Review article

Chlorine in coal: A review

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Abstract

This review embraces approximately 100 publications on chlorine (Cl) in coal. Topics reviewed in this paper include: (a) historical introduction; (b) some peculiarities of Cl environmental geochemistry; (c) estimation of the Cl coal Clarke value; (d) occurrence of high-Cl coals; (e) mode of Cl occurrence in coal; (f) factors influencing the distribution of Cl in coal; and (g) origins of Cl in coal.

1. The world average Cl contents in coals (coal Clarke of Cl) for hard and brown coals are, respectively, 340 ± 40 and 120 ± 20 ppm. The average Cl content on an ash basis is 1435 ppm which is much more than the Clarke value for sedimentary rocks (150 ppm); hence, chlorine is, on average, a highly coalphile element. Just this alone shows that the authigenic sorption fraction, Cl_{sorb}, must be dominant in coals.

Aside from "normal" coals with average Cl contents, there are "saline" coals, strongly enriched in Cl, up to 1 wt.% and more. Although there are different genetic concepts, it seems that such coals were mainly formed in epigenesis — when coal beds were influenced by basinal chloride brines (often by hot ore-forming brines, containing also some ore elements such as As, Pb, Zn, etc.).

The modes of Cl occurrence in coal are surprisingly varied. Among them are found inorganic salt-like Na and other chlorides, as well as the Cl-bearing silicates, carbonates, sulfides, as well as dissolved chlorides in pore moisture. Organic-associated Cl seems to predominate in coal. It may consist of two different types. One (minor) site ("true" Cl_{org}) may be as covalent-bonded Cl in coal organic macromolecules. The major organic Cl is represented by "semi-organic" Cl, as anion Cl^-, sorbed on the coal organic surface in pores and being surrounded by pore moisture. These are HCl-complexes bonded with bases, such as quaternary nitrogen.

If Cl in coal is mainly of syngenetic origin, a "true" Cl_{org} form may be of value, and Cl is concentrated in low-ash gelified coal macerals. If coals were submerged by epigenetic impact from basinal brines, Cl_{min} (NaCl and other salts) and "semi-organic" Cl_{sorb} forms have to be dominant. In such instances, Cl may be enriched in fusain and in high-ash coals.

There is a complicated relationship between Cl-contents in coal and coal rank. On the one hand, the coals subjected to epigenetic brine influence are, as a rule, bituminous coals that have been submerged to considerable depths where basinal brines exist. On the other hand, if coals have a rank higher than low volatile bituminous A (C^{daf} more than 86%), the Cl content decreases due to decreasing sorption capacity of the high carbonized coal organic matter.
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Contents

1. Introduction

Chlorine in coal first provoked an interest at the start of 20th century in England. In 1930's–1940's, with this country having many Cl-bearing coals, intense studies were performed concerning Cl distribution and mode of Cl occurrences in coal. A large part of these studies were outlined in the review by Kear and Menzies (1956) — the most complete by the end of the 1950's. Also, our previous outline (Yudovich et al., 1985) was mostly based on that review. Further studies added little new data about Cl contents in

coals, but highlighted some problems concerning Cl mode of occurrence in coal. The revolutionary studies of Huggins and Huffman (1991, 1995) must be especially noted.

2. Chlorine in environment

Chlorine has a high "marine-affinity"; its average content in sea water contents (1919 mg/L) is three orders-of-magnitude higher than that in fresh waters (5.5 mg/L) (Ivanov, 1994, p. 292). However, Cl differs sharply from F because its highest mobility is in the

hypergene zone: it is poorly trapped on geochemical barriers because most Cl-salts are highly soluble, and widespread clay and humic colloids being negatively charged do not capture the Cl$^-$ ion (the only mode of Cl occurrence in natural waters) (Perel'man, 1972, p. 115).[1] The only significant barrier for Cl is an evaporative one, but it occurs only in arid regions where peatbogs are not characteristic. Here, in lakes, brines may be generated with Cl-contents even higher than in seawater — from 50 to 100 g/L. Even higher Cl concentrations are known in chloride basinal brines of artesian basins — up to 200 g/L.

The main sources of Cl in natural waters are rock leaching and terrestrial volcanism. Alkali igneous rocks have an order-of-magnitude more Cl than basic and acid rocks. Among sedimentary rocks, higher Cl concentrations are found in salt-bearing strata (evaporites). Some researchers, for example, Oelschlegel (1964) hypothesized that such rocks might be a Cl source for coal-forming peatbogs.

In volcanic areas, Cl may be introduced into peatbogs from gaseous exhalations (where it is in HCl- and NH_4Cl-forms) and by being desorbed from volcanic ash particles.[2]

For example, in the 290-cm-thick low-land Keephills Fen peat (Alberta, Canada), Cl is enriched in the layer containing volcanic ash from the Crater Lake volcano eruption (Oregon, USA). This layer occurs within the interval of 240–264 cm from the peatbog surface, and the Cl content is 137 ppm versus 64 and 119 ppm in the overburden (224–40 cm) and underlying (264–270 cm) peat layers, respectively (Chagué-Goff et al., 1996).

Chlorine is an essential component of plants and animals. In his reference book, Ivanov (1994, p. 290) noted: *"Chlorine (NaCl) is a vitally important element, it controls water–salt exchange, osmotic pressure, blood and digestive juices composition of the organisms. The Cl levels in organisms are near to (those) in seawater… Estimations of Cl average contents in plants are lower (~0.33%) than in animals (~3.3%), and are higher in marine organisms (plants 0.47%, animals up to 9%) than in terrestrial (respectively, 0.2 and 0.28%)."*

Unfortunately, we do not have any Cl-values for humic organic matter, except for Selivanov's (1946) figures[3] dealing with some European Russia peatbogs. It is known also that coastal higher plants are enriched in Cl vs. those from intracontinental interiors (Perel'man, 1972). These data may be of some value for estimating the primary plant-derived Cl (Cl$_{bio}$) contribution in coal.

3. An estimation of coal Clarke value of Cl

In 1985, coal Clarke values (World averages) of Cl were calculated based on nearly 1500 analyses, as follows (Yudovich et al., 1985, p. 133):

- 300±100 and 1100±600 ppm for lignites and bituminous coals, respectively, and
- 3000–5000 ppm for their ashes.

In 2004, the Clarke value for Cl in coal was recalculated by the second author. The detailed calculation procedure was published elsewhere (Ketris and Yudovich, 2002). Modern estimations of Cl Clarke values are based on approximately 120 random samples, derived from nearly 10,700 analyses (Fig. 1):

- 120±20 and 340±40 ppm for the brown and hard coals,
- 770±120 and 2100±300 ppm for their ashes.

These new calculations show that by taking into account many more analyses, a sharp decrease is found relative to the former figures. In comparison with the 1985 figures, the Cl Clarkes for hard coals have been lowered threefold (1100 ⇒ 340 ppm) and for lignites (brown coals) — nearly threefold (300 ⇒ 120 ppm). Average Cl content in coal ash is 1435 ppm. Despite the lowered estimates, the *same trend was upheld: hard coals contain much more Cl than brown coals.*

Some regional averages are rather near to the Cl Clarke level. So, for the former-USSR, a "background" Cl content was estimated to be 100 (?) ppm, an "enhanced" content ranged from 3000 to 5000 ppm, and

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[1] Although, in lateritic weathering crusts, a sorption barrier for Cl may be generated because newly formed positively charged Al and Fe (III)-hydroxide colloids are present (Perel'man, 1972, p. 117).

[2] For example, as a result of leaching of the volcanic ash, basaltic Tolbachik volcano (Kamchatka Peninsula Russia), at a solid∶liquid ratio of 1∶1, the Cl concentration in water may be as much as 0.8 mg/L, which is appreciably more than the hydrochemical background (Yudovich and Ketris, 1988, p. 180). Perhaps, if acid (rhyolitic) ash was to be leached, the Cl concentration in water would be 5–7 times more.

[3] L.S. Selivanov was the young colleague of the great Russian scientist V.I. Vernadski. In the World War II he was a Soviet soldier and was taken prisoner. He was the insurrectionist in the Mauthausen concentration camp, and, on February 10, 1945, was killed by the Germans.
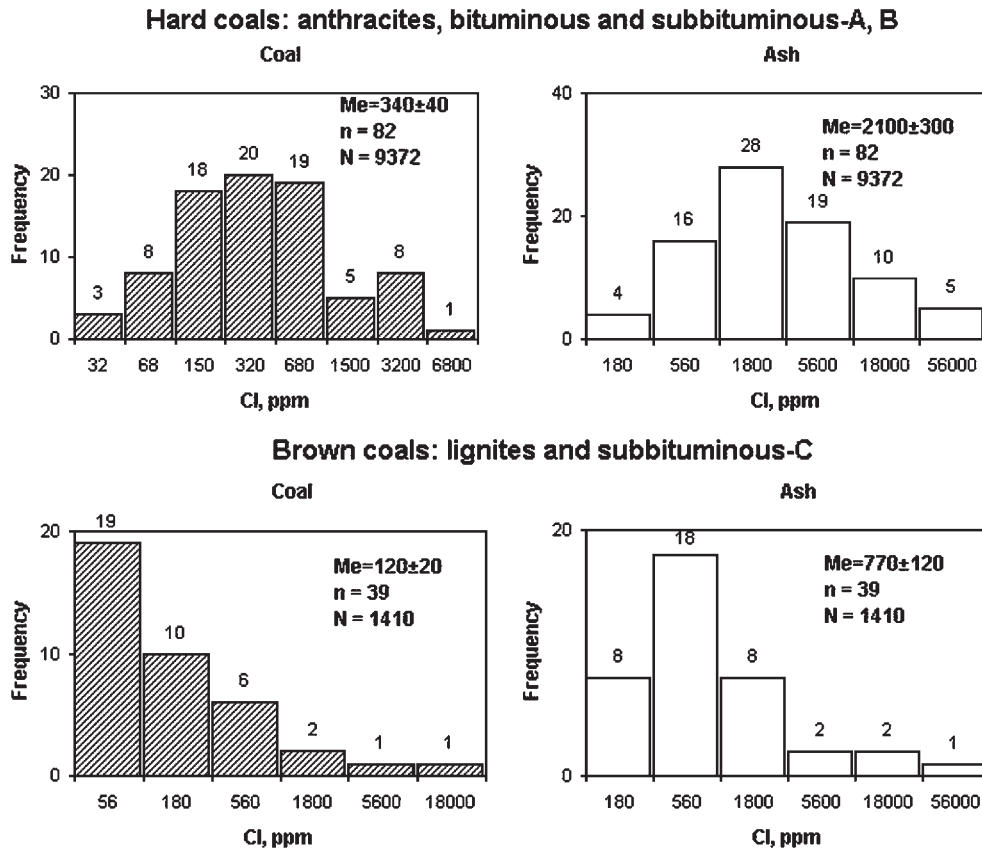
Fig. 1. Frequency distribution of Cl in world coals. N — number of analysis, n — number of random samples, Me — the median content.

the highest was found to be 12,000 ppm (Kler, 1988, p. 68). The geometric mean for 45 Chinese coals is 288 ppm Cl (from 59 to 1865 ppm) (Ren et al., 1999). According to modern estimations for world brown coals (Bouška and Pešek, 1999), the arithmetic average (1384 analyses) is only 99 ppm Cl.

