Fuel 79 (2000) 903–921

www.elsevier.com/locate/fuel

Contents, modes of occurrence and origin of chlorine and bromine in coal

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Received 30 March 1999; received in revised form 29 September 1999; accepted 20 October 1999

Abstract

Contents, modes of occurrence and origin of Cl and Br in individual coal samples from 34 deposits worldwide (Bulgaria, Australia, the United States, Japan, Canada, South Africa, China, and Ukraine) were studied. Some relationships of Cl and Br contents with chemical and mineral composition, rank, age, ash yield and geographic location of coals are described. Despite of similar chemical and geochemical properties of Cl and Br some distinct differences in the association, behaviour and occurrence of both elements in coal were found and discussed. Chlorine and Br in coal may occur, in decreasing order of significance, as organic compounds, as impurity components in the crystalline and amorphous inorganic constituents, in the fluid constituents and as discrete minerals. Both elements could have an organic occurrence and association with water-soluble (mainly ionic) and water-insoluble (ionic and covalent) organic combinations. Chlorine was identified as an impurity in minerals and inorganic phases such as clay minerals, mica, feldspars, polyhalite, gypsum, siderite, volcanic glass, phosphates and other carbonates and sulphates. A characteristic Br association with illite and to a lesser extent with mica, kaolinite and Fe-bearing minerals was also found. Water molecules, hydroxyl groups and exchangeable cations in various minerals play a leading role for the inorganic occurrence and distribution of both elements. Discrete Cl minerals such as sylvite, halite, chlorapatite and probably carnallite were also identified. Significant amounts of Cl ions may associate with solutions in the inherent moisture of the coal mesoporosity. Limited proportions of both elements may also occur in gas–liquid inclusions of different solid phases. The favourable conditions for Cl and Br enrichments in coal are also discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Coal mineralogy and geochemistry; Chlorine; Bromine

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1. Introduction

Chlorine is one of the most studied elements in coal because this harmful element may cause some technological and environmental problems during coal combustion. Data on bromine occurrence in coal are scarce and investigations about any technological and environmental impacts related to this element have not been reported. Extensive studies on contents, concentration trends, distributions, organic–inorganic affinities and modes of occurrence of elements in various coals have been conducted by many authors. Summarized data on major, minor and trace elements in coal, including halogen Cl and Br, have been reported [1–7]. A detailed review on Cl origin and mode of occurrence in coal has been done [8], while generalized data on Br are still missing.

The Clarke values for Cl and Br in coal are in the intervals 300–1100 and 5–17 ppm, respectively (Table 1). The highest concentrations of Cl associate with the so-called “salt coals” which are known in countries such as Australia, Austria, Germany, Great Britain, Poland, USA, and the former Czechoslovakia and Soviet Union. The modes of Cl occurrence in coal are variable, incompletely understood and not defined fully [8]. This statement is true to a higher extent for Br. The presence of Cl in coal comprises both organic and inorganic occurrences including the fluid constituents associated with them [5,6,8–11]. In summary, the organically associated Cl may include: a weakly bound sorption form probably as chloride ions attached to the coal substance by an ion exchange linkage; a strongly bound form probably as covalently linked chlorine. The mineral and inorganic forms may comprise: discrete chlorides such as halite (NaCl), partly sylvite (KCl) and $CaCl_2$, and in some instances chlorides of Mg ($MgCl_2$) and Fe ($FeCl_3$); other Cl-bearing minerals, namely chlorapatite ($Ca(PO_4)_3(Cl,F,OH)$), sodalite ($Na_8(AlSiO_4)_6Cl_2$) some sulphates and carbonates, and inorganic amorphous matter; and chloride ions associated with exchangeable cations in clay minerals and mica. The fluid Cl occurrence comprises chloride ions in

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PII: S0016-2361(99)00236-7

Table 1
Clarke values of chlorine (in decreasing order) and bromine for coals, rocks, soils, plants and waters (ppm)

Object	Content		Reference
	Cl	Br	
Multicellular algae	60 000	1000	Bowen, 1966 [53]
Deep-sea carbonates	21 000	70	Turekian and Wedepohl, 1961 [54]
Deep-sea clays	21 000	70	Turekian and Wedepohl, 1961 [54]
Brown algae	4700	740	Bowen, 1966 [53]
Angiospermae plants	2000	15	Bowen, 1966 [53]
Bituminous–anthracitic coals	1100		Yudovich et al., 1985 [5]
Coals	1000	17	Valkovic, 1983 [4]
		5–15	Yudovich et al., 1985 [5]
Mosses	670		Bowen, 1966 [53]
US coals	614	17	Finkelman, 1994 [55]
Lignitic–subbituminous coals	300		Yudovich et al., 1985 [5]
Coaly chondrites	260	5	Voitkevich et al, 1990 [56]
Acid rocks	240	1.7	Vinogradov, 1962 [57]
Rocks	200	3	Bowen, 1966 [53]
Granites	200	1.3	Beus and Grigorian, 1975 [58]
Shales	180	4	Turekian and Wedepohl, 1961 [54] Beus and Grigorian, 1975 [58]
Lithosphere	170	2.1	Vinogradov, 1962 [57]
	100	2	Beus and Grigorian, 1975 [58]
Clays and shales	160	6	Vinogradov, 1962 [57]
Carbonates	150	6.2	Turekian and Wedepohl, 1961 [54] Beus and Grigorian, 1975 [58]
Granodiorite	130	4	Beus and Grigorian, 1975 [58]
Magmatic rocks	130	2.5	Bowen, 1966 [53]
Intermediate rocks	100	4.5	Vinogradov, 1962 [57] Beus and Grigorian, 1975 [58]
Soils	100	5	Vinogradov, 1957 [59] Bowen, 1966 [53]
Chondrites	70	0.5	Vinogradov, 1962 [57]
Basic rocks	60	3.6	Beus and Grigorian, 1975 [58]
	50	3	Vinogradov, 1962 [57]
Ultrabasic rocks	50	0.5	Vinogradov, 1962 [57]
		1	Beus and Grigorian, 1975 [58]
Sandstones	10	1	Turekian and Wedepohl, 1961 [54] Beus and Grigorian, 1975 [58]
Sea water (mg l^{-1})	19 000	65	Bowen, 1966 [53]
Fresh water (mg l^{-1})	7.8	0.021	Bowen, 1966 [53]

the water layers adsorbed onto outer and into inner coal surfaces, and gas–liquid inclusions locked in the inorganic and organic matter.

The geochemical behaviour of Cl and Br is thought to be similar during their migration and concentration in coal [6]. For example, data for US coals indicate that Br is found in coal in a mode of occurrence closely similar to that of Cl [10,12]. Bromine is also a biophilic element and probably a significant part of this element in plants remains in the organic matter of coal [5]. Discrete mineral forms of Br in coal have not been identified, but small Br amounts could be associated with some minerals [7].

