Review Article

Selenium in coal: A review

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Abstract

The World average Se content in coals (coal Clarke of Se) for hard coals and brown coals are respectively 1.6 ± 0.1 and 1.0 ± 0.15 ppm. On an ash basis, these contents are greatly increased and are 9.9 ± 0.7 and 7.6 ± 0.6 ppm, respectively. Therefore, Se is a very coalphile element: it has strong affinity to coal matter — organic and (or) inorganic but is certainly authigenic. The "coal affinity" of Se is like that for Ge and S.

Both organic (Se_{org}) and inorganic selenium (Se_{min}) can exist in coal. In addition, Se can occur not only as a chemical-bound form, but also in sorbed (acid leachable) selenate form in the oxidized coals. The sulfidic form of Se is represented by isomorph Se in pyrite and some more rare sulfides, and the selenidic form by clausthalite PbSe. "Organic" Se may be present as both Se-organic compounds and elemental $Se°$ dissiminated through organic matter. There are some preliminary data that cleaning of high-sulfur coals, very effective for S, is less effective for Se due to enhanced contribution of the Se_{org} form (vs. S_{org}).

There are two genetic types of the Se-accumulations in coal: "reducing" and "oxidizing". In the first type, Se is enriched in high-sulfur coals, concentrating in sulfide phases. These accumulations are, in general, syngenetic, and may be epigenetic only if there are abundant hydrothermal sulfides of Fe, Cu, As, Pb. In coals of the second type, Se is enriched in the bed oxidation zones. Such coals are (or were) located in the areas with arid climate and enhanced Se content in water. Se concentrates in coal as a reduction or sorption geochemical barrier, probably, mostly as $Se°$ in oxidized organic matter and partly pyrite. This type is characterized by oxidizing zonality and close paragenesis of Se with U, Fe, Mo, V, and Pb. These Se accumulations are mostly epigenetic.

A study of Se in coal is evidently insufficient, and further detailed studies are needed, especially regarding Se forms (modes of occurrence).
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1. Introduction

Selenium (Se) was first found in Belgian coals in 1896 (Jorissen, 1896). Further, Goldschmidt and Hefter (1933) found Se in Yorkshire anthracite, and Goldschmidt and Strock (1935) showed that the most Se-enriched coals had abundant pyrite. In the 1950–60s, Se attracted attention in connection with the study of the infiltration uranium deposits (so-called "sandstone type" uranium–vanadium deposits), partly localized in the coals and often Se-bearing. Therefore, selenium hypergene geochemistry has been rather well studied. Nevertheless, the data about Se content in coals were yet scarce until the development of modern analytical techniques.

1.1. Some analytical comments

Many data on Se contents in coal are limited due to: a) low Se contents in most coals and high analytical detection limits; b) instrumental analytical interferences that may cause problems in widely used analytical tools such as inductively coupled plasma-mass spectrometry (ICP-MS); c) the appreciable loss of Se during ashing.

Swaine (1990, p. 151) noted that early methods for determining Se in coal included neutron activation analyses (RNAA — radiochemical, and INAA — instrumental) and atomic absorption spectroscopy (AAS). He also described the Australian CSRO (Commonwealth Scientific-Research Organization) wet-chemical procedure. Because wet chemical methods are too labor-intensive, instrumental methods appear to be more practical, an ICP-MS method was developed. Días-Somoano et al. (2004) noted that Se determination by ICP-MS may be interfered with by Cl (which forms ArCl in Ar-plasma), Br (BrH), Sm, Dy and Zn (ZnO), with masses that interfere with the mass of the [77]Se and [82]Se isotopes. To avoid these complications, an improved method was recommended by Días-Somoano et al. (2004) — HG (*hydride generation*)-ICP-MS. Before entering the Ar-plasma, 8.5 ml of a sample solution is added with 1.5 ml 30% HCl, for the Se transformation to Se-hydride.

2. Some peculiarities of Se geochemistry in the environment

By comparison with its nearest analogue–sulphur– Se is far less mobile due to the very easy reduction to Se° with consequent sorption and immobilisation. That is why, sulfates occur so widely in the environment, whereas selenates exist only in strongly oxidizing and alkali environments. Among the most effective geochemical barriers for Se are Fe-hydroxides (for instance, goethite) which can strongly scavenge selenite-ion SeO_3^- from solution.

A comparison of two redox reactions: $S° \Leftrightarrow S^{2-}$ (Eh = (0.47–0.58)–0.06 pH), and $HSeO_3^- \Leftrightarrow Se°$ (Eh = (0.65–0.70)–0.09 pH), shows that Se-reduction may occur in far more oxidizing environments than S-reduction. In such an environment, Fe does not yet form pyrite and exists in oxic or hydroxic forms. So, in an alkali environment and at low concentrations of Se, an association of Se-pyrite appears: "... *Se not only precipitates in native form, but substantially enrichs*

Fe-sulphides, and also selenide mineral species arise, in the first place, ferroselite FeSe$_2$" (Lisitsyn, 1980, p. 75).

In the absence of reductants, in the oxidative neutral or mild alkali waters, the most stable form of Se is the anion of the selenitic acid, HSeO$_3^-$. In fresh waters, ordinary Se concentrations are in the range 0.5–1 µg/L, but in the arid zone waters they may be enhanced two to three orders of magnitude. The ease of Se reduction results in "Se-pumping" from oxidative into anoxic hydrosulfuric waters; as was proposed for the Black Sea (Yudovich and Ketris, 1994, p. 252).

Selenium is a biophile element. Under some conditions, it can substitute for sulphur in aminoacids. Average Se content in dry plankton is 3.6 ppm, producing a very high value of the biological accumulation coefficient — 4×10^4 (Yudovich and Ketris, 1994, p. 11). The selenium Clarke value (0.5 ppm) for black shales is in the range 7.8–9.3 ppm (Yudovich and Ketris, 1994, p. 52), i.e. nearly 20 times the Se Clarke value in the soils and ordinary shales (Swaine, 1990, p. 185). Average Se content in plant ash is ∼0.5 ppm, which is either near the Se Clarke value in sedimentary rocks or slightly more (Tkalich, 1969). However, in desolate (desert) Se-biogeochemical provinces, plants are known (such as *Astragalus*), which can strongly accumulate Se, up to 1.5% Se in ash.

In the peats of Philippi deposit, eastern Macedonia, Greece, Se is contained in rather high concentration, "because of the respective mineralizations in area", and the form Se$_{org}$ dominates (Christanis et al., 1998).