However, the Cl lateral distribution has a large variation. For this reason, coals from even large regions may have mean Cl contents strongly differing from the Clarke value. For example, Permian bituminous coals of the Vorkuta coalfield (Pechora basin, Russia) contain, in general, 200–400 pm Cl (our data); various Australian coals average 150 ppm (Swaine, 1990, p. 185); and Tertiary lignites and subbituminous coals of the Western USA and Alaska have 900 ppm (Abernethy et al., 1965). The average Cl content in South African bituminous coals is no more than 300 ppm (Wyndham, 1951). Scarce data on Kuzbas coals (Russia) show, on average, nearly 400 ppm, but in Donbas coals (Ukraine and Russia) values are nearly three times higher, 1100 ppm (Gulyaeva and Itkina, 1962). Bulgarian coals are, in general, depleted in Cl; for example, feed coals of seven electric power

plants show on average from 50 to 360 ppm Cl (Vassilev et al., 1997).

4. "Coal affinity" index (coalphile index) of Cl

Direct determination of Cl in coal ash is impossible because of loss of Cl in ashing; therefore, only recalculation from a coal basis to an ash basis can be performed. According to 1985 estimations, the Clarke value of concentration (the term of V.I. Vernadski) of Cl in coal ash (i.e. coalphile index or *coal affinity index*) is in the range from 10 to 20. The new figure calculated from the improved Cl coal Clarke value is 1435 ppm (average Cl content in coal ash) relative to 150 ppm (Cl Clarke value in sedimentary rocks)=9.6. So, Cl is a *highly coalphile element* (see Yudovich and Ketris (2002), for details)[4].

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[4] However, it is of note that weighed mean of Cl content in sedimentary rocks (calculated *using the evaporites contribution*) is much more. By the different estimations in Russian literature, these weighed means make up from 2700 up to 6500 ppm Cl. If we would use these figures, the Cl coal affinity index would be sharply diminished (<1), and Cl should be attested as *non-coalphile* element!

5. Some coals enriched in Cl

Coals with above-Clarke Cl contents are known in Russia, Ukraine, England, USA, and some other countries, as can be seen from Ivanova and Krivega's (1985) monograph. For example, run-of-mine coals of England are always enriched in Cl, on average more than 1000 ppm; with "anomalous" Cl contents considered to be >3000 ppm (Kear and Menzies, 1956). The average Cl content in a representative sample of UK coals is 4400 ± 3600 ppm and the range is from 100 to 11,000 ppm (Spears and Zheng, 1999).

Strong enrichments in Cl are often characteristic of so called "saline" (salty) coals. Such coals are known on the Pacific coast of Russia (Egorov and Penzin, 1987, p. 131–132); in Northern and Western Donbas, Ukraine (Kler and Nenakhova, 1981; Ivanova and Krivega, 1985); in Eastern England; Eastern Germany; Poland; USA; and Australia (Cressey and Cressey, 1988; Daybell and Pringle, 1958; Given and Yarzab, 1978; Gluskoter and Rees, 1964; Gluskoter and Ruch, 1971; Kear and Menzies, 1956; Mielecki, 1948; Reynolds, 1948; Wandless, 1957; Ziegenhardt and Kramer, 1967). In such coals, the Cl content may be above the coal Clarke value by an order-of-magnitude, and up to as much as 1.2% (12,000 ppm). For example, in the Pennsylvanian Zwickau–Oelsnitz coalfield in Eastern Germany, from 4300 to 7700 ppm Cl were found, and 5000 ppm Cl in mine waters (Leutwein and Rösler, 1956). In North Staffordshire coals, England, the average Cl content is near 7400 ppm (Reynolds, 1948); and in the brines penetrating the coal-bearing measures from Permian overburden, Cl contents reach as high as 104 g/L (or 104,000 ppm) (Edmunds, 1975). The mean Cl content in 372 US coals is 500 ppm, but Illinois Basin (72 samples) coals are Cl-enriched: on average, 1030 ppm (Given and Yarzab, 1978).

Beside the "saline" coals of Donbas, England, Germany and the Illinois Basin, enhanced Cl contents occur in some Japanese coals due clearly to near-synchronous volcanic influence. So, Taihejo coals contain 1090 ppm Cl (or 4700 ppm calculated on ash basis) (Vassilev et al., 2000, p. 905).

6. Mode of chlorine occurrence in coal

The problem of the Cl mode of occurrence has been of interest for many years, but the problem is very complicated (Hodges et al., 1983) and the results are contradictory, partly due to poor data agreement obtained by different methods. In the middle 1940's, Crossley (1946), based on all the methods of that time, provided the most detailed concept. Based on his own experiments and taking into account other data, he concluded that Cl may occur in coal in at least four or five forms (sites):

1. Mineral chlorine, mostly as NaCl. It may be extracted via dialysis and comprises usually as much as 70–80% of the total chlorine.
   Much later, using electron microscopy, micro-inclusions of crystalline salts NaCl and KCl were found in coals (Finkelman, 1980; Cressey and Cressey, 1988; Lee et al., 1978). For example, Finkelman (1980, p. 144) observed a few small crystals of halite in the low-temperature ash light fraction (Sp. G. <2.2), prepared from Upper Freeport coal with 2200 ppm Cl. He reported also grains of sylvite (KCl) and bloedite $\{Na_2Mg(SO_4)_2 4H_2O\}$ from the low-temperature ash of the Waynesburg coal, and a grain of sylvite in the Ferron coal.[5]

2. Also mineral chlorine, existing in oxychloride form. It may be leached by weak acids and is not present in all coals. To date, this form postulated by Crossley (1946) has not been confirmed.

3. Sorbed chlorine — as Cl^- form. It is extracted from dialyzed coals by concentrated gelatin solution (or other colloids) and makes up 5–10% of the total chlorine. As it is assumed today, sorbed Cl exists on the surface of small pore walls (Caswell et al., 1984a,b; Demir et al., 1990); therefore, the extraction of such a Cl-form depends on pores opening, i.e. on the rate of coal grinding.

4. Organic chlorine, comprising 0.5% to 25% of the total Cl. Two forms of Cl_{org} were suggested: (a) hydrolyzing by boiling water, acid or alkali, and (b) non-hydrolyzing.

We now know that Crossley (1946) was not always right. In particular, it became clear that the ratio Cl_{min}/Cl_{org} varies greatly depending on geologic factors. So, Cl_{min} predominance must not be characteristic of all coals, but only for the high-Cl, saline ones. It was shown also that if NaCl is epigenetic, it is strongly attracted by fusain (Pearce and Hill, 1986).

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[5] F.E. Huggins and D.A. Spears (personal communications, in July 2005) think that chlorides and sulfates in coals and low-temperature ashes may by either artifacts (by SEM vacuum procedure and ashing) or resulted from the lab coal weathering.

6.1. Water-soluble (saline) chlorine form

As early as 1909, water-soluble chlorine was found in 32 samples from 49 USA coals examined (Parr and Wheeler, 1909). At a later time, almost all researchers (Crossley, 1946; Kear and Menzies, 1956; Edgcombe, 1956; Daybell and Pringle, 1958) assumed that water-soluble Cl exists in coal as NaCl, KCl, $CaCl_2$, and even $MgCl_2$. For example, total Cl contents in four West Canadian subbituminous coals (Whitewood, Highvale, Genesee, Battle River) were 32, 36, 32, and 95 ppm. During 18-h water extraction at ambient temperature, most (20, 32, 25 and 87 ppm Cl) was released. From Pennsylvanian Cl-rich Prince bituminous coals (Nova Scotia, Canada) 1909 ppm Cl was leached from 3704 ppm (Goodarzi, 2002).

In six Bulgarian feed coals, crushed coal (<0.1 mm) was extracted by distilled water leaching at ambient temperatures for 24 h, at a solid:liquid ratio of 1:10, with periodic agitation. In lignites (Maritsa-East and West, and Sofia basin), the water-soluble fraction was represented by gypsum, hexahydrite, and kieserite; in subbituminous (Pernik and Bobov Dol) and bituminous coals (Balkan) — mainly by gypsum. Calculated on a whole coal basis, the average contribution of the water-soluble Cl ranged from 9% (bituminous coals) to 35% (lignites), and averaged 20% of the Cl in the coals studied (Vassileva, 2004).

However, in some experiments, only a part of the total Cl was water-soluble, whereas in others almost all the Cl might be water-extracted. Kear and Menzies (1956) studied the problem in detail and concluded that the experimental regime was of importance; especially the rate of coal grinding and the duration and temperature of the leaching treatment. It was also found smaller coal particles always contained more Cl than larger ones, and the ratio "Cl extracted/Cl initial" was also higher. The extracted Cl yield increased along with experiment duration (for example, days instead of hours) and temperature increase (boiling water extracted much more Cl than cold water).

All this implies that the term "water-soluble chlorine" has no clear meaning; such a form might correspond either to easily water-soluble alkali chlorides (from larger pores), or sorbed Cl_{org}.

As was shown by Daybell and Pringle (1958), if a coal contained more than 0.25% carbonates (mainly calcite in cleats), the amount to water extractability of the Cl was close to 100%, whereas in carbonate-free coals it may that no more than 50%. They concluded that Cl is sorbed on coal as chloride anion (Cl^-), and

that the dissolving carbonate-anion exchanged with Cl^-, thereby facilitating the release of Cl^-.

Recent studies suggest that water-soluble chlorine has no simple interpretation. For example, water extracts from Novo-Moscovsk [New-Moscow] coalfield (East Donbas) "saline" brown coals, containing up to 16% Na_2O in ash, show a nearly stoichiometric ratio of Na:Cl indicating ~1% NaCl content in coal. However, neither in coal, nor in the HTA (high-temperature ash), was solid NaCl found. In coal, NaCl is dissolved in pore water: a NMR-signal from ^{23}Na appears only after coal drying. In HTA, NaCl is absent due to its decomposition during coal ashing. For the first time, NaCl was discovered in LTA (low-temperature ash), at 150 ± 5 °C. Aside from NaCl, other chlorides and sulfates were found: glauberite, kainite, and bassanite (Shendrik et al., 1997; Shendrik and Saranchuck, 2003).

