se_4 (Table 1), similar to tyrrellite $((Cu,Co,Ni)_3Se_4)$ (Stanley et al., 1990). As a mineral of this composition has not yet been found in nature or reported to date, we consider that it is possibly a transitional form of krutaite resulting from Se loss (native Se at the edges) due to decomposition (Fig. 4).

3.1.3. Klockmannite

Klockmannite is predominantly present in the fracture surface of Se-rich stone coals in which faults were developed, but they are not identified in abandoned stone coal spoils and adjacent soils. In some

Fig. 2. Occurrence of native Se, krutaite and unnamed copper-selenides in stone coal in Yutangba, China. Figures from a to d are electron microprobe secondary electron images (SEI). Numbers represent the measuring points by EMPA. (a) Native Se distributed in the conjoint boundary among fine Se-bearing chalcopyrite particles; (b) Native Se associated with krutaite or unnamed Cu-selenide mineral (Cu_3Se_4) in weathered carbonaceous mudstone; (c) Native Se with minor Cu impurity, coexisting in krutaite in stone coal; (d) Se–Cu solid solution with native Se, krutaite and unnamed Cu-selenide (Cu_3Se_4) mineral (chemical composition is listed in Table 1).

cases, they are distributed in quartz slickenfibres and brittle siliceous fine veinlets on the slickensides of the faults. The klockmannite grains are aggregates, generally anhedral, irregular, and smaller than krutaite grains in size, ranging from 5 μm to more than 100 μm (Fig. 5a, b). The results of electron microprobe analysis are shown in Table 1. The measurements reveal the presence not only of Se and Cu, but also trace Fe and S. The klockmannite contains, on average, $53.4 \pm 1.7\%$ Se and $43.8 \pm 1.4\%$ Cu by weight, and the calculated ratios of Cu to Se in the mineral formula vary in the range of 0.87–1.01, in agreement with the formula composition of klockmannite (Table 1).

3.1.4. Naumannite

Naumannite is only present in the Se-rich stone coals and is hard to find. Two naumannite grains, occurring as an aggregate, were observed under transmission electron microscope (60,000–100,000×). The smaller naumannite grain shows a short-prismatic crystal form, 50 nm–500 nm in diameter, while the whole aggregate is approximately 500 nm–900 nm in diameter. EDX analysis shows the predominance of Se and Ag, with trace Si.

3.1.5. Other Se-bearing minerals

Compared to the Cu-selenide minerals, Fe–Se minerals are hard to find. Only one tiny grain of a Fe-selenide mineral was observed in the carbonaceous mudstones by SEM-EDX. Energy spectrometric analysis

of the bar-shaped grain shows its composition to be mainly Fe and Se, but its exact chemical composition could not be determined by EMPA and thus, it cannot be determined if it is ferroselite ($FeSe_2$) or achavalite (FeSe).

Se-bearing pyrite is mostly present as rounded grains and occurs mainly in stone coal near faults. The selenium content of the pyrite varies over a wide range. In the two observed pyrite grains, the contents of Se are 3.48% and 4.26%, respectively, lower than the 6.66% Se in pyrite reported by Zheng et al. (1992, 1993) and higher than the 1.06% reported by Yao et al. (2001) for Se-bearing pyrites in stone coal. However, Se-bearing chalcopyrites were found in these samples, in coexistence with native Se (Fig. 2a).

In addition, chalcomenite ($CuSeO_3 \cdot 2H_2O$) was also found in carbonaceous shale by Yao et al. (2001) and its exact chemical composition was examined by Qian et al. (2006). Chalcomenite, with a sky blue color with vitreous luster, is generally scattered separately or occurs in radiating clusters within joint crevices and on the surfaces of carbonaceous shale, occurring as transparent elongated prisms crystals up to 200–300 μm in size (Qian et al., 2006). Qian et al. (2006) concluded that chalcomenite at Yutangba was formed in a weathering and eluviation environment. Claustalite (PbSe), although ubiquitous in coal (Finkelman, 1985), was not found in the stone coal samples, nor was chalcomenite ($CuSeO_3 \cdot 2H_2O$) described by Qian et al. (2006).

(a)