In Table 1, some data about Se-contents in plants and peats are presented for The Great Vassyugan Bog (Western Siberia) — the largest peat accumulation on our planet (Bernatonis et al., 2002). The figures were obtained by means of INAA of 53 plant samples and 306 peat samples. As seen on Table 1, Se-contents in plants change without any strong relation to plant taxonomy. However, in eutrophic and mesotrophic bogs, Se is rather strongly accumulated by woody plants. The cause of the strong Se-anomaly in valley peats (305 ppm) was not explained. Only Se-content in raised peats is comparable with initial Se-contents in plants; all other Se-content in peats are substantially higher than in plants. It is evident that Se has been particularly sorbed by peat from water.

In Pearson's (1963) terms, Se is a "soft acid" and, for this reason, tends to bond with "soft and intermediate bases" (such as Mo, Fe, Co, Ni, etc.), and, "*probably, does not form stable complexes with oxygen-bearing functional groups of the humic acids*" (Kizilstein and Shokhina, 2001, p. 437). Thus, Se tends to bond preferentially with metals in coal rather than with organics.

3. An estimation of coal Clarke value of Se

A deficit of data about Se-contents in coal is further complicated by the inaccuracy of ash data because Se may be strongly depleted by the ashing. However, until recently, coal analysis for Se without ashing was little used, although INAA and XRF-analysis (using pressed pellets)[1] substantially filled a gap in our knowledge.

In 1985, coal Clarke values of Se were only approximately calculated by Yudovich et al. (1985, p. 184) as 2–4 ppm. These figures had a low confidence level because of the limited data that were used for the statistical calculation (only 12 random statistical samples and near 400 analyses).

Recently, Marina Ketris recalculated the Clarke value for Se in coal. The detailed calculation procedure was published elsewhere (Ketris and Yudovich, 2002). The procedure involves *stepped averaging*, from minor to large: one coal bed ⇒ several coal beds ⇒ coal field (deposit) ⇒ coal area (several coal fields) ⇒ coal basin or province ⇒ totality of the coal basins, i. e. Clarke value totality, consisted of several dozen random samples representing many thousands of analyses. As a rule, the median is used for the Clarke estimation because it is very stable statistical parameter, only little influenced by large sample dispersion. Modern estimations of Se Clarkes are based on approximately 120

Table 1
The mean Se-contents in plants and peats of The Great Vassyugan Bog

Material	Peat bog type						Average content *	
	Raised peat bog		Transition peat bog		Valley peat bog			
	A^d, %	Se, ppm	A^d, %	Se, ppm	A^d, %	Se, ppm	A^d, %	Se, ppm
Trees	2.03	0.035	2.02	0.330	2.51	0.166	2.19	0.177
Bushes	2.51	0.170	2.15	0.230	6.17	0.061	3.61	0.154
Herbage	7.40	0.330	6.18	0.154	12.27	0.146	8.62	0.210
Mosses	3.17	0.290	3.45	0.252	9.78	0.057	5.44	0.200
Peats	2.95	0.25	6.20	1.08	8.30	1.17 ***	5.82	0.83 **

Compiled after Bernatonis et al. (2002, p. 209–212).
 * Our calculation.
 ** Average on the peats; the data for drained bogs were excluded.
 *** Without the anomaly, 305 ppm.

[1] J. C. Hower, personal communication (September, 2004).

random samples and, respectively, nearly 19,000 analyses (Fig. 1).

Therefore, Se coal Clarke value is lower than was earlier estimated.

Most average Se contents for large territories are rather near the Clarke level. For example, Australian, New Zealand, South African, Alaskan coals, and Paleocene lignites of the Fort Union formation (Western U.S.) contain, on average, 0.2–1.2 ppm Se. U.S. coals range from 0.5–4.0 ppm (Swaine, 1990, p. 151), on average 1.8 ppm for 7563 samples (Coleman et al., 1993).

Feed coals for the electric power plants (EPPs) in the EU countries (including coals imported from Czech Republic, Poland, and the Republic of South Africa) contain on average from 1.2 ppm Se (Czech Republic coals imported to Germany) up to 2.9 ppm Se (German coals) (Sabbioni et al., 1983). Fifteen British feed coals, representing 13 deposits, contain, on average, 2.9 ppm Se, with variations in the range from 0.3 up to 5.1 ppm. Six German feed coals contain 1.5 (0.9–2.3) ppm Se

(Goetz et al., 1981). In the Permian bituminous coals from Australia, averaging 35 samples from four boreholes, Se content is 0.5 ppm (from 0 up to 1.4 ppm) (Ward et al., 1999). According to modern estimates for the World lignites, average Se content is 0.8 ppm (2100 analyses) (Bouška and Pešek, 1999).

For the former USSR coals, the usual range of Se content in ash is 0.3–40 ppm (Kler and Nenakhova, 1981), but such figures (in ash) may be strongly underestimated because of Se depletion by the ashing. On the coals (not the ashes) a background Se content of 5 (?) ppm was estimated, with "the highest" being 20,000 ppm (Kler, 1988, p. 68). This average, in turn, seems to be overestimated. According to several studies (Golitsyn and Golitsyn, 1996; Kizilstein and Shokhina, 2001; Zharov et al., 1996), in the coal basins and deposits of the former USSR, on the small statistical samples (of 4–47 analyses), average Se content is in the range from 0.1 up to 2.4 ppm. Even for the large Eastern Donbas sample of high-sulphur bituminous coals ($n=1850$, S=2.9%), average Se
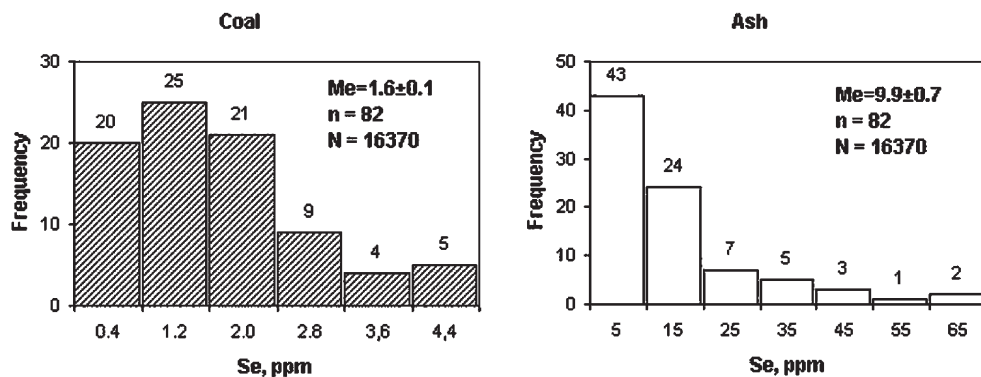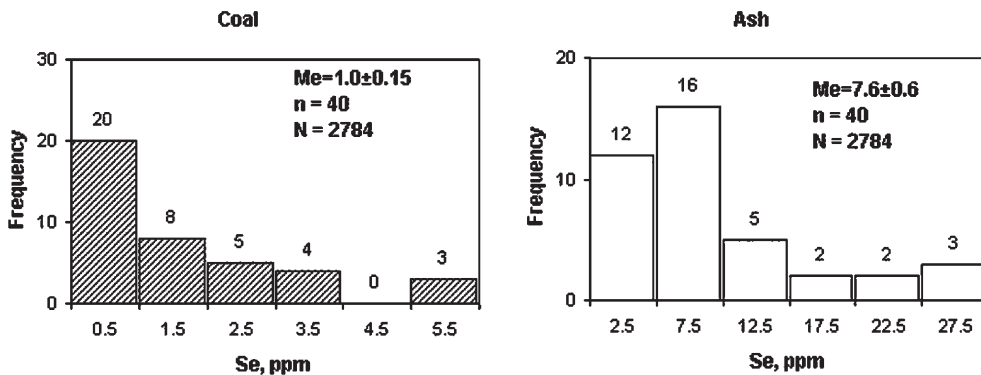