An original method for determination of water-soluble Cl-salts was used by Vassilev et al. (2000), who studied Oligocene–Miocene Bobov Dol lignites with $A^d = 31.2\%$ and Cl=360 ppm. 100 g coal was extracted with 1-L distilled water for 24 h. The solution, having the mineralization of 0.9 g/L and containing 15% of initial Cl, was dried at 80 °C, and the dry residue was examined by X-ray, SEM, and TEM. It was found that the dry residue has an assemblage of water-soluble minerals that is nearly the same as in the initial coal. Here, gypsum and bassanite were dominant, with secondary anhydrite, hexahydrite ($MgSO_4 \cdot 6H_2O$), barite, jarosite ($K–NaFe_3[SO_4]_2$ $(OH)_6$), szomolnokite ($FeSO_4 H_2O$), Na–K-sulfates, kieserite ($MgSO_4 \cdot H_2O$), polyhalite (K_2Ca_2Mg $[SO_4]_2 2H_2O$), calcite, halite, carnallite ($KMgCl_3 \cdot 6H_2O$), opal, and cristobalite. At this, Cl is present not only in chlorides but also in most sulfates. The close similarity of the dry residues and the initial coal mineral composition means that the assemblage of water-soluble minerals is in thermodynamic equilibrium (not noted by Vassilev et al. (2000)).

Theoretically, some Cl may be present in gas–liquid inclusions enclosed in clastic or authigenic minerals: such as quartz, apatite, zircon, and volcanic glass (Vassilev et al., 2000, p. 918). However, really, such "fluid" Cl contribution seems to be very minor.

6.2. "General" organic chlorine form

Organic chlorine (Cl_{org}) often makes up the main part of the total chlorine in coal. For example, Czech researchers (Klika et al., 1999) based on analyses of sink and float fractions of two coals (not described)

estimated that the Cl_{org} contribution to be: 97% (lignite, North Czech basin) and 90% (bituminous coals, Upper Silesian (= Ostrava–Karvina) basin). In 11 Indian coals with ash yields ranging from 4.83% to 30.6%, Cl contents were in the range of 3200–5500 ppm, and Cl_{org} contents were from 300 to 6500 ppm (Das Gupta and Chakrabarti, 1951). So, the Cl_{org} contribution consists of 10–25% of the total chlorine (our estimate). Outlining all the information available at that time, Finkelman (1980, p. 144) concluded: *"It seems probable that much of the chlorine in coal occurs in association with the organic matter. Different types of bonding would account for the differences in the leaching characteristics of Cl"*. The majority of previous and recent researchers also hold the same opinion (Gluskoter and Ruch, 1971; Martínez-Tarazona et al., 1988; Pearce and Hill, 1986; Saunders, 1980).

Organic chlorine may be estimated by indirect and direct methods:

a) Coal calcinations and determination of Cl loss;
b) Via selective leaching of Cl by water and organic solvents;
c) On correlation "ash yield — Cl content in coal" (or by the Cl determinations in sink–float fractions);
d) On correlation "some element content — Cl content in coal";
e) Cl distribution into zonal coalified wood inclusions.

6.2.1. Low-temperature ashing and pyrolysis

Edgcombe (1956) found that the heating of an UK coal in air at 200 °C resulted in the loss of more than half of the Cl as HCl. As chlorides are not volatile at such temperatures, the lost Cl may be attributed to Cl_{org}.

Coal pyrolysis may also indicate the Cl site in coal. In a pyrolysis device, the Cl released from coal was mostly completed during the volatiles release. This indicates a very labile chlorine form, perhaps Cl_{org} (Gibb, 1983). Pyrolysis experiments were performed with UK and USA coals treated by NaCl solution with a Cl concentration of 1%. Chlorinated coal with 0.62% Cl released chlorine as HCl in two stages: first, at T ~100 °C, and then further (more intense) at T ~300 °C. Evidently the first emission Cl peak was due to the loss of weakly bonded sorbed Cl (Cl_{org}?), and the second peak to decomposition of NaCl solutions (Fynes et al., 1988). These experiments give the flavour of thermal metamorphism of saline coals.

6.2.2. Selective leaching

Gulyaeva and Itkina (1962) determined Cl_{org} as a difference between the total Cl and Cl extracted by 1%

HNO_3 (such a form was considered to be mineral-associated). The Cl_{org} form was dominant in coals from Donbas, Kuzbas and some other basins, being on average about 90%.

The polar organic solvent DMSO (dimethyl sulfoxide) quantitatively extracts soluble chlorides, and the mix of DMSO with 0.1 M KNO_3 may extract the ion-exchangeable chlorine-ion (Cl^-), perhaps due to ion exchange of absorbed Cl^- by NO_3^-. Extraction of an Illinois Herrin No.6 coal with 4700–6000 ppm Cl resulted in the yield of 64–84% Cl from the total Cl (Cox et al., 1984).

Surface mined Chinese coals (Pennsylvanian No. 9-1 bed, and Lower Permian No. 4-1 bed), Pingshuo coalfield, Shangxi basin, North China, containing on average 360–370 ppm Cl, were sequentially leached by H_2O, DMSO, and DMSO mixed with 0.1 M KNO_3. The following Cl partitioning was obtained (percentages of total Cl content) (Zhao et al., 1999, p. 163):

Water-soluble Cl	47.6–91.6%
Ion-exchangeable Cl_{org} (removed in DMSO-extracts)	4.9–18.6
"True" Cl_{org}, retained in coal	5.1–48.3

A substantial negative correlation between Cl in coal vs. ash yield ($r = -0.42$ over 64 samples) indicated a large contribution of Cl_{org}, both ion-exchangeable and more firmly bonded.

For many years, *the non-equivalence* of extracted Cl and alkalis was considered to be evidence of Cl_{org} presence (Daybell and Pringle, 1958; Edgcombe, 1956; Harrison, 1991). For example, in Daybell and Pringle's experiments with high-Cl coal, water-soluble Na was equivalent only to 0.5–0.3 of the total chlorine. However, such results may be artifacts. In Edgcombe's (1956) experiments, although nearly all Cl was water-extracted, the amounts of alkalis released were only partly equivalent to Cl. In one instance, only 15% were extracted. Also Ca^{2+} and Mg^{2+} were present in the extracts, but this does not mean they were in chloride form in the coal. It turns out, that HCl appeared at water extraction; its reaction with carbonates might generate Ca^{2+} and Mg^{2+} not at all bonded with Cl in the initial coal.

6.2.3. Negative correlation of ash yield vs. Cl content in coal

If Cl contents in coal show a clear negative correlation with ash yield, it suggests that Cl_{org} dominates. Such a correlation has been noted for USA Pennsylvanian bituminous coals (Bragg et al., 1991; Finkelman, 1980; Gluskoter and Ruch, 1971), for Canadian

Jurassic–Cretaceous subbituminous coals (Beaton et al., 1991; Goodarzi, 1987a,b,c; Grieve and Goodarzi, 1993), for Bulgarian Paleogene subbituminous Pyrin coals (Eskenazy et al., 1998) and for many others, especially for vitrinite concentrates (Lyons et al., 1989). For example, in very low-Cl Upper Oligocene Pyrin coals (on average, 78 ppm Cl) the negative correlation between Cl and ash is found for both whole coal, and for the ash-basis calculated Cl. It is of note that Cl was not extracted by cold water (Eskenazy et al., 1998).

Finkelman (1980) reported that an X-ray fluorescence technique was developed to determine the chlorine content of the Upper Freeport coal. The Cl values, plotted against the ash content, revealed a surprisingly strong negative correlation ($r = -0.95$). This relationship was interpreted as an indication of Cl_{org} domination in this coal.

6.2.4. Correlation of Cl with other elements

Based on 16 analyses of Pennsylvanian and Lower Permian coals and host rocks from Antaibao (Shangxi province), the Cl content ranged from 10 ppm (middle-ash coal, Pennsylvanian No. 5 bed) to 106 ppm (the roof of this bed). Cl content negatively correlates with ash, and positively with S_{org}, Ca, P and Sr. Furthermore, Cl contents in vitrain and clarain lithotypes are much more than in durain. All these features seem to indicate that Cl_{org} is the dominant form (Liu et al., 2001). In two US Provinces (Rocky Mountains and Appalachian) the correlation Cl–Na is weakly negative, and in one (Gulf Coast) — positive. The latter has an ambivalent interpretation: *"This positive relationship may indicate that both Cl and Na occur as NaCl or they both are associated with the organic fraction of the Gulf Coast lignites"* (Bragg et al., 1991, p. 9).

It is well known that bromine in coal exists mainly as Br_{org} form (Yudovich et al., 1985, p. 140–142). Therefore, a positive Cl–Br correlation may indicate Cl_{org} domination. Such a correlation was found in USA coal samples (Bragg et al., 1991) and in UK coals (Spears, in press).

Based on 35 samples of New South Wales bituminous coals (Gunnedah basin, Australia), the average Cl content was 69 ppm, ranging from near zero to 230 ppm. The chlorine content was found to negatively correlate with S_{tot}, S_{pyr} and (pyritic) As and detectable Cl contents were found only in low-sulfur coals, with $S_{tot} < 1\%$. These relations and an absence of any Cl–Na correlation pose a non-trivial issue: *Cl is in ion-exchangeable Cl_{org} form*. Such form might be substituted by sulfate-ion — either in syngenesis, or in epigenesis, as pyrite undergoes oxidation (Ward et al., 1999).

In three UK coals, about 5000 ppm Cl was detected by EDX (energy dispersive X-ray) in the vitrinite but no corresponding Na was detected (Finkelman, 1980), indicating a Cl_{org} form. Finkelman (1980) also cited Minkin's unpublished data (her personal communication, 1979) concerning Cl contents in two USA coals. Using an EMP (electron microprobe), she found up to 3000 ppm Cl in vitrinite from the Upper Freeport coal and up to 40,000 ppm in the Ferron coal; as comparable levels of cations such as Na or K were not found, she postulated a Cl_{org} form.

6.2.5. Chlorine in zonal coalified wood

Three zonal coalified wood inclusions from two Bulgarian coalfields were studied (Eskenazy and Vassilev, 2001) and Cl was found to be enriched in the central zone. Such a distribution indicates primary plant-derived Cl_{org} (biogenic Cl fraction) conservation.