(b)
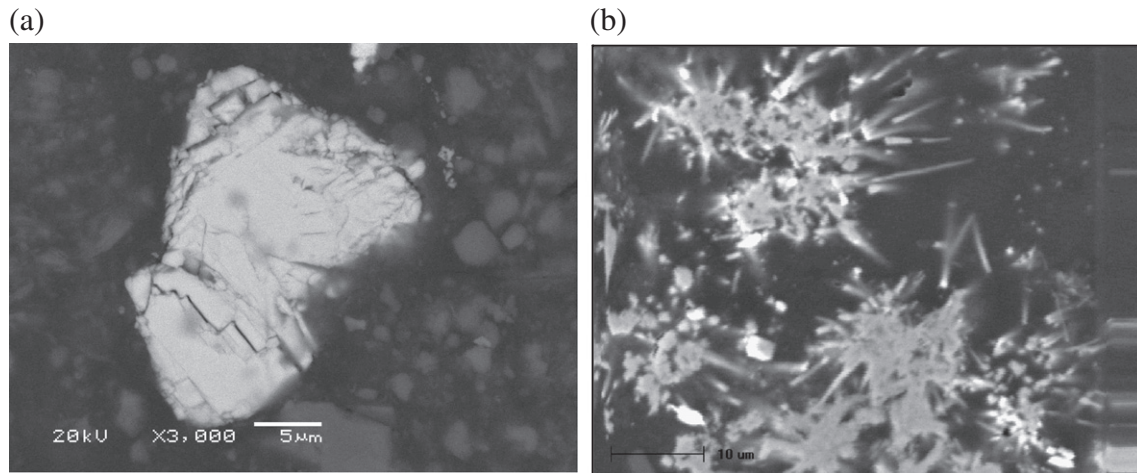
Fig. 3. Occurrence of krutaite in carbonaceous mudstone and stone coal, Yutangba village. (a) Krutaite in carbonaceous mudstone, SEM-BEC (back-scattered electron) image; (b) Acicular krutaite in Se-rich stone coal, EMPA secondary electron image.

3.2. Selenium minerals in stone coal spoils

Selenium-rich stone coal spoils mainly contain native Se and mandarinoite ($Fe_2(SeO_3)_3 \cdot 6H_2O$). Native Se is always disseminated in, or coexists with mandarinoite, occurring as a fine vein-like network (Fig. 6a, b) and granularity with Se crystal morphology (Supplementary Figs. A4 and A5). These structures indicate that the development of mandarinoite, to some extent, is probably formed by oxidation of native selenium in the presence of Fe-oxides in the spoils.

Mandarinoite is of rare occurrence in nature. The first discovery of mandarinoite was reported in 1978 (Dunn et al., 1978), and its structure was examined in detail by Hawthorne (1984). Mandarinoite in Yutangba was first reported by Belkin et al. (2003) in the exposed carbonaceous shales, occurring as small crystals from 2 to 10 μm in size. In this study, mandarinoite was mainly found within the near-surface of abandoned stone coal spoils near a discarded lime kiln. The mandarinoite occurs in three forms: crystals with certain prismatic forms (Fig. 6a), smaller granular assemblages, and veinlets filling cracks or fissures in the rocks (Fig. 6c–f). The mandarinoite crystals are rare and range from several μm to more than 100 μm in size and are easily broken during polishing. Mandarinoite granular assemblages and their vein fillings are generally larger in size, more than 10 μm in width and 100 μm in length, and are present in various forms such as round, reticular, and lamella shapes. In most cases, mandarinoite intimately coexists with native Se, which is either disseminated in mandarinoite or distributed along its boundary. Table 2 gives the results of electron microprobe analysis of mandarinoite. The element totals are less than 100%, with an average of 82.6%, revealing that the data are in good line with the formula defined by Hawthorne (1984) and the EMPA data presented by Belkin et al. (2003). The water content determined by difference is also compatible with six waters of hydration per formula unit.

3.3. Selenium minerals in Se-rich soils

There are two Se minerals occurring in Se-rich soils: native Se and krutaite. The grain size of native Se in organic-rich soils is generally much smaller than that in soils collected from the stone coal spoils. For the latter, native Se is commonly present as prismatic crystals more than 100 μm in length (Supplementary Fig. A5). In addition, native Se grains were also found within the Fe-oxides although their size is less than 5 μm (Supplementary Fig. 6). This is the first time native Se was observed to coexist with Fe-oxides in the natural environment.

Krutaite was observed in organic-rich soils that contain some detritus from Se-rich stone coal. In some cases, an eroded reticulate texture

can be observed on the surfaces of krutaite grains (Fig. 7) with more than 200 μm in length, larger than those in stone coal and carbonaceous mudstone.