Fig. 1. Frequency distribution of Se in World coals. N — number of analysis, n — number of random samples, Me — a median content.

content is 3.3 ± 0.2 ppm, with a range from 0.02 up to 9.8 ppm. The geometric-mean for 118 Chinese coals is higher than for U.S. coals — 3.6 (0.12–56.7) ppm (Ren et al., 1999).

For the U.S. coals (nearly 8700 analyses), the geometric-average Se content is 1.7 ppm over seven coal provinces, ranging from 0.42 ppm (Alaska) up to 4.6 ppm (Gulf Coast). Arithmetic figures are 3.6 and 1.1–5.6 ppm, respectively. The highest individual Se content (northern Appalachian coals and Iowa) is 75 ppm (Coleman et al., 1993).

4. "Coal affinity"(coalphile coefficient) of Se

Given the Se Clarke value in sedimentary rocks as 0.5 ppm, Clarke value of concentration (CC — the term of Vernadski (1987)) Se in ash (i.e. coalphile coefficient or "coal affinity index")[2] is estimated to be very high: 9.5 (calculated mean Se content in coal ash)/0.5 (mean Se content in sedimentary rocks)=19. Therefore, Se is considered to be a *high-coalphile* element, although less coalphile than sulphur.[3]

Average coal cleaning data from the former-USSR are consistent with a coalphile or mild coalphile behavior for Se. Data from Shpirt et al. (1990) indicate that the high ash fraction (>1.7 g/cm^3) contributes from 25% to 85% of the total coal Se. However, because of strong variation of the mean Se contents over the different coal-bearing territories, the CC_{ash} of Se can be sharply varied.

5. Some coals enriched in Se

As was proven for the U.S. coal random samples (Coleman et al., 1993), Se-bearing coals are, as a rule, high-sulphur coals. Such coals are noted also in Russia (Kler and Nenakhova, 1981; Kizilstein and Kholodkov, 1999; Zharov et al., 1996, p. 14), Ukraine (Kolker et al., 2002), Uzbekistan or Kirgizia[4] (Kler and Nenakhova, 1981, p. 154; Belopol'skaya and Serikov, 1969),

Bulgaria (Kortenski, 1994; Kortenski et al., 1999), Greece (Foscolos et al., 1989; Gentzis et al., 1996, 1997), Turkey (Tuncali et al., 2001), USA (Bragg et al., 1998; Carter et al., 1975; Clark et al., 1980; Eble and Hower, 1997; Warwick et al., 1995), China (Yang et al., 1983; Zhang et al., 2004).

Enhanced Se contents are known in both lignites or bituminous coals. For example, in contrast to the background Se content 0.5–3 ppm for Miocene–Pliocene and Pleistocene Greece lignites, the Pleistocene Megalopolis deposit (Peloponnes Peninsula) has 11.1 ppm Se (Foscolos et al., 1989). In the Neogene Ioannina high-S and high-ash lignites, the Se background content from 26 samples is 1.6–4.8 ppm, but in five samples some enhanced contents are noted in the range from 6.3 up to 13.9 ppm Se. The anomalies are related to erosion products from evaporitic gypsum- and anhydrite-bearing strata (Gentzis et al., 1997, p. 123). In the Middle Miocene high-S and high-ash lignites from Crete (S 3.5–5.7%; A^d 13.9–46.0%), from the five analyses of the drill hole samples, Se has a range from 2.1 up to 5.5 ppm (Gentzis et al., 1996, p. 145), or 24 ppm recalculated on an ash basis (A^d 27.3%).

In the United States, there are not only lignites, but also bituminous coals enriched in Se. So, high-sulphur bituminous coals of southern Illinois have high Se content: 6 ppm on the coal and 46 ppm on the ash basis[5] (Carter et al., 1975). In fifteen working seams from eastern Kentucky, average Se content is 4.3 ppm, in the range from 2.9 up to 5.5 ppm (Eble and Hower, 1997). In the Texas Paleogene lignites, average Se content is 6 ppm on the coal basis, and 77 ppm on the ash basis (Clark et al., 1980). Based on 248 analyses extracted from the U.S. Coal Quality Database, the Gulf Coast lignites contain on average ~5.1 ppm, with anomalies up to 20.3 ppm (Mississippi lignite) (Warwick et al., 1995). Paleogene lignites of the Farwell coalfield Alaska have, on average from 9 samples, 14 ppm Se; the highest value is 43 ppm Se (Bragg et al., 1998).

6. Mode of Se occurrence in coal

Dominant forms of Se are sulfidic and organic, but some others are also known. For example, in the Uzbekistan Jurassic lignites native selenium (Se°), ferroselite (FeSe$_2$), Se$_{org}$, and Se-bearing pyrite are found (Savel'ev and Timofeev, 1977).

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[2] It is of note that "coal affinity" is not the same thing as organic affinity! Coal affinity means an element's affinity to all *authigenic* coal matter (organics and inorganics, including sulfides, carbonates, silicates etc., and excluding extraneous terrigenic or volcanogenic mineral clastics).

[3] Coal Clarke value for S, by our estimation, is near 1.5%. Given mean coal ash yield of 15% and mean S content in sedimentary rocks 0.2%, sulfur CC would be calculated as: (1.5% S: 0.15)/0.2% S=50.

[4] The location is not reported in Kler and Nenakhova (1981, p. 154). In former-USSR, there were strong limitations concerning any information about specific geographic locations of uranium-bearing coals. See Yudovich and Ketris (2001, p. 41–43) for details.