Coalified wood inclusions	Central part	External part
Vitrain, Karlovo (Pliocene)	410 ppm Cl	30 ppm Cl
The same	390 ppm Cl	30 ppm Cl
Gagate, Nikolaevo (Eocene)	60 ppm Cl	30 ppm Cl

6.3. Sorbed "semi-organic" form

As was discussed above, a sorbed (weakly bonded) form, Cl_{org}, was suggested by many researchers on the basis of indirect indications but, up to 1990, such a suggestion was only probable, but not proven. The situation has been radically changed since XAFS method (X-ray absorption fine-structure spectroscopy) was used by Huggins and Huffman (1991). XAFS determines Cl in coal by means of synchrotron irradiation, with lower detection limit of near 200 ppm showed that main mode of Cl occurrence (at least, in bituminous coals) is not "true" Cl_{org}, and especially not the salt-like Cl_{min} form, but Cl-anion (Cl^-) sorbed on the maceral surfaces being, at the same time, associated with pore water (Huggins and Huffman, 1991, 1995). Such a Cl^- site may explain many earlier (some contradictory) experimental observations. On the one hand, it is not "true" Cl_{org}, because it exists only on the pore surface, not within coal macromolecular organic structure. On the other hand, it is not "true" water-soluble Cl because the characteristic Cl^- spectra persist after pore water release, at up to 300 °C coal drying.

"These observations suggest that the chloride anion–moisture complex is significantly more stable than a simple solution. It would appear that there must be significant interaction with the coal matrix to give such hydrated complexes appreciable thermal stability"

(Huggins and Huffman, 1995, p. 595). It was hypothe-sized that the anion Cl^- is held on the coal pore surface in two positions: bonded with amine N(IV),[6] as: $RNH_2 + H^+ \Rightarrow RNH_3^+$; $RNH_3^+ + Cl^- \Rightarrow RNH_3Cl$; b) bonded with any carboxyl complex, for example, with Na-carboxylate as $ClNaO^-$, where O^- is a polar oxygen group. In both positions, anion Cl^- produces HCl-complex surrounded by water molecules (in pore volume).

How are HCl-complexes related to NaCl-com-plexes? As high-Cl Illinois No. 6 coal was heated (Cl=8200 ppm), some peculiarities indicating NaCl presence in the XAFS-spectra appeared. However, as lower-Cl coal was heated (Cl=3200 ppm), NaCl was not generated. A non-trivial issue was reached:

> *"This might also imply that sodium–chlorine com-plexes are formed only after all the quaternary nitrogen is used in organohydrochloride complexes"* (Huggins and Huffman, 1995, p. 566).

Recent researchers have taken these results with enthusiasm; the form Cl_{org} became interpreted as "indi-rect" Cl_{org}. For example, results of the statistical data analysis of the 24 typical UK coals representing main coal basins were interpreted as indicating the domina-tion of such "indirect" Cl_{org} site contained in the pore moisture (Spears and Zheng, 1999).

6.4. "True-organic" form?

Although the contribution of the "true organic Cl" is minor, it is not zero. In particular, at the heating of UK coals up to 205 °C, traces of five Cl-containing organic compounds were detected in the gaseous phase (Pearce and Hill, 1986).

It was once assumed that Cl^- may be captured by any base (Oakey et al., 1991), including nitrogen-containing bases (Chou, 1991; Demir et al., 1990), such as amine (Daybell and Pringle, 1958) or pyridine (Given and Yarzab, 1978). Bethell (1962) also sug-gested that some Cl may be ionic bonded to nitrogen atoms; however, in typical UK coals studied by Pearce and Hill (1986), an absence of any correlation between Cl and N shows that such a bond (if it exists) would be unlikely interpreted as "true" Cl_{org}. Recently, in four Chinese coals containing 255 ppm

Cl, various organohalogens were found (Wei et al., 2004).[7]

Therefore, the "organic chlorine" form is heteroge-neous, and consists of two forms (Vassilev et al., 2000): a) water-insoluble Cl-organic compounds, where Cl is covalent bonded with coal organic matter (Hodges et al., 1983; Saunders, 1980); b) partly or fully water-soluble Cl which is sorbed on the pore surface of coal organic matter. Such form does not enter the coal or-ganic macromolecule and may be exchangeable (Day-bell and Pringle, 1958; Edgcombe, 1956; Gluskoter and Ruch, 1971; Saunders, 1980; Caswell et al., 1984a,b; Pearce and Hill, 1986; Oakey et al., 1991; Huggins and Huffman, 1991; Spears, in press).

6.5. Metamorphic and hypergene changes

During metamorphic and hypergene processes, the Cl mode of occurrence in coal may be changed, al-though such changes are not always easy to prove.

6.5.1. Coal rank influence

In Donbas (Ukraine and Russia) coals, the Cl mode of occurrence appears to be dependent on coal rank (Kizil'stein et al., 1983). Saline subbituminous B–C coals contain nearly all Cl (5350 ppm) in water-soluble form, and Cl content is stoichiometrically equivalent to the soluble (Na+K) contents. However, in medium volatile bituminous coals (160 ppm Cl) and anthracites (90 ppm Cl), Cl contents are about half of the alkali-equivalent contents. In saline coal, even the first water treatment extracts nearly all the Cl, whereas in higher rank coals, consequent Cl-extractions remove Cl grad-ually. Kizil'stein et al. (1983) concluded that in saline coals Cl exists in a chloride form which is nearly elim-inated in higher rank coals. However, such a methodol-ogy is dubious. How can we compare the coals having quite different initial Cl content *in entire* "coal rank sequence"? Low-rank saline coals (West Donbas) *were not the precursors* of the higher-rank coals.

In six Bulgarian feed coals (Vassileva, 2004), in general, the yield of water-soluble fraction decreases as coal rank increases:

$$1.3–8.4\%(\text{lignites}) \Rightarrow 0.9–1.2\%(\text{subbituminous})$$
$$\Rightarrow 0.6\%(\text{bituminous}).$$

---

[6] Recent studies by means of X-ray photo-electron spectroscopy showed that N(IV) contribution in coal, dependent on its rank, ranges from 3% to 16% of total nitrogen content. If an average N-content is ~1.5%, this would range from 0.05–0.25% N(IV) in coal (Huggins and Huffman, 1995, p. 566).

[7] However, F. Huggins (personal communication, July 2005) emphasizes that organochloride in coal may be artifacts: "It is quite conceivable that chemical reactions have occurred between other Cl forms and the extraction chemicals to form the organochlorine and organobromine compounds observed by GC/MS".

Chlorine contents in the insoluble residue pass, perhaps, through a maximum in subbituminous coals:

$$<130\text{–}1600(\text{lignites}) \Rightarrow 1000\text{–}5900(\text{subbituminous})$$
$$\Rightarrow 3200(\text{bituminous}).$$

Water-soluble Na shows a similar picture. Only if initial Cl-contents in coals were nearly the same, these data may really indicate some weak-bound Cl depletion due to coal metamorphism.

6.5.2. Contact heating influence

At the contact of the Cretaceous bituminous coal bed with an alkali basalt dike (Telkwa deposit, British Columbia, Canada) the coal is intensively carbonized and depleted in volatile content (Goodarzi and Cameron, 1990). The coal inorganic matter is also altered and the ash yield and Ca concentration in the heated coal are greatly increased. Many parameters reach an extreme at 5-cm distance from the contact. The contact temperature was estimated to have been 700–900 °C. The chlorine content seems to be depleted in the heated coal and some Cl is redeposited in the coke zone (Table 1).

6.5.3. Coal weathering influence

Chlorine contents in fresh and weathered British Columbia coals (Goodarzi, 1987a, p. 23, 25) are compared in the Table 2.

As is seen, coal weathering is accompanied by the ash yield increase and strong Cl content decrease, perhaps due to loss of the Cl_{org} form washed out by H_2O. In other Canadian coals some negative correlation between Cl and O contents is observed (Goodarzi, 1987a, 1995b), also indicating partial loss of the Cl_{org} form along with hypergene coal oxidation.

7. Factors affecting chlorine distribution

The distribution of Cl within a given coal bed is not well studied. For example, there are few data on traditional in coal geochemistry local (coal-bed scale) rela-

tional Cl in coal (and in ash) vs. ash yield, maceral content, position of a bench in coal bed column. More data are available about regional relationships.

7.1. Ash yield

As was discussed above, if Cl_{org} predominates in coal, Cl contents in coals may show a negative correlation with an ash yield. There are, though, some exceptions.

In Vorkuta coalfield (Pechora basin, Russia, our data) Cl contents range from 110 to 510 ppm in run-of-mine coals, middlings, tailings, and concentrates. For example, the concentrates (with an average ash yield of near 20%) may be enriched or depleted in Cl versus run-of-mine coal. However, in the high-ash Upper Rogov coalfield (average ash yield is about 40%), Cl contents in the run-of-mine coal are sharply enhanced — up to 2500 ppm (1500 ppm on average). It is not clear: is the ash yield a cause for such enrichment? Some other examples are given in the Table 3.

In Bulgarian (Vassilev et al., 2001, p. 107) and Indian (Hart et al., 1995, p. 156) coals, Cl contents are in inverse relation to ash yield, both on whole coal and ash basis, indicating the Cl_{org} domination. In Canadian coals (Beaton et al., 1992, p. 30), Cl contents in coal show a weak positive relation to ash yield; however, the minor Cl-content increase is evidently not proportional to the ash increase; this indicates substantial contribution of the Cl_{org} fraction, probably its Cl_{sorb} form. Indeed, if Cl contents are calculated on an ash basis, a characteristic decrease (typical for all the coalphile elements, see Yudovich and Ketris (2002) for details) would be obtained: $115 \rightarrow 47 \rightarrow 32$ ppm Cl.

7.2. Coal petrographic composition

Some minor, scarce data are available about irregular Cl partitioning between coal petrographic components.

In 15 xylain samples from the Miocene Maritsa-East coalfield, Bulgaria, the average Cl content (200 ppm, and up to 700 ppm) is twice that in a coals. On an ash

Table 1
Chlorine content and some other indices of a hot contact between coal and dike

Coal bed zones	Distance from contact, cm	A^d, %	C^{daf}, %	Ca, %	Cl, ppm
Coke	0	19.7	92.9	4.08	77
Coal strongly changed	5	14.7	94.2	3.46	53
Coal weakly changed	5–65	24.5 (20.8–28.1)	89.2 (86.0–90.9)	1.32 (0.29–3.46)	61 (51–69)
Unchanged coal	65–210	6.3 (5.8–7.1)	83.9 (82.4–85.4)	0.17 (0.06–0.41)	149 (131–159)

Compiled from the data of Goodarzi and Cameron (1990).

Table 2
Ash yield and Cl contents in fresh and weathered British Columbia coals (Goodarzi, 1987a, p. 23, 25)

Coals	Fording mime						Crownest mine	
	No. 47 bed		No. 61 bed		No. 64 bed		No. 10 bed	
	A^d, %	Cl, ppm	A^d, %	Cl, ppm	A^d, %	Cl, ppm	A^d, %	Cl, ppm
Fresh	4.58	57	20.90	65	14.99	79	12.28	445
Weathered	18.10	26	33.82	23	16.33	43	22.80	42

basis, the difference is more pronounced: on average 6300 vs. 270 ppm. However, this simply indicates the Cl_{org} dominance, and not some "xylain affinity" of Cl. Indeed, the highest Cl content (7500 ppm) is found in fusain ash, not xylain ash (Eskenazy and Vassilev, 2001).