4. Discussion

4.1. Origin of native Se in abandoned stone coal spoils, stone coals and adjacent soils

The formation of native Se and their forms in geological environments have been discussed in the literature (Sun, 1959; Herring, 1991; Zhu et al., 2004). Although some differences are demonstrated in the occurrence of native Se from different environments, native Se can be formed by three different pathways: microbially (biotic) mediated processes (Garbisu et al., 1996; Herbel et al., 2003; Oremland et al., 2004; Siddique et al., 2007), inorganic redox processes (abiotic) such as Se-bearing sulfide oxidation or selenate/selenite reduction (Myneni et al., 1997; Bruggeman et al., 2005; Belogub et al., 2008), and Se vapor condensed as Se crystals from natural coal combustion (Lapham et al., 1980; Kruglova and Ryabeva, 1983; Herring, 1991; Zhu et al., 2004). The native Se types occurring in the stone coal and abandoned stone coal spoils in Yutangba have been divided into three categories (Zhu et al., 2004): primary native Se occurring in carbonaceous–siliceous rocks and tiny Se crystals (100 μm–1 mm) formed in cracks in rocks close to fault planes, micro-Se crystals (<100 μm) formed on the exposed surface of Se-rich rocks, and larger Se crystals (>1 mm) derived from natural burning of
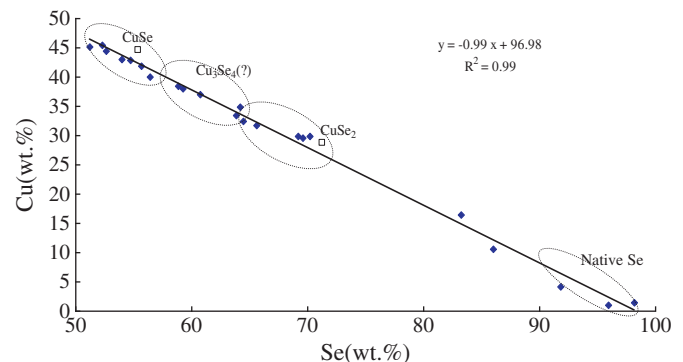
Fig. 4. Correlation trends between the Cu and Se in Cu-selenides. Open squares represent the chemical compositions of standard Cu-selenides; solid diamonds represent chemical compositions of Cu-selenides analyzed by EMPA; and dashed ovals give the range of Cu and Se content variation in the different Cu-selenides.

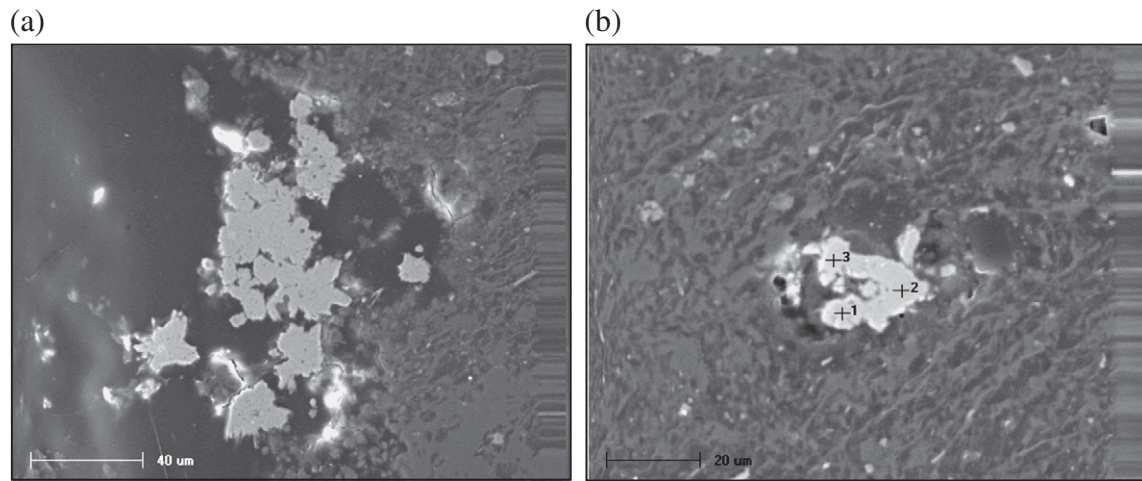(a)   (b)

Fig. 5. Klockmannite occurs as aggregates in Se-rich carbonaceous shales at Yutangba. a and b are EMPA secondary electron images. Numbers represent the measuring points by EMPA.

stone coal in the subsurface of abandoned stone coal deposits. However, the native Se found in this study is closely associated with the Se-bearing chalcopyrite (Fig. 2a), Cu-selenide minerals (Fig. 2b–d), Fe-oxide (Supplementary Fig. A6), and mandarinoite (Fig. 6a–f). For the assemblage of native Se and Se-bearing chalcopyrite or Cu-selenide minerals present in stone coals and organic-rich soils, their modes of occurrence and formation environment indicate that the native Se was either a result of oxidation of Se-bearing chalcopyrite or Cu-selenides, or reduction of Se oxyanions (SeO_3^{2-} and/or SeO_4^{2-}) in the presence of Fe^{2+} minerals such as chalcopyrite, pyrite and Fe(II, III) oxides (Myneni et al., 1997; Bruggeman et al., 2005). Microorganisms may also play an important role in reducing Se oxyanions to native Se. The aggregates of native Se shown in Fig. 2c (left) were possibly produced by biotic redox processes, exhibiting the distinct texture and chemical characteristics different from the native Se formed in an abiotic manner described previously by Zhu et al. (2004).