[5] Our average estimations.

6.1. Sulfide form

The sulfide form of Se may be identified by means of selective leaching, sink–float procedure (analyses of the high-density fraction, enriched in pyrite), direct analysis of hand-picked sulfide concentrates, and with microbeam analyses. The contribution of Se_{sulf} in total Se in coal can be estimated via calculation.

For example, for the three anthracitic samples from the i_3^B seam in the Eastern Donbas, a clear correlation of Se–S was shown, suggesting a pyritic form of Se (Kizilstein and Shokhina, 2001). Pyrite-rich high-ash fractions contain 5–17 ppm Se, whereas light "organic" fractions only contain 0.1–0.5 ppm. Pyrite concretions, extracted from coal, contain 85.4 ppm Se, and host rocks (argillites, mudstones and sandstones) have 2.1–2.7 ppm (that is, though, a higher Clarke value than for "normal" sedimentary rocks). As a result, the contribution of Se_{sulf} in the low-sulfur coal is ~35%, and in sulfur-rich coals — 85–89% of the total Se (Kizilstein and Shokhina, 2001).

Statistical analysis of 24 samples of the typical coals, representing the main British coal basins, has shown pyrite to be the main carrier of Se (Spears and Zheng, 1999).

Subbituminous Spanish coal with an ash yield 26.5%, burned at a large EPP, contains 16.7 ppm Se. Statistical analysis of the mineralogical and chemical data has shown that all of the Se exists in sulfide form (Querol et al., 1995). A distribution of the S_{pyr} and Se in three Spanish anthracites indicates a primary, but not exclusive, Se_{pyr} contribution (Martínez-Tarazona et al., 1997).

Sink–float analyses of high-sulfur Illinois coals (Ruch et al., 1974) also show an accumulation of Se (up to 21 ppm) in the pyritic-rich heavy fraction. By this, however, the ratio $(Se/S) \times 10^3$ is in the range 0.25–0.86 in initial coals and only 0.07–0.49 in heavy fractions. If all sulfidic Se has been concentrated in heavy fraction, such a change would indicate that selenium has more organic affinity than sulfur. However, such Se-carriers as PbSe particles have very small size and these "shielded" minerals will go into the light organic-rich fraction. Thus, the issue about more organic affinity of Se needs additional evidence.

Some direct analyses were made for pyrites and marcasites from different coals:

– *Eastern Donbas, Russia* — 85.4 ppm (Kizilstein and Shokhina, 2001);

– *Midland, England* — up to 1250 ppm (White et al., 1989);
– *Sydney basin, Canada* — from 7.2 up to 88 ppm (Zodrow and Goodarzi, 1993);
– *USA*, pyritic concentrates from the Pittsburgh and Upper Freeport seams — 45 and 32.2 ppm (Palmer and Lyons, 1996);

Microprobe investigation of more than 500 pyrite grains from 12 samples representing the Appalachian, Eastern Interior, and Powder River basins of the USA showed Se contents up to 1000 ppm (Kolker et al., 1997).

By means of quantitative PIXE analysis, the following Se contents (ppm) were determined in the pyrites from the Lower Kittanning coal seam Pennsylvania, over the areas with different overburden sedimentary facies:

$$114–123(\text{fresh-water facies}) \rightarrow 136(\text{brackish})$$
$$\rightarrow 68(\text{marine}).$$

As seen above, the highest Se contents are, apparently, not in the marine, but in the brackish facies. In addition, "marine" pyrites differ from "fresh-water" also in the lowered Se/As ratio. A relatively large pyrite aggregation, nearly 0.25-mm in size, showed strong Se-content dispersion in three points sampled: from 99 up to 219 ppm. Such micro-heterogeneity may indicate the multistage history of the pyrite grain's formation (Hickmott and Baldridge, 1995) (or just heterogeneity?).

In four sample sets of As- and Hg-bearing pyrite-mineralized coals from three mines in the Warrior basin, Alabama (altogether, 13 samples tested in tens of points by LAMP-ICP-MS), the highest *average* Se-content (290 ppm Se) was detected in pyrite infilling the cell cavities in fusain. The highest *individual* concentration was 510 ppm. From 12 other pyrite grains, in five samples, average Se contents were 70–280 ppm. At the same time, in the coals hosting the pyrites, the Se contents are below detection limit (Diehl et al., 2002, 2004).

– *In Northern China*, Pennsylvanian and Lower Permian coals, in 31 pyrite samples Se content is in the range from 100 ppm (detection limit) up to 4400 ppm (Liu et al., 2000). The highest Se value is noted in pyrite from the 3.2-m thick Lower Permian B_8 seam (Huainan deposit, the Liui mine). This pyrite is characterized as "automorphic granular type", with the grain size of 5–12 µm, rarely up to 30 µm, hosted by desmocollinite (Liu et al., 2000).

6.2. Micromineral form

A mineral, perhaps clausthalite (PbSe) and usually associated with sphalerite, was found in 13 of the studied 23 coal seams as microcrystals with the size not more than 3 μm, infilling pores in inertinite and vitrinite (Finkelman, 1980). Also noteworthy is an *absence* of pyrite in the association with PbSe. In the 1.25-m thick Upper Freeport seam, Pennsylvania, clausthalite was found in a 10-cm thick coaly parting, 40 cm above the floor. One probable explanation is that the coaly parting served as a shield in the way of Pb^{2+} and Se^{2-} ions moving upward.

Recently, clausthalite was found in Pennsylvanian bituminous coals from Eastern (Manchester seam) and Western Kentucky (unnamed seam) (Hower and Robertson, 2003). The mineral occurs in association with later carbonate infills of cell cavities in fusinite. With respect to the Western Kentucky coal, the mineralization appears to be Mississippi Valley Type. The Manchester mineralization has evident structural control and also is explained as epigenetic.

In contrast to evidently crystalline clausthalite in Pennsylvanian bituminous coals, the mineral found in the Uinta basin coal appears as semi-amorphous spheres 25–30 μm in diameter, with only the crystalline interior part containing acicular crystals, up to 4-μm long and nearly 100-nm thick (Hower and Robertson, 2003). It is quite probable that it is also an epigenetic mineral, but perhaps of hypergene origin, not hydrothermal (our interpretation).

As Hower and Robertson (2003) emphasized, in the routine polished section coal study, without quantitative photometry, clausthalite can be easily confused with pyrite due to similar reflectances (540 nm light, in air): 51.3% and 53.8%, respectively. Only very experienced researchers can detect the subtle difference in the mineral tints: blue for clausthalite and yellow or bronze for pyrite. However, the principal trouble lies in very small size of the clausthalite grains, only rarely exceeding 3 μm (Finkelman, 1985). There are several other Se-bearing minerals found by Finkelman in microprobe study of U.S. coals: some pyrite grains, As-chalcopyrite, galena, and some complicated, undefined sulphides (Finkelman, 1980, p. 204).