In UK bituminous coals, Cl is mainly contained in vitrinite, whereas liptinite and inertinite are strong depleted in Cl (Saunders, 1980).

The same relationship is found for USA bituminous coals (Lyons et al., 1989). In the Appalachian and Illinois bituminous coals, Cl is mainly found in vitrinite, whereas in West Canadian subbituminous coals, Cl is more or less uniformly distributed among the macerals (Harrison, 1991). In density fractions of the extremely low-ash Blue Gem coal (south-eastern Kentucky) Cl contents ranged from 1.1 to 1.5 g/mL and show a maximum (~2000 ppm) in the middle, 1.25–1.30 g/mL, fractions enriched in vitrinite (90–100%) (Hower et al., 1994).

Hodges et al. (1983), Caswell et al. (1984a,b), and Fynes et al. (1988) found that Cl in bituminous coals is positively correlated with coal moisture, which, in turn, is dependent on coal porosity. Because bright coals enriched in vitrinite have greater porosity, such coals are enriched in Cl (Caswell et al., 1984a). On the other hand, in saline South Yorkshire coals, Cl is enriched in durain vs. vitrain and clarain. By the grinding fusain-bearing coals, the fines produced were enriched in fusain and in Cl versus a (ordinary) coals (Kear and Menzies, 1956).

On the Pingshuo coalfield (Shangxi basin, North China), a 24% ash, 13.45-m thick bituminous coal bed is open mined. Analyses of 44 samples from three drill holes showed an average Cl content of 374 ppm (from 41 to 833 ppm). By EDX-SEM method, the following Cl distribution was revealed (Zhao et al., 1999, p. 163): — Table 4.

Such distribution indicates the prevalence of the Cl_{org} form and Cl depletion in liptinite group macerals. Appreciable Cl content in calcite and positive Cl–Ca correlation ($r=+0.71$ from 15 samples) indicates an epigenetic Cl nature in these coals (Zhao et al., 1999, p. 163).

7.3. Position of a bench within coal bed column

There are only scarce and contradictory data about Cl vertical distribution within a coal bed.

In the Upper Oligocene Pyrin coalfield (Bulgaria), in contrast with other trace elements, Cl is depleted in the marginal zones of the coal beds (Eskenazy et al., 1998). A similar Cl distribution has been noted for some Canadian coals (Goodarzi, 1988). In the column of a Miocene Maritsa-East lignite (Bulgaria), Cl is distributed without clear trend, with possible enrichment in the middle part. A rather strong Cl–Na correlation was noted, due to, perhaps, not NaCl, but the

Table 3
Chlorine content and ash yield: some relationships

Coals	Ash yield set (A^d, %)	Set of the Cl contents	Reference
Bulgaria, Oligocene subbituminous coals and related products, Pernik coalfield	18.9% (a feed concentrate, the power station "Republic") →54.9% (sludge) →57.8% (initial coal) →59.9% (coal fines, <30 mm) →72.4% (tailings)	Cl, ppm on coal basis: 74→56→53→26→46; Cl, ppm on ash basis: 392→102→92→43→64	Vassilev et al., 2001, p. 107
India, Gevra high-ash coals, Madhja-Pradesh state	"Coal-like" ($A^d<45\%$) → "non-coal-like" ($A^d>45\%$)	~150 ppm Cl→ ~65 ppm Cl	Hart et al., 1995, p. 156
Canada, Yukon, Division Mountain subbituminous coals	19.1% (coal) →46.4% (carbonaceous shale) →84.8% (partings)	Cl, ppm on coal basis: 22 (9–43) →22 (10–67) →27 (17–73); Cl, average ppm on ash basis: 115→47→32	Beaton et al., 1992, p. 30

Table 4
Cl contents in macerals and inorganics

Material	Cl, ppm	Material	Cl, ppm	Material	Cl, ppm
Telocollinite	1460	Semifusinite	1000	Clay matter	163
Desmocollinite	900	Sporinite	200	Calcite (epigenetic)	467
Fusinite	1240	Cutinite	440		

After Zhao et al. (1999, p. 163).

presence of organic forms (Cl_{org} and Na_{org}) (Eskenazy and Vassilev, 2001).

In the 149-cm thick, high-sulfur ($S_{tot} = 5.45\%$, $A^d = 12.91\%$) high volatile bituminous Springfield bed (Indiana, USA), sampled in five benches, the weighted average Cl content is 600 ppm. The highest Cl content was noted in the near-roof (0–31 cm) bench — 1000 ppm (Mastalerz et al., 2004), possibly indicating a specific marginal (post-sedimentation) enrichment (Yudovich, 1978; 2003).

7.4. Metamorphic influence

The problem of metamorphic influences on Cl content in coal is very complicated. On the one hand, primary Cl may be partly lost from coal during coal metamorphism; on the other hand, the coal Clarke value of bituminous coals is much more than that of lignites (see Section 3); this may be due to epigenetic Cl input in coal from saline connate waters.

7.4.1. General considerations

One can think that Cl behavior during coal metamorphism may be similar to other coalphile elements (such as Ge). *If thermal coal metamorphism is not accompanied by epigenetic Cl input from reservoir brines*, two synchronous processes may occur:

a) The loss of Cl from lignites where present in water-soluble chlorides, sulfates, and carbonates, and also in ion-exchangeable sorbed "semi-organic" form surrounded by the pore moisture (water-associated form);
b) Redistribution of retained Cl following its transformation into more firmly bonded species, such as covalent-bound Cl-organic, and also water-containing silicates and oxides (illite, kaolinite, chlorite, muscovite, and Fe-hydroxides) (Vassilev et al., 2000). In particular, against background decrease of the water-soluble Cl in macropore moisture (the pore

size of >300 Å), an increased Cl-contribution is noted in mesopores (30–12 Å).

If a thermal coal metamorphism is accompanied by Cl input from brines, the bituminous coals would be enriched in Cl vs. lignites. For example, such a trend is noted in Canadian coal basins where Cl contents increase along with coal rank (Goodarzi, 1995a), and in eastern Kentucky, on the footwall of the Pine Mountain Thrust zone (Hower et al., 1991; Hower and Gayer, 2002). At the same time, such a trend should be non-linear: in high-rank coals, Cl contents drop due to decrease of the pore sizes (Skipsey, 1974, 1975).

Therefore, for a correct evaluation of the thermal coal metamorphism role in the coal geochemistry of Cl, it is necessary "to delete" any epigenetic Cl inputs in the low-temperature connate brines.

Some materials may illustrate these issues, although other factors (aside from metamorphism) often might influence the Cl content.

7.4.2. Russia

Sharp difference in average Cl content between Vorkuta (275 ppm) and Upper Rogov coalfields (1500 ppm) may be resulted from their different rank: high volatile B/A bituminous and subbituminous B, respectively. However, other factors controlling Cl-contents might be involved here (see above: Section 7.1).

7.4.3. Bulgaria

In 219 samples from eight Bulgarian coalfields, the average Cl content shows a rough increasing trend along with coal rank: 130 ppm (lignites) $\Rightarrow$ 100 ppm (subbituminous coals) $\Rightarrow$ 820 ppm (bituminous coals). However, strong Cl anomalies are noted in Pliocene Karlovo lignites (up to 15,900 ppm), evidently without any relation to their rank (Eskenazy and Vassilev, 2001).

7.4.4. UK and USA

In UK coalfields, lateral increases in Cl contents are observed, from west to east, along with a deepening of Carboniferous strata (Wandless, 1957). The highest Cl contents are found in central England (Daybell and Pringle, 1958). A similar relationship (though less clear) is found in the Illinois Basin, USA (Gluskoter and Rees, 1964).

However, if the coal rank is high and C^{daf} exceeds 86%, the sorption capacity of the coal organic matter would be sharply decreased (Skipsey, 1974, p. 264), and very rarely do such coals contain >0.2% Cl.

8. Genetic problems

Cl may accumulate in coal due to either syngenetic or epigenetic processes.

8.1. Syngenetic processes

Two main processes account for Cl enrichment in the peat-stage of coal formation: marine transgression and near-synchronous volcanism.

8.1.1. Facies influence

As was seen in Section 2, Cl has the highest "marine affinity": its Clarke in seawater is recognized as a global geochemical constant and constitutes 1.9% (19,000 ppm by weight). In addition, many plants may accumulate Cl. In near-shore regions, even rainwater is Cl-bearing (up to 200–300 mg/L Cl), therefore Cl may not only be introduced into low-land but also into the domed peatbogs. That is why, in early English studies, syngenetic concepts were put forward: Cl in coal was considered either biogenic (plant-derived) or derived from seawater (Kear and Menzies, 1956). This concept also was accepted by Russian researchers (Gulyaeva and Itkina, 1962, p. 349); indeed, relatively low Cl contents were found in fresh-water intra-continental peatbogs (Selivanov, 1946).

In Pacific coastal NE Russia, the Anadyr' coalfield is known to have high-Cl coals. Russian geologists describe the process as "evaporation" (Egorov and Penzin, 1987, p. 131–132): *"In buried coal-forming peatbog, a concentration of natural chloride waters occurs: as direct evaporation through sheared zones, as "evaporation" by dissolving in migrating gas, especially methane, and as water loss in mineral hydration."*

Using quantitative PIXE (particle-induced X-ray emission) analyses, Cl was determined in vitrinites of the Lower Kittanning seam (western Pennsylvania) in the areas where the seam is covered by the rocks of differing facies (Hickmott and Baldridge, 1995, p. 252). This resulted in recognition of a progressive increase in the Cl-content with increasing salinity of depositional environment:

$$1179–1855 \text{ ppm(fresh water facies)}$$
$$\rightarrow 1120–3090(\text{brackish}) \rightarrow 2144–3080 \text{ ppm (marine)}.$$

Therefore, the Cl maximum appears to be noted in vitrinites from marine environments.

An idea about facies-controlled Cl accumulation in coals is in good agreement with low Cl contents in young lignites (mostly fresh-water) versus Permian–Pennsylvanian bituminous coals (mostly near-shore, marine influenced).

8.2. Volcanic influence

It is well known that ammonium chloride is present in fumarole gases. If peatbogs are situated near volcanic areas, a Cl enrichment is possible from volcanic exhalations and thermal waters, as well as from Cl leaching from volcanic ash. As was noted in Section 2, the Keephills Fen peatbog in Canada may exemplify some recent (6800 years ago) volcanic enrichment in Cl (Chagué-Goff et al., 1996). Similar Cl input is proposed for some Cl-bearing coals of Bulgaria (Bobov Dol) and Japan (Taihejo), with evident features of the synchronous volcanism, such as volcanic ash particles (Vassilev et al., 2000).