Systematic studies on the geochemistry and mineralogy of Cl and Br simultaneously in various coals and their combustion products are restricted. Such investigations are important: in elucidating Cl and Br occurrence and origin in coal; in understanding their behaviour during coal processing and burning; and in predicting and evaluating possible utilizations and environmental impacts related to coal use. The present study provides a characterization and comparison of contents, concentration trends, modes of occurrence and origin of Cl and Br in coals worldwide and especially in Bulgarian coals. A detailed understanding of the origin and occurrence of Cl and Br in coal may contribute to eliminate, reduce or immobilize their mobile forms during coal processing and subsequent coal combustion. A similar characterization of Cl and Br in combustion wastes from coal-fired power stations will be reported in another paper.

2. Material and methods

Individual coal samples from 34 deposits of Bulgaria (7), Australia (8), the United States (7), Japan (6), Canada (3), South Africa (1), China (1), and Ukraine (1) were examined. The coal specimens exhibit a wide variety of characteristics

Table 2
Chlorine and bromine contents in coal and coal ash samples from 34 coal deposits world-wide (ppm)

Sample	Coal		Coal ash (A^d basis)[a]			A^d (wt %)	C^{daf} (wt %)
	Cl	Br	Cl	Br	Cl/Br		
Bulgaria							
1 Maritza West	150	110	290	210	1.4	52.0	62.9
2 Sofia	80	90	290	330	0.9	27.5	63.0
3 Elhovo	90	12	210	28	7.5	43.5	64.2
4 Maritza East	200	180	500	450	1.1	39.7	65.5
5 Bobov Dol	360	1330	1150	4260	0.3	31.2	73.9
6 Pernik	50	1130	100	2240	0.04	50.4	74.3
7 Balkan	150	850	390	2220	0.2	38.3	85.7
Australia							
8 Ebenezer	370	20	2910	160	18.2	12.7	79.9
9 Wambo	360	12	2950	98	30.1	12.2	81.9
10 Blair Athol	440	20	3930	180	21.8	11.2	83.3
11 Lithgow	480	6	2250	28	80.4	21.3	83.8
12 Newlands	250	17	1660	110	15.1	15.1	84.1
13 Wallarah	370	12	2640	86	30.7	14.0	84.1
14 Moura	710	37	6890	360	19.1	10.3	85.5
15 Entham	580	18	5270	160	32.9	11.0	85.6
USA							
16 Usibelli	90	8	970	86	11.3	9.3	64.2
17 Beluga	80	3	560	21	26.7	14.4	70.2
18 Montana	190	15	1470	120	12.3	12.9	70.6
19 Black Thunder	200	11	3170	170	18.6	6.3	72.5
20 Colowyo	190	15	3330	260	12.8	5.7	77.2
21 Illinois	750	2	6470	17	380.6	11.6	78.2
22 Plateau	100	7	1020	71	14.4	9.8	79.7
Japan							
23 Taiheiyo	1090	6	4700	26	180.8	23.2	73.8
24 Akabira	110	7	220	14	15.7	50.3	76.4
25 Horonai	140	3	420	9	46.7	33.0	76.7
26 Sunagawa	200	14	660	47	14.0	30.1	78.3
27 Ashibetsu	180	7	560	22	25.5	32.2	80.8
28 Takashima	230	10	2800	120	23.3	8.2	82.2
Canada							
29 Coal Valley	140	11	1370	110	12.5	10.2	81.6
30 Fording River	280	15	2720	150	18.1	10.3	83.4
31 Coal Mountain	280	8	1620	46	35.2	17.3	85.0
Others							
32 Ermelo[b]	260	6	2430	56	43.4	10.7	78.8
33 Datong[c]	210	13	1590	98	16.2	13.2	82.3
34 Donbass[d]	500	1620	3420	11 100	0.3	14.6	86.6
Mean for all samples	290	170	2090	690	34.4	21.0	77.5

[a] Calculated from coal data.
[b] South Africa.
[c] China.
[d] Ukraine.

such as chemical and mineral composition, rank, age, genesis and geographic location, which make them suitable for some investigations. The used samples have been studied earlier for relationships between their composition and ash fusibility [13], coal rank [14] and ash yield [15].

The low-temperature (LTA) and high-temperature ashes (HTA) were prepared in an oxygen plasma asher and in an electric furnace, respectively. The temperature in oxygen plasma ashing was estimated to be <200°C. Ashing in the electric furnace was performed at 815°C for 1 h in an atmosphere of static air. Sieving, heavy liquids, and magnetic separations, as well as hand picking under a binocular microscope were applied to concentrate the minerals and phases present in some coals. Dry water-soluble residues (DWSR) from Bulgarian and Ukrainian coals were generated from 100 g material of ground coal (≤ 100 μm). Each sample was placed in a glass tank with 1 l distilled water for 24 h. The suspension was periodically stirred and after that filtered. The pH value was potentiometrically measured in the generated water solution, and then the solution was placed in a drying furnace at 80°C until resulting DWSR.

Powder X-ray diffraction (XRD) analyses were

Table 3
Mean chemical compositions (based on 34 coal samples) for groups in increasing order of Cl and Br contents in coal ash (wt%)

Group	Proximate analysis (as received)				Ultimate analysis (daf)					High-temperature ash analysis									Cl in coal (ppm)	Cl in ash (ppm)	n^{a}	Br in coal (ppm)	Br in ash (ppm)	n^{a}
	W	VM	FC	A	C	H	N	O	S	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	TiO_2	SO_3						
Chlorine group																								
Low (Cl =≤ 660 ppm)	6.8	29.0	29.1	35.1	72.5	5.6	1.2	17.2	3.4	54.48	20.62	7.75	2.01	7.30	1.97	0.78	0.85	4.23	130	380	11			
Moderate (Cl = 970–1660 ppm)	5.2	33.0	47.6	14.1	77.7	5.1	1.3	14.9	1.0	53.78	22.09	5.51	1.84	8.83	1.21	0.60	1.09	3.90	200	1360	8			
High (Cl = 2250–3420 ppm)	5.3	32.8	50.8	11.1	81.0	5.2	1.2	11.8	0.8	54.95	24.09	6.33	1.72	5.87	1.39	0.90	1.18	3.43	320	2860	10			
Very high (Cl =≥ 3930 ppm)	5.2	32.9	49.2	12.8	81.3	5.3	1.2	11.2	1.0	54.66	26.17	8.15	1.26	4.26	1.29	0.88	1.20	2.14	710	5450	5			
r^{b}	− 0.28	0.07	0.36	− 0.29	0.36	0.01	− 0.08	− 0.35	− 0.18	0.13	0.26	0.07	− 0.30	− 0.25	0.01	0.06	0.29	− 0.28	1.00	0.83	34			
r^{c}	− 0.14	0.18	0.57	− 0.60	0.46	− 0.19	− 0.10	− 0.40	− 0.31	− 0.03	0.27	0.13	− 0.21	− 0.15	− 0.20	0.19	0.40	− 0.13	0.83	1.00	34			
Bromine group																								
Low (Br =≤ 28 ppm)	5.7	33.6	33.4	27.3	75.4	5.8	1.1	15.7	2.0	57.83	23.02	6.70	1.57	4.77	1.83	0.94	0.98	2.36				6	21	8
Moderate (Br = 46–120 ppm)	4.3	33.9	48.8	13.1	79.4	5.2	1.2	13.6	0.6	54.00	24.43	5.32	1.86	7.77	1.07	0.80	1.12	3.46				11	87	12
High (Br = 150–450 ppm)	8.5	31.7	42.8	17.0	75.9	5.2	1.2	15.5	2.2	50.64	21.88	7.91	1.92	9.06	1.20	0.81	1.09	5.49				52	240	10
Very high (Br =≥ 2220 ppm)	3.6	20.5	43.6	32.2	80.1	5.1	2.0	9.9	2.9	58.82	21.80	9.22	1.56	2.24	3.06	0.41	0.94	1.95				1230	4960	4
r^{d}	− 0.13	− 0.57	0.04	0.31	0.09	− 0.16	0.53	− 0.23	0.24	0.13	− 0.13	0.33	− 0.07	− 0.23	0.62	− 0.22	− 0.18	− 0.13				1.00	0.89	34
r^{e}	− 0.15	− 0.49	0.24	0.08	0.19	− 0.26	0.33	− 0.29	0.18	0.05	− 0.12	0.40	− 0.08	− 0.18	0.50	− 0.13	− 0.16	− 0.11				0.89	1.00	34