In addition, some irregular, veined native Se filling the fissures of Se-rich stone coal (Supplementary Fig. A3) is considered to be a precipitation from Se-enriched fluids produced during rock deformation due to tectonic activity. Thus, native Se can precipitate via different pathways. One pathway is that Se-enriched hot fluids from fault propagation cool quickly in fracture surface, causing precipitation of elemental Se resulting from Se reduction by organic matter in cracks or fissures forming native Se veins. If the space is large enough, the native Se would form Se crystals. However, as nano to micro-grained native Se were distinguished in the fresh stone coal in our previous study (Zhu et al., 2004), we cannot exclude the exsolution of elemental Se in the stone coal owing to its low melting temperature (196 °C) and injection of melted Se into minerals or fissures in the rocks. In addition, we also found some very tiny acicular Se crystals developed on the fracture surfaces of some Se-rich stone coal, especially in the small cavities or cracks. As for these newly found Se crystals, we considered their formation mechanism to be abiotic reduction, similar to that of the micro-grained Se crystals.

4.2. Origin of copper-selenides in Se-rich stone coal and adjacent soils

The occurrence of Cu-selenides at Yutangba includes krutaite and klockmannite. These minerals do not only occur as individual mineral grains, but also as selenide mineral assemblages. The assemblage of klockmannite, krutaite, and native Se was observed only in the deformed Se-rich stone coals near the fault plane where milk-white, bead-like quartz (slickenfibres) and hair-like aggregates of native Se crystals had developed. This indicated that during the development of

faults through the Se-rich stone coal a sudden shearing action occurred. The drastic descending of the upper part of the fault probably caused the fault plane temperature to suddenly increase, which led to the exsolution of silica and Se from stone coal. As a result, quenched quartz, native Se and Se mineral assemblages were formed during the following process of condensation. The Se mineral assemblages can be considered as a good geothermometer (Simon et al., 1997), indicating that its temperature of formation would not exceed 220 °C. In particular, this assemblage reveals that the solid solution between CuSe and $CuSe_2$ could be formed in the acidic, weakly reducing to mildly oxidative environment (Figs. 4 and 8). In the mineral formula of krutaite, the coefficient of Cu varies over a certain range, but generally around 1.000. However, in the mineral grains in which native Se coexists with krutaite (Fig. 2b, d), we calculated a chemical formula with the proportion of Cu to Se of 1:1.3 (Cu_3Se_4) (Table 1), similar to trustedtite (Ni_3Se_4) and tyrrellite (($Cu,Co,Ni)_3Se_4$) (Stanley et al., 1990). Although intermediate (Cu_3Se_4) has not been named and is not clear if the Cu end member exists, webmineral.com/chem/Chem-Se.shtml lists this as a form of tyrrellite (Mineral Species containing selenium, 2012). More work needs to be conducted.

The Se mineral assemblage in the weathered carbonaceous mudstones in the stone coal and adjacent organic-rich soils consists principally of krutaite and native Se. As observed from the characteristics of these minerals (Fig. 2b), some of them seem to have been decomposing instead of growing, because tiny native Se particles occurred at the rim of larger krutaite grains. In contrast to krutaite, klockmannite cannot be found in carbonaceous mudstone and organic-rich soils. Based on the stable range of native Se, Cu-selenides, and Fe-selenides in pH–Eh diagram of Cu–Fe–Se–H$_2$O system (Fig. 8), the pH value may be the key factor affecting krutaite's and klockmannite's growth. The occurrence of krutaite indicates pH values within the local environment of carbonaceous mudstone and organic-rich soils should be less than 2 (Fig. 8). However, the measured pH is generally 4.2 to 5.3 (as measured in seep water from the stone coal) with an average of 4.7, this means that krutaite ($CuSe_2$) is more stable than expected based on thermodynamics calculation (Elrashidi et al., 1987; Masscheleyn et al., 1991), or that it is metastable, a remnant of different pH conditions.

The Fe–Se minerals, usually formed under relatively strict thermodynamic conditions, are very rare in the Se-rich stone coals and adjacent soils. The measured pH values of the carbonaceous mudstones (wet samples) are in the range of 4.2–4.6, which is not favorable to the formation of Fe–Se minerals. Thermodynamic calculations in the system Cu–Fe–Se–H$_2$O (Fig. 8) show that both $CuSe_2$ and CuSe can precipitate in a supergene environment, even under oxidizing conditions with low pH value. Klockmannite can occur in the general acidic environment

(a)

(b)

(c)

(d)

(e)