6.3. Organic form

Organic form of Se can be identified by means selective leaching (see Section 6.5), but more often

indirectly by the Se-enrichment of the light fraction without visible sulfides or selenides.

For example, in the C-1 borehole, which penetrated Cenozoic sediments in the rift-derived Tunkin depression (near the south end of the Lake Baikal, Russia), in the depth interval 961.5–996.0 m, lignites and coaly clays are found. From six analyses, Se contents are 0.406–0.816 ppm, on average 0.598 ppm (and 5.63 ppm on an ash basis). Strong Se–C_{org} correlation ($r = +0.79$ for 29 samples) indicates Se bonding with coal organic matter (Troshin et al., 2001).

Low-temperature ashing (LTA) of the Upper Freeport coal showed the depletion of more than 50% of Se, apparently, in Se_{org} form (Finkelman, 1980). In the six bench samples of this seam, Se content is in the range from detection limit up to 2.9 ppm, however, without connection with pyritic S content (Minkin et al., 1984), may be, indicating Se_{org} form. Semiquantitative estimation of the Se modes of occurrence in 25 coals by means of selective leaching, microprobe, and SEM-EDS analyses showed that Se_{org} contribution makes up no less than 50%; with most of the remaining Se associated with pyrite (Finkelman et al., 1999). In the low-sulfur, low-ash subbituminous Powder River Basin coal, Wyoming, arbitrary balance of Se-forms was estimated (percent from total Se content) (Dreher and Finkelman, 1992; Coleman et al., 1993):

in pyrite	5–10
in other sulfides or selenides	1–5
Se_{org}	>60
water-leacheable compounds	0–15
ion-exchangeable form	0–15

Therefore, in low-sulfur coals Se_{org} must be the dominant form: either as native Se° dispersed in coal matter (Savel'ev and Timofeev, 1977), or as some organic compounds, for example, similar to organic sulfur.

In contrast to the sulfidic Se-form, which can be observed with electron microscope, the existence of Se_{org} form may be indicated usually only by means of indirect data. For example, selective leaching of 10 coals from nine US states showed that Se was immobile. This may be due to extremely firm bonding of Se with coal organics (Palmer et al., 1989).

Although the *concentrations* of Se_{org} are usually lower than Se_{sulf}, the bulk *contribution* of the former can be more than the later (Table 2). Thus, Se_{org} contributes from 5% up to 58%, without clear relation to ash content of coals studied.

Table 2
"Selenium organic affinity" values (a contribution of Se_{org} in the gross Se-content in coal)

Coal seam	LTA, %	Se, ppm	Se_{org}, %
Herrin No 6, Illinois	20.37	4.3	28
Pittsburgh No 8, West Virginia	12.87	1.6	53
Blue Creek, Alabama	12.67	3.0	58
Rosebud, Montana	14.49	0.93	5

Compiled after Fiene et al. (1979, p. 37–40).

6.4. Silicate (and other?) forms

Aside from authigenic forms Se_{sulf} and Se_{org}, there is also clastogenic (terrigenic) Se in some coals. This is indicated from the sink–float fractions of Texas lignites (Clark et al., 1980). The primary Se contributors are there "organic" fractions (<1.80 g/cm^3), but "mineral" fractions (>2.0 g/cm^3) are also present. Such partitioning indicates that the main part of total Se is Se_{org} but mineral Se may be present in terrigenic ash too. In the samples from two boreholes (as seen on the plots of Clark et al., 1980), Se contents show no correlation with S_{pyr} and S_{org} (although, some peaks seem to be congruent).[6]

For all U.S. coals (20 regions), there are correlations between Se–S_{tot}, Se–S_{pyr} and Se–S_{org}, however, the latter correlation is the weakest (Coleman et al., 1993, p. 222).[7] The Se/S_{org} ratio is higher in the low-S_{org} coals than in the S_{org}-rich coals (number of analyses in brackets):

S_{org}	Se/S_{org}
$>2\%$ (203)	2.5
$1–2\%$ (1245)	2.6
$<1\%$ (5425)	6.0

This relationship seems to be explained either by different chemical structure of high-S coals (that hinders from Se entering coal organic matter), or by different concentrations Se and S in ancient peat accumulation (Coleman et al., 1993).

We suppose a relation between Se/S_{org} ratio and S_{pyr}/S_{org} ratio. As is known (Kizilstein, 1975), the sul-

furization of the peat organic matter occurred by diagenetic sulfate reduction with a deficiency of Fe^{2+}. In such an environment, the excess sulfide-ion (or elemental S), not bound to pyrite, may penetrate the organic matter structure and be fixed there. The process appears to be quite independent of the Se concentration in the peat waters, but, at equal status, must be characteristic for paralic high-sulfur coals with lowered Fe-content.

Perhaps, the sorbed mineral form of Se exists; for example, Se bonded with authigenic minerals such as carbonates. However, there are no suggestions about such a form by the leaching experiments (see below).

6.5. Form ratios

For different coals, the ratio of different Se-forms varies considerably. In high-S coals with abundant sulfides, a substantial part of Se exists in sulfide (and selenide) sites, in the elemental form (as micro-inclusions in pyrite) (Minkin et al., 1984); and, also, as probable admixture in the Cu, As and Pb-sulfides. In low-sufur coals Se_{org} and/or Se_{clay} may occur as the dominant forms. Recently, the ratio of Se-forms has been determined by means of stepped leaching (=acid demineralization) of coals (Finkelman et al., 1990; Palmer et al., 1998; Querol et al., 2001; Senior et al., 2000).

Selective leaching (over 18 h at room temperature, and a solid : liquid ratio 1 : 7) of crushed to 60 mesh (0.25 mm) nine USA coals and seven concentrates, by means of four solutions (1N $CH_3COONH_4 \Rightarrow$ 3N HCl $\Rightarrow$ 48% HF $\Rightarrow$ 2N HNO_3) showed that only two Se forms are dominant: pyritic (up to 80%, HNO_3-leachate), and organic (up to 95%, residual non-dissolved Se) (Palmer et al., 1998).

In three samples of Australian and USA steam coals, via complex procedure (sink–float followed by the selective leaching), Se partitioning was semiquantitatively estimated (Table 3).

As seen from Table 3, mineral-bonded Se contributes nearly 80% of the total, and Se_{org} the remaining 20%. Among the minerals, sulfides contribute from 25% to 100% in two coals, and clay matter — from 25–50% (Herrin No. 6, Illinois) and even 75–100% (Australian coal) (Querol et al., 2001).