In Carboniferous Dobrudzha bituminous coals (Bulgaria), enhanced Cl content may be partly accounted for by volcanism because of an association of the coals with tuffs. In addition, a coal bed has been intruded by a subvolcanic dike (Eskenazy and Vassilev, 2001).

8.3. Epigenetic processes

The most controversial topic in Cl coal geochemistry is the origin of so called saline (salty) coals. Some researchers argued for a syngenetic formation of such coals, others for an epigenetic nature, due to Cl input from salt-bearing strata, by saline basinal waters. Detailed analysis of both the concepts is made in Ivanova and Krivega's (1985) discussion of West Donbas saline coals and in Yudovich and Ketris (2002).

Epigenetic formation of saline coals is noted in northern Donbas, England, East Germany, Poland, Illinois Basin (USA), and some other localities. Some features may indicate epigenetic Cl accumulations in coal: (a) the presence of NaCl and other Cl-bearing minerals; (b) abundant weakly bonded sorbed Cl$^-$ form; and (c) the relation between the Cl contents in coal and geological structure and basinal (hot) brines.

Sometimes, the "epigenetic" explanation is forwarded as an alternative to the "volcanic" one. For example, against the background Cl contents over seven Bulgarian coalfields, from 10 ppm (Lower Oligocene lignites, Vulche Pole) to 240 ppm (Pliocene lignites, Karlovo), the Dobrudzha Pennsylvanian bituminous coals show 2430 ppm Cl. Aside from syngenetic volcanism (see above, Section 8.2), an epigenetic Cl enrichment from Na–Cl brines appears to be as likely (Eskenazy and Vassilev, 2001).

8.3.1. Cl-bearing minerals as epigenetic indications

In western Donbas (Ukraine) and Bobov Dol (Bulgaria), saline lignites were influenced by basinal brines. In Bobov Dol coals, in the bedding-parallel fractures, individual crystals and cubic crystalline aggregations (sized from 3 to 10 μm) of sylvite and halite were found, associated with volcanic glass and epigenetic gypsum and polyhalite (Vassilev et al., 2000, p. 912).

Chlorine may be present not only in chlorides but also in other coal minerals. In samples of high-Cl coals (including some Australian, Japanese, Illinois, and western Donbas coals), very common minerals are Cl-bearing: such as micas (up to 2% Cl), feldspars (up to 2.3% Cl), siderite (up to 0.2% Cl), and gypsum (up to 0.4% Cl). Evidently, these minerals might sorb Cl from brines (Vassilev et al., 2000, p. 912). In particular, montmorillonite and mixed-layer clay minerals have a high sorption capacity to Cl that even allows them to be used for the Cl-bearing waters cleaning (Vassileva et al., 1996). Aside from such (as minor admixtures) Cl form, *micromineral chlorides* seem to be present in mineral matter, as particles of <1 μm in size (Vassilev et al., 2000).

In Pennsylvanian bituminous coals from the Sydney and Stellarton basins, Nova Scotia, Canada, Cl is partially present in epigenetic sulfides which have been formed from mineralized brine derived from dissolution of the Windsor Group evaporites (Mukhopadhyay et al., 1998).

In UK coals, the main part of the weakly bonded Cl^-, considered to be derived from brines, sublimates from coal (as HCl) at $T > 170$ °C (Pearce and Hill, 1986). This is in good agreement with NaCl occurrence in host rocks; as NaCl occurs in host rock, it is very likely that coal has been influenced by dissolved Cl^- ion, which is weakly bonded with coal matrix and can be sublimated.

Within the coal bed, Cl is enriched in fusain. It is well known that fusain may act only as a physical sorbent (Yudovich, 1978). This indirectly indicates an epigenetic Cl nature.

8.3.2. Relation of the Cl contents to geologic factors

In eastern Germany, saline coals are laterally related with salt dome tectonics that indicate an epigenetic process (Ziegenhardt and Kramer, 1967).

Chlorine enrichments in South Yorkshire coals are clearly epigenetic because brines penetrate coal beds from overlying salt-bearing Permian–Triassic strata (Skipsey, 1974, 1975). In Pennsylvanian coals of Eastern Midland, Yorkshire and Northumberland, UK, Cl content clearly correlates with the salinity of connate waters, reaching up to 211 g/L (and Cl content — up to 131 g/L). This relationship has two exceptions. First, high-rank coals have sharply decreased sorption capacity and may not hold much Cl (see above: Section 6.5.1). Second, enrichment may occur if brines penetrate coal-bearing strata *from above*, as is seen in SE Durham, where brines move from overlying Permian evaporites (Skipsey, 1974).

As seen above, positive correlation "Cl content in coal vs. Cl content in basinal brines" argues for epigenetic process.

Mapping of the Cl contents in the Herrin coal (Illinois) shows a remarkable picture: the Cl (and Na) contents follow the synclinal bed structure, increasing from its uplifted periphery (<0.1–0.1% Cl) to its submerged central part ($0.2 \Rightarrow 0.4 \Rightarrow 0.5 \Rightarrow 0.6\%$ Cl) (Harvey and Ruch, 1986). As Harvey and Ruch (1986, p. 26) noted, such Cl and Na distributions reflect the depth-trend in chemical composition of the basinal water (and, in our opinion, is epigenetic).

In the Appalachians, a clear "stratigraphic" relationship is found: older Pennsylvanian coals are richer in Cl than younger ones (Table 5).

As proposed by Bragg et al. (1991, p. 8), such a relationship is due to the regressive character of the sedimentary sequence; older coals were formed in more marine environments than younger ones. However, another explanation suggests itself from the point-of-view of epigenesis, by analogy with that suggested for Illinois coals (Gluskoter, 1967). Besides, the syngenetic concept is based on some oversimplification of sedimentology and does not consider tectonic complications that may have occurred in the Appalachian basin.

Based on 51 samples the Pennsylvanian Western Kentucky Lisman and Baker coal beds (Illinois Basin), Cl contents correlate positively with burial depth and coal rank (vitrinite R_{max}): $r(Cl - \text{depths}) = 0.73$, and $r(Cl - R_{max}) = 0.45$. The correlation with R_{max} values is weaker than in a normal geologic setting due to local

Table 5

Stratigraphic relationship of the mean Cl contents in south Appalachians, USA (Bragg et al., 1991, p. 8)

Geologic age	Formation	Number of analyses	Cl in coal, ppm
Lower Permian (?)	Dunkard [a]	44	162
Upper Pennsylvanian	Monongahela	73	477
	Conemaugh	41	828
Middle Pennsylvanian	Allegheny	709	1097
	Kanawha	36	1408
Lower Pennsylvanian	New River	56	1503

[a] Group.

thermal waters that caused Mississippi Valley-Type mineralization. Such a thermal influence raised coal rank parameters above the regional background, and adds Cl to coal along with Zn, Ni, V, Cu, and Co. Although in Eastern Kentucky such mineralization appears not to be known, a similar picture is also observed here: the Cl contents appear to depend on two factors: (a) burial depth, and (b) distance from the Pine Mountain Thrust fault zone. Hence, in both the Interior and Appalachian basins, a tectonic factor operated, forcing hot Cl-bearing brines through the coal-bearing strata (Hower et al., 1991; Hower and Gayer, 2002).

In 29 whole-bed samples the 75×60 km eastern Kentucky area where the Pennsylvanian Manchester coal bed (and its stratigraphic analogues) is mined, Cl contents ranged from 600 to 4700 ppm, with an obvious increasing trend from NW to SE (Sakulpitakphon et al., 2004). Because coal rank (vitrinite R_{max}) and the contents of Hg, As, and Pb showed the same trend (being evidently structural dependent), it is very possible that all the elements entered coal-bearing strata through sheared zones, from the basement. Therefore, the process occurred synchronously with coal metamorphism (Sakulpitakphon et al., 2004). At the same time, attempts to find primary facies influence on the Cl contents in Kentucky coals were unsuccessful: correlations of the Cl-content with the S-content or other "marine indicators" have not been found (Hower et al., 1991).

With respect to the possible origin of epigenetic Cl enrichment, Hickmott and Baldridge (1995, p. 253) noted that vitrinites from the Lower Kittanning bed (western Pennsylvania) have Cl/Br ratios much lower (10–170) than in fresh, marine (289), or thermal waters, but are comparable with *fluid inclusions* in ores and metamorphic rocks. Such similarity raises a paradoxical question — are these fluids related to volatiles escaping during coal metamorphism?

9. Conclusions

1. The world average Cl content in coals (coal Clarke of Cl) for hard and brown coals are, respectively, 340 ± 40 and 120 ± 20 ppm. On an ash basis, these contents are greatly increased to 2100 ± 300 and 770 ± 120 ppm, respectively. The average Cl content on an ash basis is 1435 ppm which is much more than the Clarke value for sedimentary rocks, 150 ppm; hence, chlorine is, on average, a *highly coalphile element*. Just this alone shows that the authigenic sorption fraction, Cl_{sorb}, must be dominant in coals.

2. A strong lateral dispersion of the average Cl contents over numerous coal basins and coalfields has been noted. Perhaps, a substantial part of the dispersion may be accounted for by primary facies factor — the different depositional environments where intracontinental (limnic) and near-shore (paralic) coals were formed. The latter, even with other conditions equal, have to be more enriched in Cl. Therefore, Cl, like other "thalassophile" (strong marine affinity) elements, such as boron and sulfur, may serve as an indicator of the near-shore coal-forming environment. The other important factor indicated for syngenetic Cl accumulation was volcanism, near-synchronous with peat formation.

3. At the same time, there are saline coals, strongly enriched in Cl, up to 1 wt.% and even more. Although there are different genetic concepts, it seems that such coals were mainly formed in epigenesis — when coal beds were influenced by basinal chloride brines (often hot ore-forming brines, containing also ore elements such as As, Pb, Zn, etc.).

4. The modes of Cl occurrence in coal are surprisingly varied. Among them are found inorganic salt-like Na and other chlorides, as well as the Cl-bearing silicates, carbonates, sulfides, as well as dissolved chlorides in pore moisture. Organic-associated Cl seems to predominate in coal.

5. Organic-associated Cl has two different sites. One site ("true" Cl_{org}) may be as covalent-bonded Cl in coal organic macromolecules, but such a form seems to be only a minor Cl contributor in coal. Main organic Cl is represented by "semi-organic" Cl, as anion Cl^-, sorbed on the coal organic surface in pores and being surrounded by pore moisture. These are HCl-complexes bonded with bases, such as quaternary nitrogen (Huggins and Huffman, 1991, 1995).