(f)
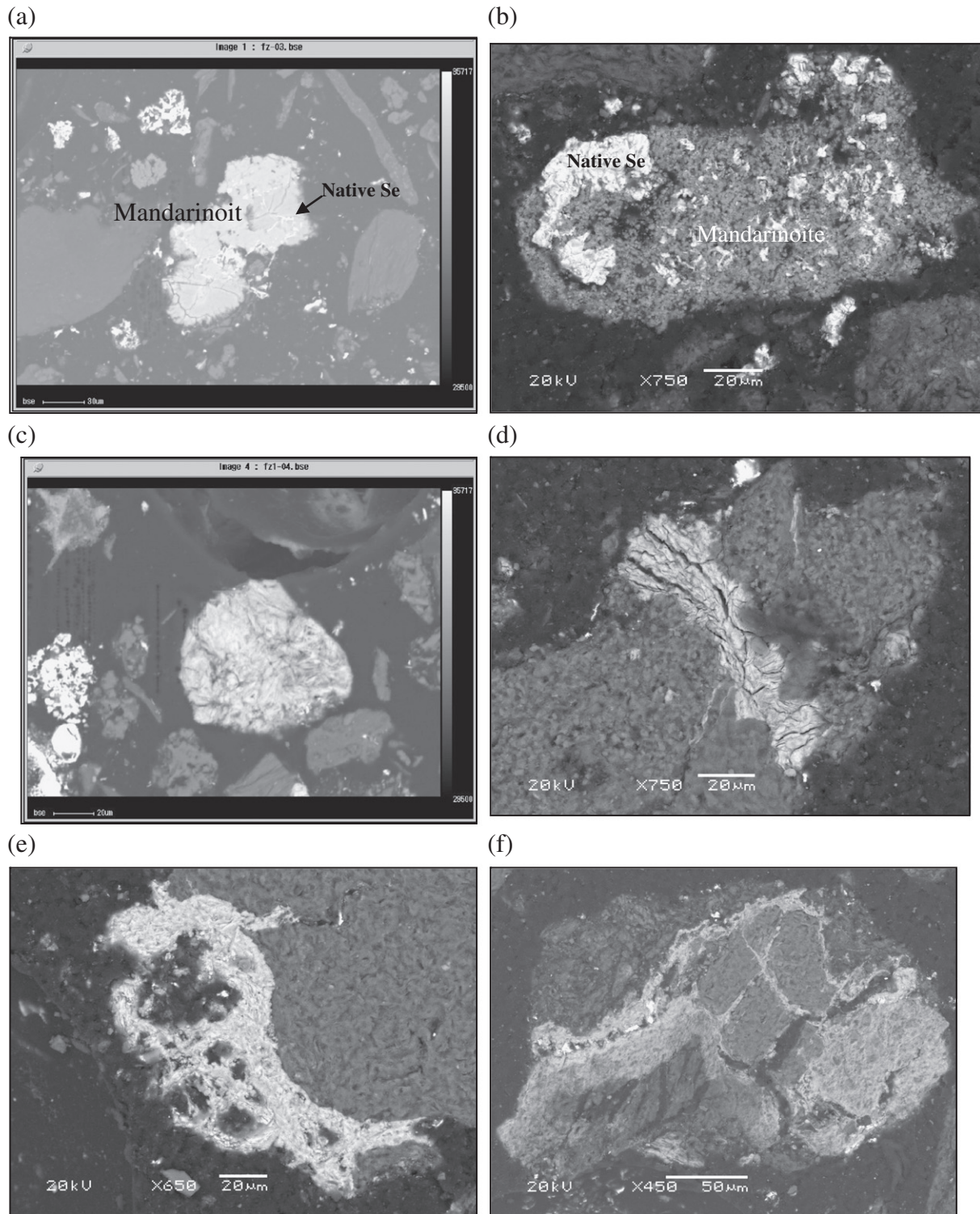
Fig. 6. Occurrence of native Se and mandarinoite in near-surface of abandoned stone coal spoils in Yutangba. a and c are EMPA-BEC images, while figures b, d, e and f are SEM-BEC images. (a) Mandarinoite coexisting with native Se (white fine veins, black arrow); (b) Native Se (white) coexisting with the large aggregates of tiny mandarinoites, which are presented as pseudomorph of Se crystal; (c) Mandarinoite crystals; (d) Large mandarinoite veins distributed within fracture of carbonaceous siliceous groundmass; (e and f) Random shape and net veins of mandarinoite distributed the boundary and within fracture of carbonaceous siliceous groundmass.

while krutaite is formed in the strongly acidic condition. However, the occurrence of native Se in large amounts indicates that the Se content is substantially greater than the Cu concentration. Therefore, Fe–Se minerals could be formed under nearly neutral and slightly reducing environment

and it is theoretically possible that this Fe–Se mineral would be ferroselite. However, the extremely rare occurrence of Fe–Se minerals and the extensive occurrence of krutaite indicate that the chemical conditions in the stone coal and adjacent soil in Yutangba are favorable to the formation

Table 2
Electron microprobe analyses of mandarinoites from abandoned stone coal spoils.