Study of four typical USA steam coals by means of sequential leaching ($CH_3COONH_4 \Rightarrow$ HCl $\Rightarrow$ HF $\Rightarrow$ HNO_3) showed that in high-sulfur bituminous coals (three beds, S_{tot} in the range 0.82–3.60%) Se exists in three or four forms, and in low-sulfur subbituminous

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[6] As J. C. Hower noted, in such high-ash fractions as <1.80 g/cm^3, Se-bearing minerals may also occur (personal communication, September, 2004).

[7] "*This is surprising, as the dominant mode of occurrence of selenium+ appears to be in organic association when it substitutes for organic sulphur*" (Coleman et al., 1993, p. 222).

Table 3
Semiquantitave estimation of the Se distribution

Coal seam	Se, ppm	Se, % from gross content in coal		Se, % coal from minerals, in:		
		Organics	Minerals	Sulfides	Carbonates	Others [a]
Gascoine Wood, Australia; $A^d=15.9$, S=1.21%	<2	17	83	75–100	–	
Herrin No 6, Illinois, USA; $A^d=10.2$, S=3.27%	<2	21	79	25–50	–	25–50
Wyee, Australia; $A^d=23.1$, S=0.36%	<2	20	80		–	75–100

Compiled after Querol et al. (2001).
[a] Primary, aluminosilicates.

coal (S_{tot} 0.22%) in three forms (Table 4; after Senior et al., 2000).

6.6. Metamorphic change?

It is well known that many organic-bonded trace elements change their mode of occurrence due to coal metamorphism. Such changes are especially well studied for Ge (Yudovich, 1978; Yudovich and Ketris, 2002). By analogy, perhaps, Se_{org} may be partly lost in the higher rank coals versus initial Se_{org} content in lignites. So, a subtle decrease of Se emission at the ashing of the higher rank bituminous coals vs. lower rank coals was found. Such decrease seems to be connected with lower contribution of Se_{org} in the former coals (Finkelman et al., 1990).[8]

However, some part of such (liberated) Se may be redistributed and fixed in coal in inorganic forms. Such opportunity can be suggested by ashing experiments with the Argonne Premium coals (Finkelman et al., 1990). In the LTA- and by 550 °C-ashing experiments, with the expectation of partial emission of Se (up to 30% from total, in Paleocene Beulah–Zap lignite), a paradoxical addition of Se was discovered: 50% in LTA-regime and 78% in 550°-ashing. The researchers concluded that Se was resorbed by ash from hot gases. In reality, low-temperature ashing of the Wilcox lignite, previously leached by the 1 N ammonium acetate for the exchangeable cations removal (which can scavenge Se), resulted in loss of an initial 94% (Finkelman et al., 1990). It is rather obvious that Se_{org} exists in the lignite. By the analogy with other anion-producing elements (such as P or B) (Yudovich et al., 1985), we suggest that the Se_{org} form in the coal is not a true "Se-organics" compound, but

a compound of Se with the sorption coal inorganics (represented by Ca, Mg, etc.).

7. Factors controlling Se distribution

The factors controlling Se distribution include: S contents, ash yield and a position of a bench within coal bed column.

7.1. Possible influence of S content

As was shown above, for a large set of U.S. coals (20 regions), a significant positive correlation was found between Se–S_{tot}, Se–S_{pyr} and Se–S_{org} (Coleman et al., 1993, p. 222).

In the Illinois No. 6 seam, 1% S and 1 ppm Se are found. The heavy fraction (>2.88 g/cm^3) with 24% pyrite contains 5 ppm Se, and light one (<1.62 g/cm^3) — only 0.8 ppm Se. The values for the Elkhorn/Hazard seam, Kentucky, are different: pyrite contents of 1.0%, 87%, and 0.8% in the coal, heavy, and light fractions, respectively; with Se contents of 0.9, 2.0, and 0.9 ppm, respectively. This difference is due to different Se-partitioning in two coals; as selective leaching showed, the contribution of the Se_{pyr} form in the Illinois No. 6 seam is 50%, but in the Elkhorn/Hazard seam it is only 20% (Senior et al., 2000). Thus, this example shows that the relations "Se–S" may be complicated worsening their correlation in coal. Evidently, the correlation "Se–S" must be more, the more the ratio Se_{pyr}/Se_{org} is.

Table 4
Se forms in typical U.S. steam coals, percent from total Se value

Seam	Se-bearing phases			
	Pyrite	HCl-leached sulfides	Clay	Organics or "shielded minerals"
Pittsburgh	80	5	10	5
Illinois No 6	50	–	–	50
Elkhorn/Hazard	20	15	5	60
Wyodak	5	5	–	90

Compiled after Senior et al. (2000, p. 233).

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[8] «The subtle decrease in Se volatility… between the high-volatile coals… and medium-to low-volatile coals… may be due to a lower proportion of organically bound Se in the higher rank coals» (Finkelman et al., 1990, p. 758).

7.2. Ash yield

In a random sample of East Donbas coals ($n = 97$), the following regression equation was calculated:

$$Se(ppm) = -0.023 \text{ A}\% + 3.1 \text{ S}\% - 2.1.$$

The calculated average Se (1.7 ppm) approximately corresponds to the analytical determined average ($n = 240$): 2.2 ppm (Kizilstein, 2002, p. 111–112).

For the U.S. coals examined by Coleman et al. (1993), a significant but weak positive correlation was found between "Se in coal–ash yield" ($r = 0.21$). The strongest correlation ($r > 0.5$) is observed in Western U.S. coals. This relationship may be explained by the same terrigenous source for Se and clastics; the peat was accumulated, in general, in a fresh-water environment, not complicated by marine ingressions. Nevertheless, for some coals (SE Utah, etc.) the correlation is negative. Oman et al. (1988) found a positive correlation ($r = 0.62$) between Se and ash yield for 732 coal samples from the Powder River Basin. Epigenetic processes resulting in Se redistribution and depletion may greatly weaken the "Se-ash" correlation (Coleman et al., 1993).

In three U.S. coal deposits, average Se content tends to slightly increase along with ash yield increase (Fig. 2). By this, it is seen that average Se increase is not proportional to average ash content increase, indicating the presence of a non-ash-influenced Se_{sulf} form. It is also of note that Se content on ash basis decreases as the ash increases. This is typical for "coalphile" elements with abundant autigenic-form contribution in coal (Yudovich, 1978; Yudovich and Ketris, 2002).

In the Eocene Vermillion Creek lignite bed, Se content (Hatch, 1987) does not show a definitive pattern but, again, Se-content *in ash* decreased with increasing ash yield (Fig. 3).