[a] Number of samples.

[b] Correlation coefficient with Cl in coal.

[c] Correlation coefficient with Cl in ash.

[d] Correlation coefficient with Br in coal.

[e] Correlation coefficient with Br in ash. The correlation coefficient between Cl and Br is 0.00 in coal and 0.03 in coal ash.The significant correlation coefficient is >0.33 and <-0.33 at 95% confidence level.

conducted for all coals, their density, magnetic and size fractions, DWSR and LTA using a diffractometer with CuK_α and CoK_α radiation. The XRD procedures have been described earlier [13,14]. Polarizing microscopes were used for optical observation under reflected and transmitted light. Polished sections were prepared by mounting samples in epoxy and duracryl pellets. Particles smaller than 63 μm from each sample and separated fraction were placed in glycerine immersion medium and observed under transmitted light. Scanning (SEM) and transmission electron microscopic (TEM) studies were carried out on electron microscopes equipped with an energy dispersive X-ray (EDAX) analyser. Samples for SEM examination and element determination were prepared from polished blocks and powder pellets, broken sample fragments and grain mounts. Mineral and phase identifications by SEM were based on morphological features and elemental compositions. Samples for TEM examination were prepared from alcohol suspensions of powder. Mineral and phase identifications by TEM were based on electron diffraction patterns and elemental composition. Semi-quantitative and quantitative determinations of the mineral and phase proportions in samples were performed using separation and ashing procedures, light microscopy (point counting method), XRD (semi-quantitative analysis) and SEM (micromorphometric particle analysis).

Chemical analyses for Cl and Br were conducted by X-ray fluorescence (XRF) on pelletized coal samples and standards. The XRF procedures have been described earlier [16]. The lowest limit of detection is 30 ppm for Cl and 2 ppm for Br, and the coefficient of variation is approximately 10%. The duplicate measurements for 20% of all the samples show that the reproducibility is similar and the deviation is normally $\leq 10\%$. Chlorine, Br and other elemental determinations were also carried out with SEM and TEM equipped with EDAX, wet chemical analysis and atomic absorption spectroscopy (AAS).

3. Results and discussion

3.1. Chlorine and bromine contents and concentration trends

The elements found in coals are commonly classified as major (>1 wt%), minor (1–0.1 wt%) or trace (<0.1 wt%) elements. The range of Cl for most coals is probably 50–2000 ppm [7] and rarely to about 1% in certain UK coals [8,17]. Bromine range from 0.5 to 90 ppm for most coals seems reasonable [7], whereas the main exceptions being some Belgian [18] and Canadian [7] coals with up to 6900 and 3550 ppm Br, respectively. The present results show that Cl and Br contents determined in the coal samples (Table 2) range from 50 to 1090 ppm (mean value 290 ppm) and from 2 to 1620 ppm (mean value 170 ppm), respectively. Hence, Cl and Br are trace and occasionally minor elements in the coal specimens studied.

The chlorine and bromine Clarke values for coals, rocks, soils, plants and waters are given in Table 1. Chlorine is present in all plants except conifers [3]. Coals have lower Cl and Br contents than algaes, angiospermae plants (for Cl) and deep-sea carbonates and clays. However, coals have higher Cl and Br concentrations in comparison with the other rocks, soils and mosses. This is due to the influence mainly of organic matter in coal, which contains some inherited biophilic Cl and Br. Nevertheless, certain organic and inorganic materials may also be a favourable environment for the capture, fixation and accumulation of these elements from aqueous solutions circulating in the swamp or through coal seams (see below). In addition, sea water is abundant in Cl and Br in comparison with fresh water (Table 1). The aforesaid observations emphasize a leading role of plants and sea water sediments as a precursor for Cl and Br enrichment in coal.

A number of coal deposits worldwide have Cl and Br concentrations greater than the respective Clarke values for coals. For instance, the highest contents (with concentrations ≥ 3 times greater than the Clarke values) show Taiheiyo coal for Cl, and Bulgarian (without Elhovo) and Ukrainian coals for Br. However, each deposit has individual plant constituents, regional, depositional and paleoenvironmental conditions which may cause a specification in enrichment or depletion of Cl and Br contents. Thus, the Cl and Br concentrations and modes of their occurrence may vary widely for different coals. Some vertical and horizontal variation of mobile Cl and Br within coal seams was also found [3,16,19–21].

The calculated Cl and Br concentrations in coal ashes (Table 2) range from 100 to 6890 ppm and from 9 to 11 100 ppm, respectively. On the basis of these values the samples studied are arranged in four major groups for comparison (Table 3), namely with low, moderate, high and very high concentrations. The specified groups were divided according to the Cl and Br content proximities for the samples into each group and to the distinct Cl and Br content intervals between the groups divided.

3.2. Relation between bulk chemical composition and chlorine and bromine contents

Chlorine and Br can correlate positively with each other in coal [21–23]. Such relationship indicates that these nonmetals may have been derived from the same source and may have similar modes of occurrence in coal [21]. A positive correlation between Cl and Na or a clear lack of correlation between these elements have been reported for different series of Illinois coals [24]. Negative correlations between Cl, Na, and moisture for US coals have been also detected [21].