| Sample	FZ-01	FZ-03	FZ1-04	FZ-05	FZ-06	Average	C1p[1]	Formular composition[1]
SeO_2 (wt.%)	55.16	55.46	56.02	55.81	60.55	56.60	56.97	55.68
Fe_2O_3	23.89	25.41	26.27	24.11	24.56	24.86	25.33	26.86
SO_3	0.21	1.21	1.75	1.88	0.43	1.10	0.13	–
Total	79.26	82.08	84.10	81.80	85.54	82.56	82.43	82.84
H_2O by difference	20.74	17.92	15.90	18.20	14.46	17.44	17.57	17.16
Calculated number of cations in mineral based on EMPA								
Se	3.083	2.955	2.900	2.960	3.130	3.038	3.076	3.000
Fe	1.832	1.881	1.887	1.777	1.764	1.825	1.892	2.000
S	0.016	0.089	0.125	0.138	0.031	0.081	0.010	–
Total	4.931	4.926	4.910	4.875	4.926	4.944	4.968	5.000

Note: Total iron as Fe_2O_3; total sulfur as SO_3; [1]: C1p and formula from Belkin et al. (2003) and Hawthorne (1984), respectively.

of Cu–Se selenide minerals rather than Fe–Se selenide minerals. This implies that Cu plays a very important role in the precipitation, transport, and immobilization of Se in the supergene environment.

4.3. Origin of mandarinoite in abandoned stone coal spoils at Yutangba

The modes of occurrence of mandarinoite in the abandoned stone coal spoils indicate that it is a secondary mineral. Previous studies had reported that mandarinoite was a rare mineral resulting from the oxidation of more reduced Se species or Se-bearing minerals such as pyrite (Dunn et al., 1978; Belkin et al., 2003). However, mandarinoite in this study was closely associated with native Se in almost all cases, which showed that the formation of mandarinoite occurs either by simultaneous precipitation with native Se or the precipitation of aqueous ferric ions reacting with selenite species derived from the oxidation of native Se. The abandoned stone coal spoils underwent local combustion in 1995 owing to anthropogenic disturbance (Zhu et al., 2004). Such combustion can lead to large amounts of Se being released. Most of the released Se vapor condensed as crystals of native Se at the cooler near-surface of the stone coal spoils, while some of the released Se was oxidized to SeO_2, which is very unstable in the surface environment (Finkelman and Mrose, 1977) and further reacted with the water from rain or moisture to immediately form selenous acid (Herring, 1991). Fe-oxides would have been easily produced in such a strong oxidizing environment, and many were observed in our samples. For example, Fig. 6a–c shows the aggregate of the smaller mandarinoite crystals, while Fig. 6d–f possibly indicates that the mandarinoite crystallized out of solution in various forms after flowing into fissures, and then

developed cracks as it dehydrated (Fig. 6c). This geochemical process could be illustrated by the following chemical reaction between selenous acid (H_2SeO_3) and Fe-oxides:

$$Fe_2O_3 + 3H_2SeO_3 + 3H_2O \rightarrow Fe_2(SeO_3)_3 \cdot 6H_2O. \tag{1}$$
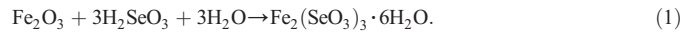
The range of pH and Eh conditions for a typical soil environment is approximately 3.5–9 and −0.2–0.8 V, respectively (Herring, 1991). The pH–Eh conditions near the surface of the stone coal spoils should be similar or slightly higher in Eh. Furthermore, the logarithm of the solubility product (K_{sp}) of mandarinoite was found to be −41.6, less than any other reported ferric selenite by more than 10 orders of magnitude (Rai et al., 1995). This indicates that strong interaction may occur between the selenite species and aqueous ferric iron in such environment, which will be strongly favored in the formation of mandarinoite owing to partial oxidation of Fe-bearing Se-rich stone coals. However, mandarinoite is extensively distributed in the stone coal spoils of Yutangba although it is rare species worldwide, suggesting that ferric selenite or selenite adsorbed onto ferric oxides and ferric hydroxides plays a significant role in fixing Se during oxidative weathering of Se-rich stone coal in the Enshi Prefecture, China.
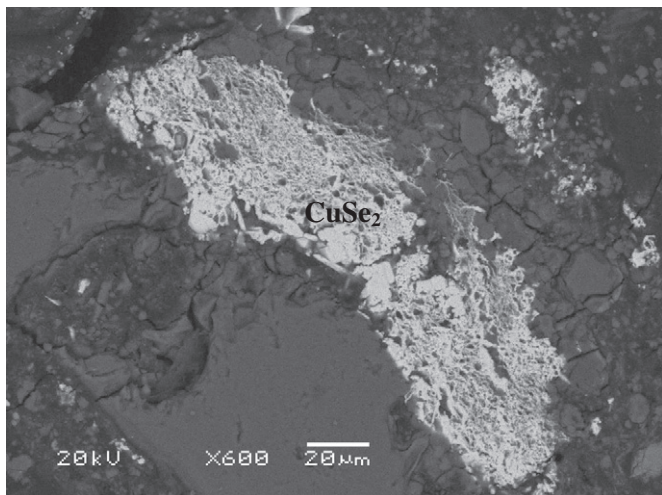