6. The ratio of mineral Cl : organic Cl (as well as the Cl distribution among the coal macerals) is different in different coals and, perhaps, has a genetic dependance. If Cl in coal is mainly of syngenetic origin, a "true" Cl_{org} form may be found, and Cl is concentrated in low-ash gelified coal macerals. If coals were submerged by epigenetic impact from basinal brines, Cl_{min} (NaCl and other salts) and "semi-organic" Cl_{sorb} forms have to be dominant. In such instances, Cl may be enriched in fusain and in high-ash coals.

7. There is a complicated relation between Cl-contents of coals and coal rank. On the one hand, coals influenced by epigenetic brines are, as a rule, bituminous coals that have been submerged to

considerable depths where basinal brines occurred. On the other hand, if coals have a rank higher than low volatile bituminous A (C^{daf} more than 86%), the Cl content is decreased due to decreasing sorption capacity of the highly carbonized coal organic matter.

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References

Abernethy, R.F., Gibson, F.H., Frederic, W.H., 1965. Phosphorus, chlorine, sodium and potassium in U.S. coals. U.S. Bur. Mines Rep. Invest. 6579, 34 pp.

Beaton, A.P., Goodarzi, F., Potter, J., 1991. The petrography, mineralogy and geochemistry of a Paleocene lignite from southern Saskatchewan, Canada. Int. J. Coal Geol. 17, 117–148.

Beaton, A., Cameron, A.R., Goodarzi, F., 1992. Petrography, geochemistry and utilization potential of the Division Mountain coal occurrence, Yukon territory. Can. Geol. Surv. Pap. 92-1E, 23–32.

Bethell, F.V., 1962. The distribution and origin of minor elements in coal. Mon. Bull. Br. Coal Util. Res. Assoc. 26 (12), 401–429.

Bouška, V., Pešek, J., 1999. Quality parameters of lignite of the North Bohemian Basin in the Czech Republic in comparison with the world average lignite. Int. J. Coal Geol. 40, 211–235.

Bragg, L.J., Finkelman, R.B., Tewalt, S.J., 1991. Distribution of chlorine in United States coal. In: Stringer, J., Banerjee, D.D. (Eds.), Chlorine in Coal. Coal Sci. Technol., vol. 17. Elsevier, Amsterdam, pp. 3–10.

Caswell, S.A., Holmes, I.F., Spears, D.A., 1984a. Total chlorine in coal seam profiles from the South Staffordshire (Cannock) Coalfield. Fuel 63, 782–787.

Caswell, S.A., Holmes, I.F., Spears, D.A., 1984b. Water-soluble chlorine and associated major cations from the coal and mudrocks of the Cannock and North Staffordshire coalfields. Fuel 63, 774–781.

Chagué-Goff, C., Goodarzi, F., Fyfe, W.S., 1996. Elemental distribution and pyrite occurrence in a freshwater Peatland, Alberta. J. Geol. 104, 649–663.

Chou, C.-L., 1991. Distribution and forms of chlorine in Illinois Basin coals. In: Stringer, J., Banerjee, D.D. (Eds.), Chlorine in Coal. Coal Sci. Technol., vol. 17. Elsevier, Amsterdam, pp. 11–29.

Cox, J.A., Larson, A.E., Carlson, R.H., 1984. Estimation of the inorganic-to-organic chlorine ratio in coal. Fuel 63, 1334–1335.

Cressey, B.A., Cressey, G., 1988. Preliminary mineralogical investigation of Leicestershire low-rank coal. Int. J. Coal Geol. 10, 177–191.

Crossley, H.E., 1946. The inorganic constituents of coal; occurrence and industrial significance. The Chemical Age, 629–636.

Das Gupta, H.N., Chakrabarti, J.N., 1951. Estimation of chlorine in organic combination in the coal substance. J. Indian Chem. Soc. 28, 664–666.

Daybell, G.N., Pringle, W.J.S., 1958. The mode of occurrence of chlorine in coal. Fuel 37, 283–292.

Demir, I., Chou, C.-L., Chaven, C., 1990. Abundances and leachabilities of sodium and chlorine in lithotypes of Illinois Basin coals. In: Chyi, L.L., Chou, C.-L. (Eds.), Recent Advances in Coal GeochemistryGeol. Soc. Amer. Spec. Pap., vol. 248, pp. 73–85.

Edgcombe, L.J., 1956. State of combination of chlorine in coal. I. Extraction of coal with water. Fuel 35, 38–48.

Edmunds, W.M., 1975. Geochemistry of brines in the coal measures of northeast England. Inst. Min. Met. Trans. B 84, 39–52.

Egorov, A.I., Penzin, Yu.P., 1987. Cenozoic Coal Formation in NE USSR. Rostovsk. un-t [Rostov university], Rostov-na-Donu [Rostov on the Don river]. 184 pp.

Eskenazy, G., Vassilev, S., 2001. Geochemistry of chlorine and bromine in Bulgarian coals. Spis. Bulg. Geol. Druzh. [Proc. Bulg. Geol. Soc.] 62 (1–3), 37–46.

Eskenazy, G., Vassilev, S., Karaivanova, E., 1998. Chlorine and bromine in the Pirin coal deposit, Bulgaria. Spis. Bulg. Geol. Druzh. [Proc. Bulg. Geol. Soc.] 50 (2), 67–72.

Finkelman, R.B., 1980. Modes of occurrence of trace elements in coal. Ph. D. Thesis. Dept. Chem., University of Maryland, College Park. 302 pp.

Fynes, G., Herod, A.A., Hodges, N.J., Stokes, B.J., Ladner, W.R., 1988. The thermal emission of chlorine-containing compounds from coal following brine and chlorine gas treatments. Fuel 67, 822–830.

Gibb, W.H., 1983. The nature of chlorine in coal and its behaviour during combustion. In: Meadowcroft, D.B., Manning, M.I. (Eds.), Corrosion Resistant Materials for Coal Conversion Systems. Appl. Sci., London, pp. 25–45.

Given, P.H., Yarzab, R.F., 1978. Analysis of the organic substance of coals: problems posed by the presence of mineral matter. In: KarrJr. Jr., C. (Ed.), Analytical Methods for Coal and Coal Products, vol. 2. Academic Press, New York, pp. 3–41.

Gluskoter, H.J., 1967. Chlorine in coals of the Illinois basin. Trans. Soc. Min. Eng. 238, 373–379.

Gluskoter, H.J., Rees, O.W., 1964. Chlorine in Illinois coals. Ill. Geol. Surv. Circ. 372, 23 pp.

Gluskoter, H.J., Ruch, R.R., 1971. Chlorine and sodium in Illinois coals as determined by neutron activation analyses. Fuel 50, 65–76.

Goodarzi, F., 1987a. Comparison of elemental distribution in fresh and weathered samples of selected coals in the Jurassic–Cretaceous Kootenay Group, British Columbia, Canada. Chem. Geol. 63, 21–28.

Goodarzi, F., 1987b. Concentration of elements in lacustrine coals from Zone A Hat Creek deposit No. 1, British Columbia, Canada. Int. J. Coal Geol. 8, 247–268.

Goodarzi, F., 1987c. Elemental concentrations in Canadian coals. 2. Byron Creek collieries, British Columbia. Fuel 66, 250–254.

Goodarzi, F., 1988. Elemental distribution in coal seams at the Fording Coal Mine, British Columbia, Canada. Chem. Geol. 68, 129–154.

Goodarzi, F., 1995a. Geology of trace elements in coal. In: Goodarzi, F., Swaine, D. (Eds.), Environmental Aspects of Trace Elements of Coal. Kluwer Acad. Publ., Dordrecht, pp. 51–75.

Goodarzi, F., 1995b. The effects of weathering and natural heating on trace elements of coal. In: Goodarzi, F., Swaine, D. (Eds.),

Environmental Aspects of Trace Elements in Coal. Kluwer Acad. Publ., Dordrecht, pp. 76–92.

Goodarzi, F., 2002. Mineralogy, elemental composition and mode of occurrence of elements in Canadian feed-coals. Fuel 81, 1199–1213.

Goodarzi, F., Cameron, A.R., 1990. Organic petrology and elemental distribution in thermally altered coals from Telkwa, British Columbia. Energy Sources 12, 315–343.

Grieve, D.A., Goodarzi, F., 1993. Trace elements in coal samples from active mines in the Foreland Belt, British Columbia, Canada. Int. J. Coal Geol. 24, 259–280.

Gulyaeva, L.A., Itkina, E.S., 1962. Halogens, vanadium, nickel and copper in coals. Geokhimiya [Geochemistry] 4, 345–355.

Harrison, C.H., 1991. Electron microprobe analysis of coal macerals. Org. Geochem. 17, 439–449.

Hart, B.R., Powell, M.A., Sahu, K.C., Tripathy, S., Fyfe, W.S., 1995. Mineralogy and geochemistry of coals from the Gevra mine, Korba, Madhya Pradesh, India. In: Pajares, J.A., Tascón, J.M.D. (Eds.), Coal Science. 8th ICCS Proc., vol. II. Elsevier, Amsterdam, pp. 155–158.

Harvey, R.D., Ruch, R.R., 1986. Mineral matter in Illinois and other U.S. coals mineral matter and ash in coal. In: Vorres, K.S. (Ed.), Washington, American Chemical Society Symp. Ser., vol. 301, pp. 10–40.

Hickmott, D.D., Baldridge, W.S., 1995. Application of PIXE microanalysis to macerals and sulfides from the Lower Kittanning Coal of western Pennsylvania. Econ. Geol. 90, 246–254.

Hodges, N.J., Ladner, W.R., Martin, T.G., 1983. Chlorine in coal: a review of its origin and mode of occurrence. J. Inst. Fuel 56, 158–169.

Hower, J.C., Gayer, R.A., 2002. Mechanisms of coal metamorphism: case studies from Paleozoic coalfields. Int. J. Coal. Geol. 50, 215–245.

Hower, J.C., Riley, J.T., Thomas, G.A., Griswold, T.B., 1991. Chlorine in Kentucky coals. J. Coal Qual. 10, 152–158.

Hower, J.C., Taulbee, D.N., Rimmer, S.M., Morrell, L.G., 1994. Petrographic and geochemical anatomy of lithotypes from the Blue Gem coal bed, southeastern Kentucky. Energy Fuels 8, 719–728.

Huggins, F.E., Huffman, G.P., 1991. An XAFS investigation of the form-of-occurrence of chlorine in U.S. coals. In: Stringer, J., Banerjee, D.D. (Eds.), Chlorine in Coal. Elsevier Sci. Publ. Co., New York, pp. 43–61.

Huggins, F.E., Huffman, G.P., 1995. Chlorine in coal: an XAFS spectroscopic investigation. Fuel 74, 556–559.