The present results show that there is no correlation between Cl and Br in the coals and coal ashes studied (Table 3). The samples in the fourth Cl group (with very high Cl contents) show maximum concentrations of C,

Table 4
Mean ratios of some chemical components for groups in increasing order of Cl and Br contents in coal ash (wt%)

Group	Ratio				I^a	n^b
	SiO_2/Al_2O_3	$(MgO + CaO)/K_2O + Na_2O)$	CaO/MgO	K_2O/Na_2O		
Chlorine group						
Low (Cl $=\leq$ 660 ppm)	2.69	5.09	3.40	4.03	5.46	11
Moderate (Cl = 970–1660 ppm)	2.45	6.53	4.69	3.17	4.87	8
High (Cl = 2250–3420 ppm)	2.37	4.19	3.02	5.45	10.00	10
Very high (Cl $=\geq$ 3930 ppm)	2.14	3.33	3.27	1.44	7.62	5
r^c	− 0.17	− 0.23	− 0.14	0.03	0.19	34
r^d	− 0.28	− 0.13	− 0.05	− 0.14	0.04	34
Bromine group						
Low (Br $=\leq$ 28 ppm)	2.56	2.81	3.18	5.72	11.41	8
Moderate (Br = 46–120 ppm)	2.36	5.84	4.07	2.00	5.48	12
High (Br = 150–450 ppm)	2.41	6.98	4.11	2.87	5.57	10
Very high (Br $=\geq$ 2220 ppm)	2.70	1.12	1.53	8.23	6.12	4
r^e	0.17	− 0.24	− 0.32	0.23	− 0.06	34
r^f	0.11	− 0.20	− 0.23	0.13	− 0.08	34

[a] Detrital–authigenic index = $(SiO_2 + Al_2O_3 + K_2O + Na_2O + TiO_2/Fe_2O_3 + MgO + CaO + SO_3)$.
[b] Number of samples.
[c] Correlation coefficient with Cl in coal.
[d] Correlation coefficient with Cl in ash.
[e] Correlation coefficient with Br in coal.
[f] Correlation coefficient with Br in ash.

Al_2O_3, Fe_2O_3 and TiO_2 (Table 3). An interesting case is the gradual increasing of Cl concentrations with decreasing SiO_2/Al_2O_3 ratios for the specified Cl groups (Table 4). The lower value of this ratio is informative for coals formed under stable conditions of deposition. Coals or their ashes in the group with very high Br contents reveal maximum values of A, C, N, S, SiO_2, Fe_2O_3, K_2O, SiO_2/Al_2O_3, and K_2O/Na_2O (Tables 3 and 4). Some of the above mentioned indications were confirmed by the calculated correlation coefficients (Table 3). For instance, significant positive correlations between Cl and FC, C, TiO_2, and between Br and N, Fe_2O_3, K_2O; as well as significant negative correlations between Cl and A, O, and between Br and VM in coals or coal ashes were found (Table 3). Due to the wide variety of coal samples used such significant correlations are infrequent cases, but of great interest for the consideration of some basic relationships in coal. Content distributions of some important components versus Cl and Br concentrations are illustrated in Fig. 1.

The data show that there are distinct differences in the association of Cl and Br with the bulk chemical composition of coals and coal ashes. However, the total chemical composition of HTA is insufficient for a reliable genetic explanation of Cl and Br enrichment in coal. Most important are the modes of Cl and Br occurrence (minerals and phases), their amount and origin in coal, as well as their behaviour during coalification process.

3.3. Relations between coal rank, age, geographic location and chlorine and bromine contents

The Clarke values for Cl in bituminous–anthracitic coals are higher than in lignitic–subbituminous coals [5]. For example, the concentration of Cl gradually increases with increase of rank for Canadian coals [25]. Skipsey [17] also indicated that rank has a major influence on Cl contents and illustrated a decline in Cl above ~86% C^{daf}. The author suggested that the low porosity offered an explanation for the limiting value for Cl-holding capacity in high-rank coals [26]. The present results confirmed that Cl contents in the coal samples studied depends significantly on the coal rank (62.9–86.6% C^{daf}). For instance, Cl has relatively strong positive correlations with FC and C (Table 3 and Fig. 1). Bromine contents in coal depend on the coal rank to a lesser extent because of the relatively weak positive correlations with these components.

According to the age of coals it can be noted that Permian and Carbonic coals are normally more enriched in Cl than younger coals of Cretaceous and Tertiary ages. More abundant Cl concentrations were also found in the older US coals [27]. In contrast, coals of Tertiary age are commonly more abundant in Br than older coals. An exception is the Carbonic Donbass coal, which is highly enriched in Br.

It was noted that Cl contents of British [17] and United States [21] coals varied in a wide range depending on their geographic locality. The present samples studied were divided in five coal groups (Bulgaria, Australia, North America, Japan and others) according to their spatial distribution (Table 5). The results show that the geographic location of coal deposits affects the Cl and Br contents strongly. Some indicative Cl and Br content similarities and distinctions are observed for the geographic coal groups specified. For example, the orders of decreasing abundance (mean values) are: Australia > Japan > North America >