Fig. 7. Krutaite grains showing eroded reticulate weathering characteristic in organic-rich soil, EMPA-BEC image.
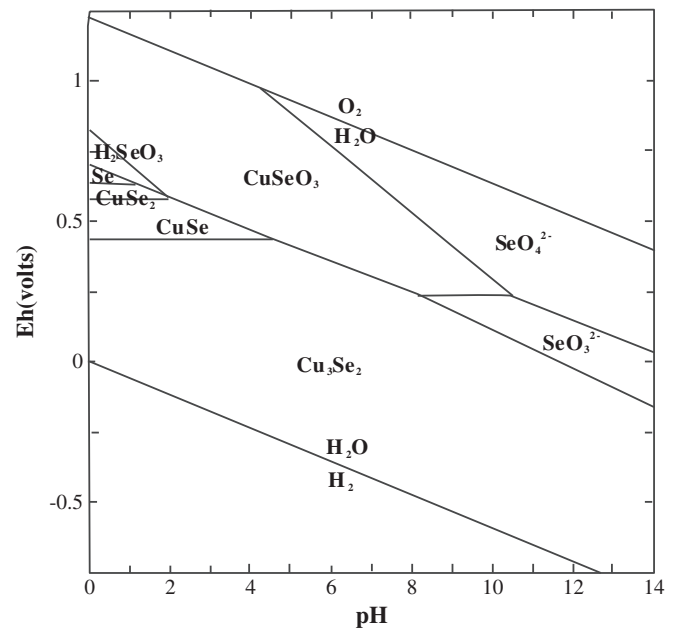

Fig. 8. Eh–pH diagram of Cu–Fe–Se–H_2O systems at 25 °C 1 atm pressure and $\Sigma Se = 10^{-6}$ M, $\Sigma Cu = 10^{-4}$ M, $\Sigma Fe = 10^{-1}$ M. (Calculated from The Geochemist's Workbench ® (Bethke, 2001)).

4.4. Geological and environmental implications

"The independent Se-ore deposits" in Yutangba have been documented in detail in previous studies (Song, 1989; Wang and Li, 1996; Yao et al., 2002; Wen and Carignan, 2011). However, particularly in the sites where Se is extremely enriched, up to 8%, the mechanism of Se enrichment in stone coal is still being debated. Liu et al. (2005) suggested that Se enrichment was closely related to the carbonaceous cherts with the characteristics of biochemical and submarine exhalative sedimentation. Wen and Carignan (2011) suggested that either secondary hydrothermal or supergene alteration was the key factor controlling Se enrichment in stone coals, which is consistent with Wang and Li's (1996) investigation. The occurrence of Se mineral assemblages in our study provides a new insight into understanding the formation mechanisms of Se-ore deposits hosted in stone coals in Yutangba. The assemblage of klockmannite, krutaite, and native Se shows that they are precipitated from secondary hydrothermal solutions produced during fault activities. The formation temperature of the Se-ore deposits should be less than 220 °C (Simon and Essene, 1996; Simon et al., 1997). The assemblage of krutaite and native Se indicates that the depositional environment pH should be lower than or similar to the measured value of 4.6. These observations show that the original Se-rich stone coals must have undergone oxidative weathering. Pyrite and other sulfides/selenides in stone coals were oxidized, releasing acids to cause lower pH. Thus, the oxidation of reduced Se (Se^{2-}) and later reduction of mobile, downward-percolating Se oxyanions in the subsurface environment will lead to the formation of Se minerals at various depths, particularly near or below the water table (Herring, 1991; Seby et al., 2001). Because the water table varies with the season, Se might undergo repeated oxidation–reduction cycles. Over time, Se was continuously leached from the top of the stone coal and gradually moved deeper to become extremely enriched in the thermodynamically favorable, reducing environment. Hence, the Se ore deposits are secondary and derived from the supergene weathering process of primarily Se-rich stone coal.

However, it is emphasized that, unlike the ubiquitous native Se, the occurrence of the Cu-selenide minerals and their assemblages are limited to local sites close to faults developed in the stone coal strata, where the average Se content is over 1500 mg/kg and Se-ore deposits were discovered. These Se minerals and assemblages may be found in other parts of the Enshi area, but it does not mean that they are of extensive occurrence in the whole Se-rich stone coal strata. The strata of Se-rich stone coal in Yutangba stand nearly vertical, and normal faults exist in the strata. Over geological time and with the variation of ancient and current water tables, it is possible locally that extremely Se-rich ore bodies were formed especially in favorable structure positions where faults developed, but this possibility is not applicable to the whole strata. Therefore, in the study of Se-ore deposits, care should be taken to deal with the difference between "original Se-rich stone coal" and "Se-ore deposits". For the former, average Se concentrations are 200 ppm with a few higher Se concentration layers (>500 ppm), and the latter is characterized by Se concentrations greater than 1000 ppm (Song, 1989; Wang and Li, 1996; Wen and Carignan, 2011). As for the accumulation of Se in stone coal in Yutangba, our current viewpoint is that the secondary enrichment of Se is still underway and that Cu plays an important role in precipitating the reduced Se ions.