Fig. 3. Plot of Se content vs. ash content for seven Vermillion Creek coals. Plotted after Hatch (1987).

In the Lava deposit coals (SW Greece), arranged by increasing ash (xylites ⇒ raw coals ⇒ xylitic lignites ⇒ lignites ⇒ marl interbeddings), contents of Se are varied (Georgakopoulos et al., 1995). As is seen on Fig. 4, there is no relationship for coals but Se is enriched (relative to the Clarke level for carbonate rocks) in the host marls (the right point, with conventionally assumed ash yield near 90%).

At the average Se content of 4.5 ppm in Lower Eocene Sorgun lignites (Turkey, $A^d \sim 18\%$), contents of Se distinctly increase along with an ash increase:

$$1.8 \text{ ppm } (A^d = 5.2\%) \Rightarrow 3.3 \text{ ppm } (A^d \sim 10.5\%)$$
$$\Rightarrow 6.9 \text{ ppm } (A^d \sim 30\%)$$

(Karayigit et al., 2000), due to abundant Se_{pyr}.

In Belgium raw coals, arranged by increasing ash (domestic fuel, $3.7 \pm 0.8\% \Rightarrow$ coking coal, $5.4 \pm 2.3\% \Rightarrow$ industrial coal $6.0 \pm 0.9\% \Rightarrow$ steam coal, $32.5 \pm 9.9\%$), contents of Se in coals are nearly equal at low ash coals and some enhanced in high-ash coal ($1.0 \Rightarrow 1.0 \Rightarrow 1.2 \Rightarrow 2.0$ ppm) (Block and Dams, 1975, p. 148). However, recalculated on an ash
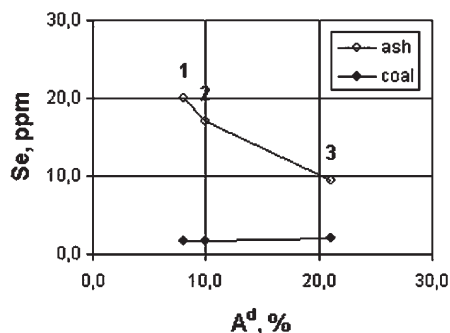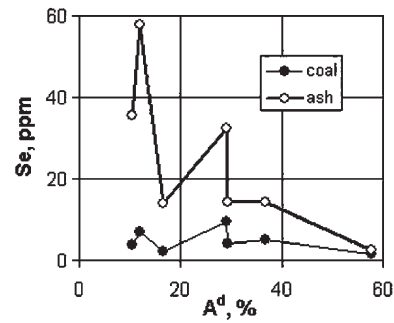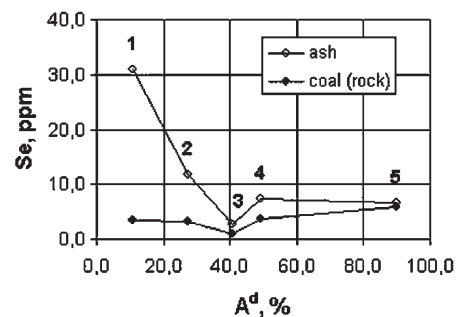

Fig. 2. Plot of Se content vs. ash content for three U.S. coals. Compiled after Hatch and Swanson (1976) (cit. after: (Lindahl and Finkelman, 1984, p. 29). 1 — Black Mesa, 2 — Powder River, 3 — San Juan.

Fig. 4. Plot of Se content in coal and ash (calculated), Greek lignites. Plotted after Georgakopoulos et al. (1995). 1 — xylites ($n = 2$), 2 — raw coals (3), 3 — xylitic lignites (3), 4 — lignites (3), 5 — marl bands (3). Ash content for marl bands is conditionally estimated.

Table 5
Distribution of Se in columns of the four anthracitic beds, the eastern Donbas (Shakhtisko–Nesvetayevsky geologic-industrial region)

Benches	Seam i_2^1			Seam i_3^H			Seam i_3^B			Seam l_6		
	A^d, %	S, %	Se, ppm	A^d, %	S, %	Se, ppm	A^d, %	S, %	Se, ppm	A^d, %	S, %	Se, ppm
Near the roof	18.0	2.5	2.3	21.4	3.0	7.1	25.5	2.5	7.5	30.2	3.5	Not analysed
Upper	11.0	2.1	1.1	18.2	1.9	1.0	16.6	2.4	5.3	15.3	2.5	4.1
Lower	7.5	1.1	0.7	14.2	2.9	6.2	12.5	1.5	4.1	13.2	1.5	2.7
Near the bottom	16.8	1.1	0.1	16.4	1.5	Not detected	48.0	1.7	10.1	52.3	1.8	0.8

Compiled after Kizilstein (2002, p. 63–64).

basis, these contents clearly decreased: $27.0 \Rightarrow 18.5 \Rightarrow 20.0 \Rightarrow 6.1$ ppm.

7.3. Position of a bench within coal bed column

In Kizilstein's (2002) textbook, the data from bench sampling are cited, dealing with sampling of four coal beds, each consisting of two benches with different petrographic composition.[9] In addition, thin (1–2 cm) marginal coal layers were sampled near the bottom and roof of the beds. As is seen from Table 5, ash, S, and Se are non-uniformly distributed across seam section; with a distinct enrichment in the near-roof layer observed (two instances). This seemingly corresponds better to the S content than to the ash yield. Thus, there is a specific "marginal enrichment" (Yudovich, 1978, 2003). In one instance, however, the near-bottom bench is enriched, corresponding better to the ash yield than to the S content content. In this instance, the enrichment seems to be not specific (Se$_{clay}$ form?).

In the 1-m thick Paleocene Beulah lignite (North Dakota), Se is distinctly enriched in the ∼0.4-m thick lower bench (4.28 ppm vs. 0.55–1.42 ppm). The bench has a significantly increased S content (1.78% S vs. 0.6–1.19% S). The other sulphophile elements (Zn, Co, Se, and Sb) are also accumulated in the lower bench (Karner et al., 1986, p. 73). However, the Se enrichment is not proportional to the increase of S.

In the Dean Seam, eastern Kentucky, with total thickness of 112.5 cm and average S content of 3.11%, two uppermost benches (17.1 and 19.9 cm) have enhanced S content: 4.94% and 2.21% versus underlying benches with S content ranging from 0.73% up to 1.04%. Correspondingly, the Se contents are here 10.3 and 4.9 ppm vs. 1.5–4.3 ppm (Mardon and Hower, 2004).