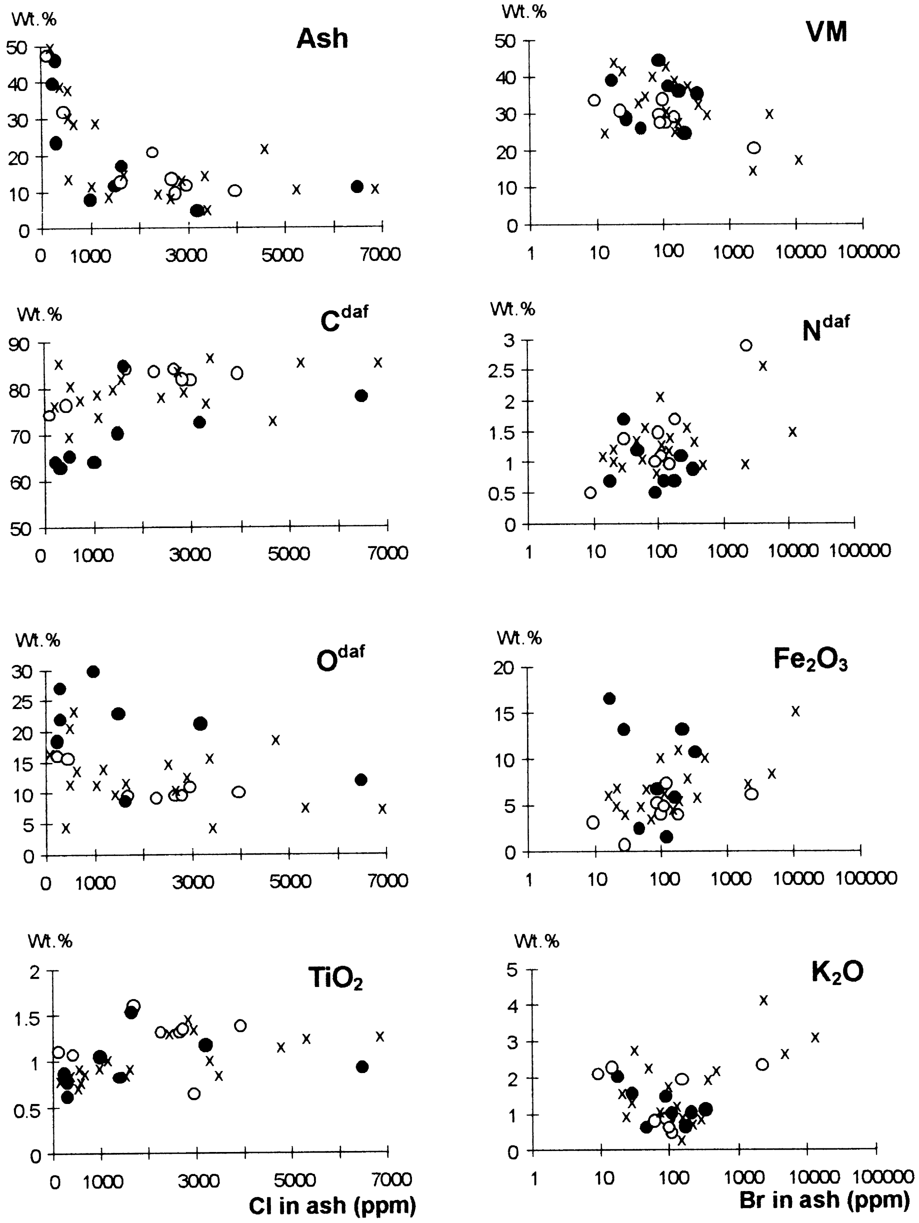

Fig. 1. Distributions of some chemical components in coals and high-temperature ashes versus Cl and Br contents (ash basis): ○, samples with the highest detrital tendency ($I > 8$) of ash; ●, samples with the highest authigenic tendency ($I < 3$) of ash; ×, samples with an intermediate tendency of ash.

Table 5
Mean Cl and Br contents for coal groups divided according to the geographic locality of 34 coal samples used (ppm)

Coal group	Coal		Coal ash (A^d basis)			n^a
	Cl	Br	Cl	Br	Cl/Br	
Bulgaria	150	530	420	1390	1.6	7
Australia	450	18	3560	150	31.0	8
North America	230	10	2270	110	54.3	10
Japan	330	8	1560	40	51.0	6
Others	320	550	2480	3750	20.0	3
Mean for all groups	300	220	2060	1090	31.6	5

[a] Number of samples.

Bulgaria for Cl; and Bulgaria > Australia > North America > Japan for Br (Table 5). The different sequences and lack of correlation between Cl and Br indicate that these elements may have been derived from different sources and may have various modes of occurrence in these groups. The present results emphasize again some distinct differences in the association of Cl and Br in coal.

3.4. Relations between ash yield, mineral composition and chlorine and bromine contents

Negative correlations of ash yield with Cl [18,21,28] and Br [18,19,22,23,29] have been mentioned. The present study confirmed the observation for Cl, while Br shows a

Table 6
Mean mineral proportions in the crystalline matter of coal groups (based on XRD of 34 coal and LTA samples) in increasing order of Cl content in coal ash (vol.%)

Mineral	Chlorine group			
	Low (Cl =≤ 660 ppm)	Moderate (Cl = 970–1660 ppm)	High (Cl = 2250–3420 ppm)	Very high (Cl =≥ 3930 ppm)
Silicates				
Quartz	35–36	36	34–35	33
Kaolinite	7	9–10	10	13
Illite	4	4	3–4	4–5
Montmorillonite	1–2	1–2	1–2	1–2
Biotite + muscovite + chlorite	2–3	3–4	3–4	4
Plagioclase + K-feldspar	5–6	3–4	3–4	4
Zeolite + amphibole	2–3	2–3	2–3	2
Oxides and hydroxides				
Hematite + goethite + lepidocrocite	4	6	5	6
Spinel	< 1	< 1	< 1	< 1
Corundum + diaspore	3	2–3	3–4	2–3
Rutile	1	1–2	1–2	1–2
Portlandite	< 1	< 1	< 1	< 1
Brucite	1–2	2	1–2	1–2
Carbonates				
Calcite + aragonite	8–9	7–8	7–8	5–6
Dolomite + ankerite	2–3	3	3–4	1–2
Siderite	1	1–2	2–3	2
Magnesite	< 1	< 1	< 1	< 1
Witherite	1	< 1	1–2	1
Sulphides				
Pyrite + marcasite + pyrrhotite	4–5	3–4	3–4	4
Sulphates				
Gypsum + anhydrite	4–5	3	3	3
Jarosite + rozenite + melanterite + coquimbite	3–4	3–4	3–4	2–3
Alunite	1–2	1	< 1	< 1
Hexahydrite	1–2	1	1	1
Barite	1	1	< 1	< 1
Phosphates				
Apatite + vivianite + goyazite	2	3	2–3	3–4
Number of samples	11	8	10	5

relatively weak positive correlation with ash yield (Table 3). The total ash and mineral contents, as well as the correlation trends of an element with ash yield are informative, but they have less significance in understanding the actual element association and affinity in coal. The ash in coal comprises a sum of various genetic ash classes and subclasses and their distribution in coal have to be considered separately [15]. An approximate index based on the chemical composition of HTA samples has been used [14] to assess dominant detrital or authigenic ash nature of coal samples used. The index (*I*) does not indicate (Table 4) any significant relationships between the ash nature and Cl and Br concentrations. However, certain distinct sub-trends for Cl and Br with the dominant authigenic or detrital tendency of ash can be distinguished (Fig. 1).

In general, the qualitative composition, mode of localization and supposed dominant genesis of the minerals in coal show that sulphides, sulphates, carbonates, chlorides, and some phosphates and clay minerals (mainly kaolinite and occasionally illite) are commonly authigenic in origin. Minerals such as quartz, feldspars, mica, Fe oxyhydroxides, other silicates and oxyhydroxides, and some phosphates and clay minerals (mainly montmorillonite and illite) are considered to have mostly detrital nature in coal [14,30–32]. It should be stated that organics, authigenic, heavier and especially accessory minerals in coal are normally concentrating phases for most of the trace elements. However, the accessory minerals are commonly present in trace quantities and their contribution to the enrichment of trace elements in the whole coal is rarely of great significance [11]. Therefore, the distribution of a number of trace elements, including Cl and Br, is controlled mostly by the abundant organic matter and clay minerals, and in some cases by sulphides and carbonates, which are dominant carriers and matrix phases of trace elements in coal. Table 6 shows that coals with very high concentrations of Cl are enriched in kaolinite, illite, mica and phosphates, and depleted in carbonates. Some of these observations are in consistent with the concentration trends for Al_2O_3, CaO and MgO (Table 3). Table 7 reveals that coals with very high concentrations of Br are enriched

Table 7
Mean mineral proportions in the crystalline matter of coal groups (based on XRD of 34 coal and LTA samples) in increasing order of Br content in coal ash (vol.%)