A sudden prevalence of human Se poisoning in Yutangba in the early 1960s was reported by Yang et al. (1983) and the main reason for this accident appeared to be the excessive Se intake by local people derived from the release of Se during weathering and/or combustion of Se-rich stone coals. However, the Se-rich stone coal strata extend several tens of kilometers in SW Hubei, while Se poisoning occurred in specific regions and only specific groups of local residents were affected (Fordyce et al., 2000; Zhu et al., 2008). More recent studies revealed that human Se poisoning was closely related to the exploitation and utilization of stone coal by local people, since almost all high-Se plants are distributed in the cultivated sites and cropland near discarded stone coal spoils or mining sites (Zhu et al., 2008). The occurrence of krutaite and native Se assemblage in stone coal and their adjacent soils indicate that Cu can facilitate precipitation of reduced Se ions, and prohibit Se release into the surrounding environment under acidic and reducing to weakly oxidative conditions, thus constraining the solubility, mobility, and bioavailability of Se (Herring, 1991; Seby et al., 2001). However, in order to promote local economic development for improving people's living conditions and meeting fuel or fertilizer requirements in recent years, local people have privately mined stone coal as a fuel to make lime and as a fertilizer to improve cropland. Meanwhile, application of lime was used to neutralize the acidity in cropland produced by the weathering of the stone coal fertilizer. These activities will break the stable equilibrium range of these Se minerals and result in their dissolution and mobilization of the Se and further introduce more amounts of Se into the soil and ultimately in the food chain.

During chemical weathering of the stone coals, Se is easily oxidized. Its geochemical behavior is largely controlled by iron oxides in adsorbed or precipitated forms. The occurrence of mandarinoite indicates that there are strong interactions between selenite species and aqueous ferric ions, confirming the previous experimental work that adsorption on hydrous ferric oxides can remove more than 95% of selenite from solution under suitable pH conditions (Balistrieri and Chao, 1990). The assemblage of native Se and mandarinoite implies that the native Se crystals are less stable than recognized, and that the current conditions in Yutangba are strongly favorable for the formation of mandarinoite during partial oxidation of Se-rich stone coals, which can significantly restrict the bioavailability of Se during stone coal weathering and prevent Se release into the air from stone coal combustion. This work demonstrates that selenite is strongly associated with Fe-oxides in precipitated minerals and adsorbed or complexed forms in a near-surface oxidizing environment. Iron-oxides thus play a significant role in the geochemical behavior of Se in the supergene environment in Enshi, China, and likely in most other locations where Se-rich rocks occur.

5. Conclusions

Several Se minerals and their assemblages have been found in Se-rich stone coal, stone coal spoils, and their adjacent soils. These Se minerals include native Se, krutaite, klockmannite, naumannite, Se-bearing pyrite, Se-bearing chalcopyrite, and mandarinoite. The native Se has characteristics of both abiotic and biotic formation. Most abiotic native Se, found in crystalline forms, coexisted with Cu-selenide minerals and mandarinoite, while biologically formed native Se exhibits a more massive structure and contains Cu impurities. The coexistence of native Se and Fe-oxides suggests that the native Se could be formed via interaction between Se oxyanions and Fe-oxides containing Fe (II). Copper-Se minerals show two different assemblages. One is native Se, krutaite, and klockmannite, which could form via precipitation from secondary hydrothermal fluids during movement of faults within the stone coal strata; another is native Se and krutaite, which was formed during the weathering processes of stone coal. The above assemblages indicate that the formation temperature of these mineral should have been less than 220 °C and at a pH below 4.6, and imply that Cu likely plays an important role in precipitating reduced Se ions and constraining Se geoavailability under acidic, weakly reducing to mildly oxidizing conditions. The occurrence of the assemblage of native Se and mandarinoite demonstrates that either dissolved Fe ions or Fe-oxides could play a significant role in the geochemical behavior of Se in oxidative environment or coal combustion processes. It is also apparent that Cu played an important role in the precipitation, transport and immobilization of Se. The occurrence of the Se minerals indicates that the present geological environment in Yutangba is favorable to the formation of Cu-selenides rather than Fe-selenides.

Knowing the occurrence and quantity of Se minerals in Yutangba is important for investigating the geochemical behavior of Se in the surface environment and for assessing the relationship between excessive Se levels in the environment and in humans. Our study indicated that the formation of extremely high-Se ore bodies at Yutangba is

most likely the result of weathering and leaching of original stone coal strata. The secondary enrichment of Se is currently still underway. Therefore, rationally managing the mining of Se-rich stone coal, the disposal of spoils and encouraging proper precautions when using stone coals are important for preventing Se poisoning from occurring again in Enshi Prefecture, China.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2012.08.023.

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