In the low-S Danville Coal Member, Indiana, with total thickness of 148 cm and average S content of

0.08%, two upper benches (15 and 28 cm) also have enhanced S content: 0.82% and 0.59% versus two underlying benches with S content of 0.53–0.63%. Se-contents also follows S-contents: 1.40 and 1.30 ppm vs. 0.47–0.70 ppm (Mastalerz et al., 2004).

These examples show that Se is enriched in the uppermost parts of coal beds, where S contents are also enhanced. Similar picture is seen also from Se distribution in a high-S Indiana coal, the 149 cm-thick Springfield Coal Member, with calculated mean S content of 5.45% (Mastalerz et al., 2004). Against a high S content (2.94–6.85%), the highest S content (6.85%) is found in fourth (from the top) 31 cm-thick bench. This bench has also the highest Se content — 5.2 ppm vs. Se content ranging from 2.4 up to 5.2 ppm.

8. Genetic topics

The multiple sources of Se provide an interesting peculiarity in the Se geochemistry, including: (a) arid territories with abundant Se in waters and red-coloured sediments; (b) volcanic exhalations and ashes; (c) hydrothems; d) aureol waters of the sulfide deposits. Some of these sources can be distinguished in the Se-bearing coals.

For example, syngenetic Se accumulation might be formed via input of the Se-bearing clastics to the peat bogs. In the Paleocene Powder River Basin subbituminous coal, average Se contents in coals decreases from South (1.7 ppm) to North (0.7 ppm), accompanied by positive correlation between the contents of Se, ash, S, and other ash-forming elements. It is thought that Se-bearing Cretaceous strata along the southern boundary of the coal basin were the source rocks. Oman et al. (1988) concluded that the river flowed from S to N and inputted the soluble and particulate material into the peat-accumulation area.

As Kizilstein and Shokhina (2001) suggest, "*the source of Se (and S, too) in the typical Donbas paralic peat-accumulation was marine water*". By means of comparison of Se content in the Eastern

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[9] The bench thickness is not showed; it is unclear also, if there is a splitting parting or the benches differ from each other only by their petrographic composition.

Donbas anthracite macerals (three samples from i_3^B seam), they concluded that Se concentration increased in the peat facies line: high-moor ⇒ transitional ⇒ valley. Such increase is explained by increasing hydrodynamics, i.e. more Se input in the solution and particulates.

Especially well studied are epigenetic infiltration uranium–vanadium deposits (Bed Oxidation Type), known in arid zones, containing sedimentary or volcanic-sedimentary formations, often red-coloured, with above-Clarke Se contents. For this reason, in oxic infiltration waters, Se and its companions (U, Mo, V, Pb) are concentrated. Coal beds (or coalified wood inclusions) serve as reduction or sorption barriers for the dissolved elements; forming in zones, Se is first precipitated in the uppermost, most oxidized parts of the coal beds, in association with Mo and V (Kondrat'eva et al., 1980, p. 154).

In an unnamed brown coal deposit with high Mo, U and Se contents (perhaps, Kirgizia or Kazakhstan; location not specified in former USSR report), also containing Se-bearing coal pyrite, trigonal tubular crystals of elemental Se are described, with a length up to 2 cm. They are found in the ash of burned coal bed, in the overlying unburned (or partly burned) coal bed, as well as in the sandy roof of the coal beds (Exogenic selenium deposits, 1962; Kruglova and Ryabeva, 1983). Evidently, they are all produced by the Se sublimation from coal organics or pyrite followed by Se reduction.

In Yutangba (Hubei Province China), the aggregations of hollow and tubular trigonal Se crystals are described. As shown on the microphoto, they reach up to 3-mm long and 0.2–0.4-mm thick and accumulated in the roof of underground-burned Permian bituminous coal bed, within a zone of 15-m long and near 20-cm thick, in spent mine (beneath 10 cm of its surface).[10] Se, most likely, was evaporated from the coal pyrite due to underground firing of coal resulted from agricultural activity (grass burning out for crops). It is of note, that Se-bearing black shales were also burning here; however, Se-crystals sublimated from black shales have different morphology. As Zhu et al. (2004) note, these results indicate an ability of Se° (that is known as very stable in wide range of the pH–Eh conditions) to migrate substantially.

Se enrichment in a bituminous coal bed (Pitkin County, Colorado) was described, over the range 15–75 cm from the dike/coal contact, evidently resulted in the Se sublimation from the most heated zone of the coal bed (Finkelman et al., 1992).

9. Conclusion

1. The World average Se content in coals (coal Clarke of Se) for the hard coals and brown coals are respectively 1.6 ± 0.1 and 1.0 ± 0.15 ppm. On an ash basis, these contents would be greatly increased and are 9.9 ± 0.7 and 7.6 ± 0.76 ppm, respectively. Therefore, Se is a very *coalphile element*: it has strong affinity to coal matter — organic and (or) inorganic but is obligatory authigenic (see monograph by Yudovich and Ketris (2002) for details). The "coal affinity" of Se is like that for Ge, As, and S.

2. Both organic (Se_{org}) and inorganic selenium (Se_{min}) may exist in coal. Besides, Se can occur not only as a chemical-bound form, but also in sorbed (acid leachable) selenate form in the oxydized coals. Sulfidic form of Se is presented by isomorph Se in pyrite and some rare sulfides. The selenidic form is represented by clausthalite (PbSe). "Organic" Se may be represented by both Se-organic compound (which are only little studied) and elemental Se°, dissiminated through organic matter. The latter, ambivalent mode of Se occurrence has once more to distinguished among *virtual* (genetic) and *modal* (real) fractions of coal inorganic matter (see monograph by Yudovich and Ketris (2002) for details).

There are some preliminary data suggesting that high-sulfur coal cleaning (very effective for S) is less effective for Se due to enhanced contribution of the Se_{org} form (vs. S_{org}).

3. There are two genetic types of the Se-accumulations in coal: "reducing" and "oxidizing".

In coals of the first type, Se is enriched in high-sulfur coals, concentrating in sulfide phases. These accumulations are in general syngenetic; they may be epigenetic only if abundant hydrothermal sulfides of Fe, Cu, As, etc. are present.

In coals of the second type, Se enriched in the *bed oxidation zones*. Such coals are (or were) located in the areas with arid climate and enhanced Se content in water. Se is concentrated on coal as a reduction or sorption geochemical barrier; probably, mostly as Se° in oxydized organic matter and partly pyrite. This type characterized by *oxidizing zonality* and a close paragenesis of Se with U, Fe, Mo, V, and Pb. These Se accumulation are mostly epigenetic.

4. A study of Se in coal is now evidently insufficient, and further detailed studies are needed, especially regarding to Se forms (modes of occurrence).

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[10] Unfortunately, no data about coal are reported.

Acknowledgements

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