Mineral	Bromine group			
	Low (Br =≤ 28 ppm)	Moderate (Br = 46–120 ppm)	High (Br = 150–450 ppm)	Very high (Br =≥ 2220 ppm)
Silicates				
Quartz	43	34–35	28–29	37–38
Kaolinite	7	10–11	10	8–9
Illite	4	4	3–4	5
Montmorillonite	1	1–2	2	1–2
Biotite + muscovite + chlorite	3	3–4	3–4	3–4
Plagioclase + K-feldspar	5–6	3–4	4–5	4
Zeolite + amphibole	2–3	3	2–3	2
Oxides and hydroxides				
Hematite + goethite + lepidocrocite	5	6	5	3–4
Spinel	< 1	< 1	< 1	1
Corundum + diaspore	2–3	3	4	1–2
Rutile	1	1–2	1–2	2
Portlandite	< 1	< 1	< 1	0
Brucite	1	1–2	1–2	2
Carbonates				
Calcite + aragonite	7	7–8	8–9	6–7
Dolomite + ankerite	2–3	3–4	2	3
Siderite	1–2	1–2	2	2
Magnesite	< 1	< 1	< 1	< 1
Witherite	< 1	1	2	< 1
Sulphides				
Pyrite + marcasite + pyrrhotite	3–4	3	5	4–5
Sulphates				
Gypsum + anhydrite	4–5	3	3–4	2–3
Jarosite + rozenite + melanterite + coquimbite	2–3	3–4	3–4	4
Alunite	1	1	1	1–2
Hexahydrite	1	1	1–2	1
Barite	< 1	1	1	1
Phosphates				
Apatite + vivianite + goyazite	2	2–3	3	3–4
Number of samples	8	12	10	4

in illite, rutile (TiO_2), brucite ($MgOH_2$), phosphates, Fe-sulphides -sulphates. Some of these observations are also in consistent with the concentration trends for K_2O and Fe_2O_3 (Table 3). These results show that the mineral composition has certain influence (see below) on Cl and Br contents and distributions in coal.

3.5. Water-soluble chlorine and bromine components

The water extraction can give to a certain extent preliminary information of some elemental modes of occurrence in coal. Chlorine and bromine anions exhibit high migration ability during exogenetic processes. For example, aqueous leaching experiments have shown that a large proportion of Cl can be washed out of coals [8]. These experiments have demonstrated differences in the rates of release of Na and Cl, and suggested that both elements were largely independent of each other [33]. For instance, the fraction of the chlorine extractable by water from Illinois coals was mostly in the range 30–35% and Cl was more than equivalent to the water-soluble Na and K found [24]. Coal microstructure factors such as pore-size distribution, permeability and wettability also control the ease of access of water to the internal surfaces for Cl removability [8,34].

For this purpose, more detailed studies were performed on DWSR derived from seven Bulgarian and Ukrainian coals (Table 8). The generated water solutions show pH in the range 2.2–7.5 (from highly acid to slightly alkaline), whereas the amount of the resulted DWSR is in the range 0.2–8.4% (from salty to brine total mineralization). The detected elemental composition of DWSR (Table 8), in decreasing order of significance, is normally Ca, S, Mg, Na, Fe, K, Si, Cl, Al, Br, plus others (O, H, C, N, P, trace elements). The water-extractable Cl and Br from coal samples were in the range <1–35% and <1%, respectively. This leaching indicates that substantial Cl parts (13–35%) in five samples (mainly with lower coal rank) are related to the presence of water-soluble salts and organic materials. In contrast, Br behaviour for the all samples studied can be explained by the occurrence in strongly bound organic

Table 8
Chemical composition (wt%) for DWSRs generated from some coals (in increasing order of C^{daf})

Sample	Quantity	pH	Cl[a]	Leached[b] Cl	Br[a] ppm	Leached[b] Br	Ca[c]	S[a]	Mg[c]	Na[d]	Fe[d]	K[d]	Si[e]	Al[e]	Others
1. Maritza West	3.7	6.8	0.14	35	< 5	< 1	26.0	15.4	5.5	2.6	0.03	0.15	≤ 0.1	≤ 0.1	50.0
2. Sofia	1.3	7.2	0.16	26	25	< 1	24.2	8.3	4.3	0.5	0.06	0.22	≤ 0.1	≤ 0.1	62.1
4. Maritza East	8.4	2.2	0.01	4	< 5	< 1	8.1	18.0	5.4	3.2	2.05	0.07	≤ 0.1	≤ 0.1	63.0
5. Bobov Dol	0.9	5.2	0.59	15	12	$\ll 1$	16.0	15.7	5.9	7.3	0.07	0.77	0.5	0.3	52.9
6. Pernik	1.2	4.1	0.10	24	24	$\ll 1$	13.4	15.7	6.3	6.6	1.35	0.88	0.9	0.4	54.4
7. Balkan	0.6	6.7	0.32	13	30	$\ll 1$	26.0	17.4	10.3	2.9	0.05	0.91	1.3	≤ 0.1	40.7
34. Donbass	0.2	7.5	0.05	< 1	nd[f]	nd[f]	28.3[e]	23.0[e]	≤ 0.1[e]	0.9[e]	0.3[e]	0.3[e]	0.7	≤ 0.1	46.3

[a] Determined by XRF.
[b] Percentage of the total content leached from the initial coal sample.
[c] Determined by wet chemical analysis.
[d] Determined by AAS.
[e] Determined by SEM–EDAX.
[f] No data.

and inorganic water-insoluble forms. A similar observation for Br was also found [12]. The elemental X-ray map distributions in the Bobov Dol DWSR confirmed that the water-soluble Cl and Br have strong association with extractable S, Ca, Na, Mg, K, P, Fe and Al (Fig. 2). The additional XRD, SEM and TEM studies on the all DWSR generated show that the samples are composed mainly by gypsum, to a lesser extent by minerals such as bassanite ($CaSO_4 \cdot 0.5H_2O$), anhydrite, hexahydrite ($MgSO_4 \cdot 6H_2O$), calcite, barite ($BaSO_4$), jarosite ($K–NaFe_3(SO_4)_2(OH)_6$), szomolnokite ($FeSO_4 \cdot H_2O$), sylvite, halite, carnallite ($KMgCl_3 \cdot 6H_2O$), Na–K sulphates, phosphates, and rarely by kieserite ($MgSO_4 \cdot H_2O$), polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$), opal ($SiO_2 \cdot nH_2O$), and cristobalite ($SiO_2$) (Figs. 2 and 3a–c). Traces of fine-dispersed (<5 μm) mechanical contaminations, namely inclusions of feldspars (Fig. 3b), kaolinite and mica were also detected in DWSR. Most of the listed minerals are also originally present in these coals [32]. Interesting phenomena are the close composition to stoichiometric sylvite and parallel enrichment trends for water-soluble K, Cl and Br detected in most of the DWSR samples (Table 8). Nevertheless, the multicomponent composition of DWSR indicates a more complex nature of halogen elements in coal (see below).

3.6. Modes of occurrence

Elements may occur in both organic and inorganic occurrences in coal and each element has dominant associations and affinities to different phases in coal. The present data reveal that Cl and Br in coal may occur, in decreasing order of significance, as organic compounds, as impurity components in the crystalline and amorphous inorganic constituents, in the fluid constituents, and as discrete minerals. Some Cl and Br occurrences are illustrated in Figs. 2–4.