Ivanov, V.V., 1994. Environmental Geochemistry of Elements: Reference Book, 2. Main p-Elements. Nedra [Entrails Publ. House], Moscow. 303 pp.

Ivanova, A.V., Krivega, T.A., 1985. Saline Coals of Western Donbas. Naukova dumka [Scientific Thought Publ. House], Kiev. 124 pp.

Kear, R.W., Menzies, H.M., 1956. Chlorine in coal. Its occurrence and behaviour during combustion and carbonization. Mon. Bull. - Br. Coal Util. Res. Assoc. 20 (2), 53–64.

Ketris, M.P., Yudovich, Ya.E., 2002. Calculation procedure of the coal Clarkes. Lithogenes i geochimiya osadochnykh formatsiy Timan-Ural'skogo regiona. Syktyvkar, 111–117. (Tr. In-ta geol. Komi nauch. tsentra UrO Ross. Acad. nauk, vyp. 111). [Proc. Inst. Geol. Komi Sci. Center, issue 111].

Kizil'stein, L.Ya., Vyalov, V.I., Gal'chikov, V.V., 1983. Soda distribution in coals of northern part of the Donetsk basin. Izb. vyssh. ucheb. zaved. Geol. i razvedka [High Scool Proc. Geology and Exploration], vol. 2, pp. 70–77.

Kler, V.R., 1988. Minor element concentrations in the coals and coal-bearing formations. In: Kler, V.R., Nenakhova, V.F., Saprykin, F.

Ya., Shpirt, M.Ya., Rokhlin, L.I., Kulachkova, A.F., Iovchev, R.I. (Eds.), Metallogeny and Geochemistry of Coal-Bearing and Oil Shale-Bearing Strata of the USSR: the Regularities of the Element Concentrations and Methods of their Study. Science Publ. House, Moscow, Nauka, pp. 67–142.

Kler, V.R., Nenakhova, V.F., 1981. Paragenetic Complexes of Mineral Resources of the Oil–Shale- and Coal-Bearing Strata. Science, Moscow, Nauka. 175 pp.

Klika, Z., Mrozek, S., Kolomazn(k, I., 1999. Distribution of the trace elements in Czech coal. In: Li, B.Q., Liu, Z.Y. (Eds.), Prospects for Coal Science in the 21st Century. Sci. Technol. Press, Shanxi, pp. 81–184.

Lee, R.J., Huggins, F.E., Huffman, G.P., 1978. Correlated Mössbauer, SEM studies of coal mineralogy. Scan. Electron Microsc. 1, 561–568.

Leutwein, F., Rösler, H.J., 1956. Geochemische Untersuchungen an paläozoischen und mesozoischen kohlen Mittel-und Ostdeutsch-lands. Freib. Forsch., C, vol. 19. Akademie Verlag, Berlin. 196 SS.

Liu, D., Yang, Q., Tang, D., Kang, X., Huang, W., 2001. Geochemistry of sulfur and elements in coals from the Antaibao surface mine, Pingshuo, Shanxi Province, China. Int. J. Coal Geol. 46, 51–64.

Lyons, C., Palmer, C.A., Bostick, N.H., Fletcher, J.D., Dulong, F.T., Brown, F.W., Brown, Z.A., Krasnow, M.R., Romankiw, L.A., 1989. Chemistry and origin of minor and trace elements in vitrinite concentrates from a rank series from the eastern United States, England and Australia. Int. J. Coal Geol. 13, 481–527.

Martínez-Tarazona, M.R., Palacios, J.M., Cardin, J.M., 1988. The mode of occurrence of chlorine in high volatile bituminous coals from the Asturian Central coalfield. Fuel 67 (12), 1624–1628.

Mastalerz, M., Hower, J.C., Drobniak, A., Mardon, S., Lis, G., 2004. From in-situ coal to fly ash: a study of coal mines and power plants Indiana. Int. J. Coal. Geol. 59, 171–192.

Mielecki, T., 1948. Przyczynek do poznania zawartości chloru w polskich węglach. Biul. Inst. Nauk.-Bad. Przem. Węgl. Komun. 36, 5 pp.

Mukhopadhyay, P.K., Goodarzi, F., Grandlemire, A.L., Gillis, K.S., MacNeil, D.J., Smith, W.D., 1998. Comparison of coal composition and elemental distribution in selected seams of the Sydney and Stellarton Basins, Nova Scotia, eastern Canada. Int. J. Coal Geol. 37, 113–141.

Oakey, J.E., Minchener, A.J., Hodges, N.J., 1991. The use of high-chlorine coals in industrial boilers. J. Inst. Energy 64, 3–11.

Oelschlegel, H.G., 1964. Geochemische Untersuchungen an nord-westdeutschen und nordhesslischen tertiären Braunkohle. N. Jahrb. Min. Abh. 101, 67–96.

Parr, S.W., Wheeler, W.F., 1909. Unit Coal and the Composition of Coal Ash. Univ. Ill. Eng. Exp. Stat. Bull., vol. 37. 69 pp.

Pearce, W.C., Hill, J.W.F., 1986. The mode of occurrence and combustion characteristics of chlorine in British coal. Progr. Energy Combust. Sci. 12, 117–162.

Perel'man, A.I., 1972. Elemental Geochemistry in Hypergene Zone. Nedra [Entrails Publ. House], Moscow. 288 pp.

Ren, D., Zhao, F., Wang, Y., Yang, S., 1999. Distribution of minor and trace elements in Chinese coals. Int. J. Coal Geol. 40, 109–118.

Reynolds, F.M., 1948. The occurrence of vanadium, chromium, and other minor unusual elements in certain coals. J. Soc. Chem. Ind. 67, 341–345.

Sakulpitakphon, T., Hower, J.C., Schram, W.H., Ward, C.R., 2004. Tracking mercury from the mine to the power plant: geochemistry of the Manchester coal bed, Clay County, Kentucky. Int. J. Coal Geol. 57, 127–141.

Saunders, K.G., 1980. Microstructural studies of chlorine in some British coals. J. Inst. Energy 53 (416), 109–115.

Selivanov, L.S., 1946. Geochemistry and biogeochemistry of the dispersed bromine. Tr. Biogechim. Lab. AN SSSR [Proc. Biogeochim. Lab. USSR] 8, 5–72.

Shendrik, T.G., Saranchuk, V.I., 2003. Salty Coals. Skhidniy vidavnichiy dom [East Publ. House], Donetsk. 296 pp.

Shendrik, T.G., Simonova, V.V., Pashchenko, L.V., 1997. The mineral matter of Ukrainian salty coals in connection with the environmental problem of their application. In: Ziegler, A., et al. (Ed.), Proc. 9th Intern. Conf. Coal Sci. (Essen: 7–12 Sept. 1997), vol. 1. DGMK, Essen, pp. 409–412.

Skipsey, E., 1974. Distribution of alkali chlorides in British coal seams. Fuel 53 (4), 258–267.

Skipsey, E., 1975. Relation between chlorine in coal and the salinity of strata waters. Fuel 54 (2), 121–125.

Spears, D.A., in press. A review of chlorine and bromine in some UK coals. Int. J. Coal. Geol. doi:10.1016/S0166-5162(98)00012-3.

Spears, D.A., Zheng, Y., 1999. Geochemistry and origin of elements in some UK coals. Int. J. Coal Geol. 38, 161–179.

Swaine, D.J., 1990. Trace Elements in Coal. Butterworths, London. 278 pp.

Vassilev, S., Eskenazy, G., Karaivanova, E., 1997. Chlorine and bromine in Bulgarian coals and their combustion wastes. C. R. Acad. Bulg. Sci. 50 (7–8), 54–48.

Vassilev, S.V., Eskenazy, G.M., Vassileva, C.G., 2000. Contents, modes of occurrence and origin of chlorine and bromine in coal. Fuel 79 (8), 903–921.

Vassilev, S.V., Eskenazy, G.M., Vassileva, C.G., 2001. Behaviour of elements and minerals during preparation and combustion of the Pernik coal, Bulgaria. Fuel. Proc. Technol. 72, 103–129.

Vassileva, C.G., 2004. Some environmental aspects related to water-soluble fractions in Bulgarian coals and fly ashes. C. R. Acad. Bulg. Sci. 57 (7), 71–76.

Vassileva, B., Vassilev, S., Vassileva, C., 1996. Effective use of mineral sorbents for purification of waste waters from thermoelectric power stations. C. R. Acad. Bulg. Sci. 49 (4), 59–62.

Wandless, A.M., 1957. British coal seams: a review of their properties with suggestions for research. J. Inst. Fuel 30, 541–552.

Ward, C.R., Spears, D.A., Booth, C.A., Staton, I., Gurba, L.W., 1999. Mineral matter and trace elements in coals of the Gunnedah Basin, New South Wales, Australia. Int. J. Coal Geol. 40, 281–308.

Wei, X.Y., Wang, X.H., Zong, Z.H., Zhang, L.F., Ji, Y.F., Xie, K.C., Lee, C.W., Liu, Z.X., Chu, N.B., Cui, J.Y., 2004. Identification of organochlorines and organobromines in coals. Fuel 83, 2435–2438.

Wyndham, J.L.P., 1951. The minerals and metals in coal. S. Afr. Min. Eng. J. 62-2 (3070), 659–661.

Yudovich, Ya.E., 1978. Geochemistry of Fossil Coals. Nauka [Science Pub. House], Leningrad. 262 pp.

Yudovich, Ya.E., 2003. Notes on the marginal enrichment of germanium in coal beds. Int. J. Coal Geol. 56, 223–232.

Yudovich, Ya.E., Ketris, M.P., 1988. Geochemistry of Black Shales. Nauka [Science Pub. House], Leningrad. 272 pp.Yudovich, Ya.E., Ketris, M.P., 1997. Geochemistry of Black Shales. Prolog, Syktyvkar. 212 pp., See also English short outline with a large bibliography.

Yudovich, Ya.E., Ketris, M.P., 2002. Inorganic Matter of Coals. URO RAN [Ural Division of the Russian Acad. Sci.], Ekaterinburg. 422 pp.

Yudovich, Ya.E., Ketris, M.P., Merts, A.V., 1985. Trace Elements in Fossil Coals. Nauka [Science Publ. House], Leningrad. 239 pp.

Zhao, F., Ren, D., Zhang, W., Tang, Y., 1999. The geochemical characteristics of chlorine in coal from Pingshuo surface mine, Shanxi province. In: Li, B.Q., Liu, Z.Y. (Eds.), Prospects for Coal Science in 21st Century. Sci. Technol. Press, Shanxi, pp. 161–164.

Ziegenhardt, W., Kramer, H.-J., 1967. Die Verteilung der Salzgehalte in den Braunkohlenflözen der Egelner Südmulde. Ein Beitrag zur Salzkohlengenese. Z. Angew. Geol. 13, 465–473.