3.6.1. Chlorine and bromine as element-organic compounds

Organically bound Cl or Cl dominantly associated with the organic coal fraction have been emphasized [7,16,21,22–24,28,29]. Most of the Cl is fairly evenly distributed within the vitrinite, whereas Cl levels in the exinite and inertinite are similar, but significantly lower than that in vitrinite [9]. It was also assumed an equal distribution between organic and inorganic forms of Cl in some British, US and Canadian coals [35–37]. It was supposed that Cl associates with organic matter: in a water-insoluble covalent combination as organochlorine compounds [5,8,9]; or as ions adsorbed on the coal's surface, possibly through an ion exchange linkage [9,24,33,35,38,39] with basic surface groups [33] and nitrogen functional groups [20,34] such as amino [35] or hydrochlorides of pyridine bases [36].

It is generally agreed that Br is predominantly associated with organic matter in coal [7,16,19,22,23,28,29,37], especially in the vitrinite concentrates [40]. It was found that Br normally was among the elements with the highest organic affinities in US coals [1]. It was stated that the dominant part of Br probably occurs as organic complexes in coal [6].

Most of the studied coals could have major organic Cl and Br association. For instance, Cl has significant negative correlation with ash yield, and positive correlation with FC and C (Table 3). Bromine also shows a dominant organic affinity, however, this element also demonstrates a positive correlation with ash yield, Fe_2O_3 and K_2O (Table 3). Iron is a characteristic element of sulphides, sulphates and oxides in coal, while potassium is a typical element of illite, feldspars, jarosite and sylvite in coal (see below). In addition, organically bound Br probably has similar modes of occurrence to N because there is a strong positive correlation between both elements (Table 3). Nitrogen is mostly bound organically in pyrrolic, pyridinic and quaternary functional groups in polycyclic aromatic compounds in coal [41,42].

Two of the most enriched in Cl and Br coal samples (Bobov Dol and Donbass) were studied in detail by SEM and TEM, for a confirmation of some of the above-mentioned indications. Both elements, in particular Cl, were found to be uniformly distributed and dispersed in the relatively homogeneous organic matter. SEM observations

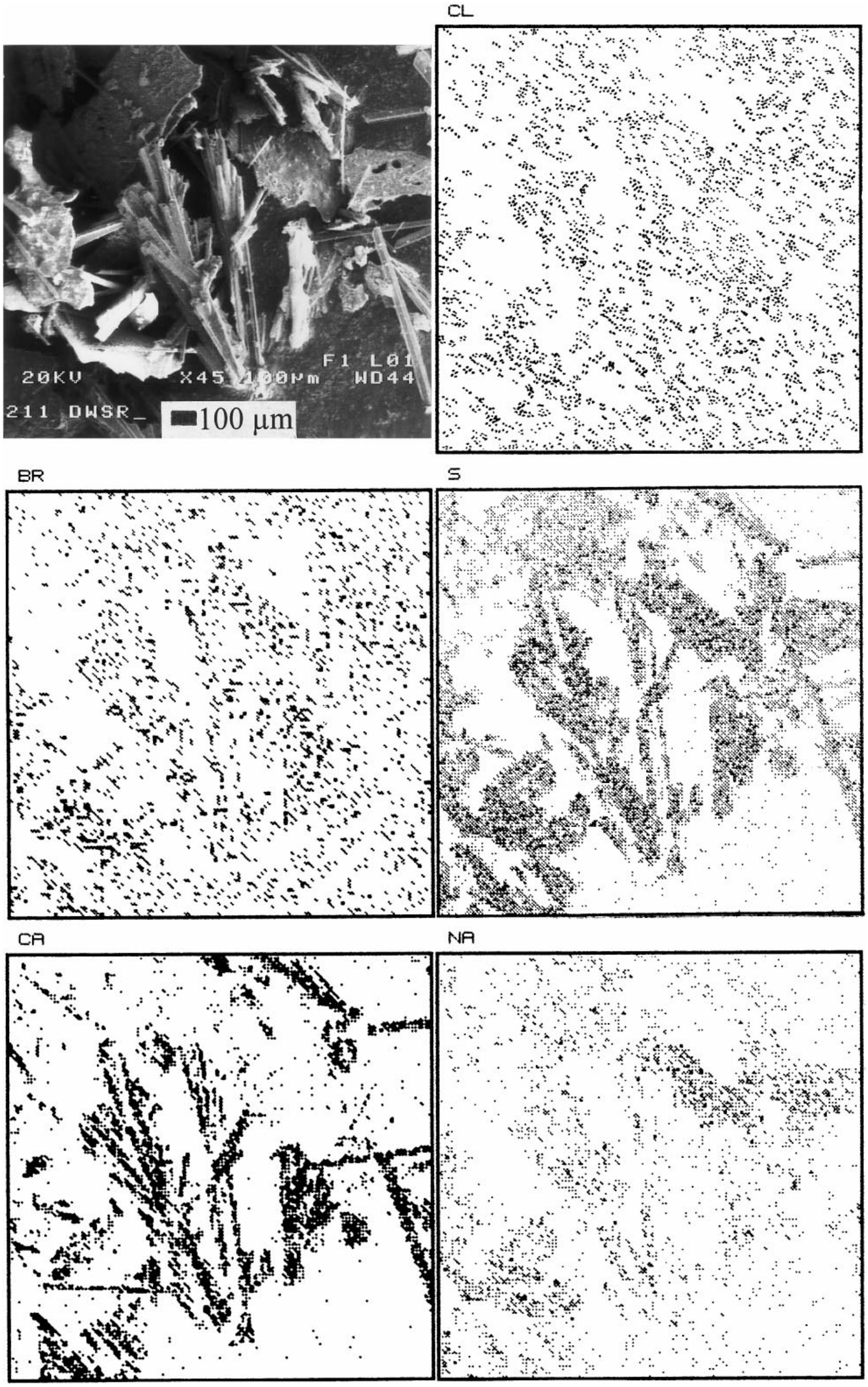

Fig. 2. SEM–EDAX dot image with an elemental distribution of Cl, Br, S, Ca, Na, Mg, K, P, Fe, and Al in the DWSR generated from Bobov Dol coal.

and electron microprobe analyses performed on several selected, visibly homogeneous vitrinite particles demonstrate relatively low variations in the contents of Cl and Br. It is also noticeable that the established contents of Cl and Br are in the same order of magnitude to their bulk values in both coal samples. Only some analyses exhibit a greater variation in Cl and Br contents, which suggests the presence of finely sized mineral inclusions of Cl- and Br-bearing minerals (see below). TEM observations and microprobe analyses of a great number of visible homogeneous

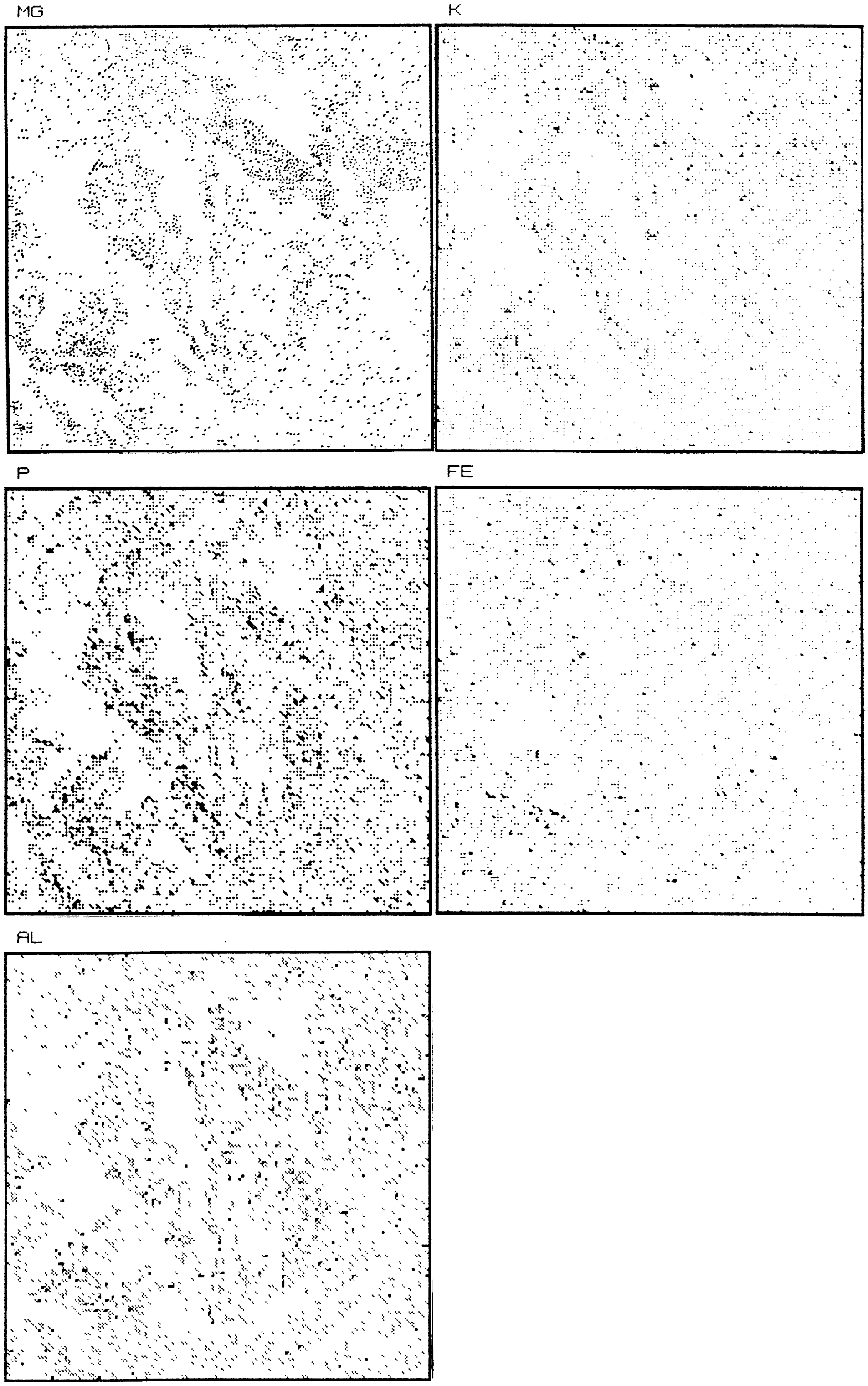

Fig. 2. (*continued*)

organic particles also show that the concentrations of Cl and Br are occasionally above the detectable limit. These particles transmitted for the electron beam do not have mineral inclusions above 0.01 μm in size.

Broken Bobov Dol sample fragments enriched in organic and inorganic matter were also studied for an illustration of the aforesaid observations. X-ray map distribution for Cl and Br (Fig. 4) clearly shows that Cl, and to a lesser extent Br, exhibit a relatively homogeneous distribution and association with characteristic organically bound elements

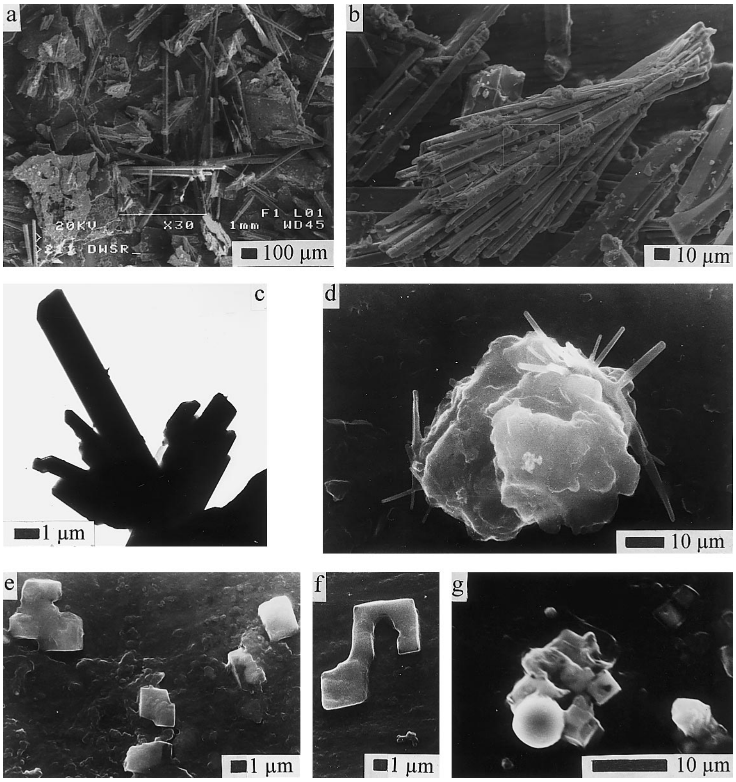

Fig. 3. (a) SEM image of a general view of DWSR generated from Bobov Dol coal, secondary electrons; (b) SEM image of a chlorine-containing radial gypsum aggregate and K-feldspar grains adhered onto its surface in the DWSR generated from Donbass coal, secondary electrons; (c) TEM image of a chlorine-containing prismatic gypsum aggregate in the DWSR generated from Donbass coal; (d) SEM image of an epigenetic chlorine-containing polyhalite aggregate in Bobov Dol coal, secondary electrons; (e) SEM image of epigenetic cubic sylvite and halite crystals in Bobov Dol coal, secondary electrons; (f) SEM image of an epigenetic cubic sylvite crystal with a skeletal and step-shaped growth in Bobov Dol coal, secondary electrons; (g) SEM image of epigenetic sylvite and halite crystals covering a volcanic alumino-silicate glass sphere in Bobov Dol coal, secondary electrons.

such as S, P, Mg, Ca and Na throughout the coal matrix. A relatively equal distribution between organic and inorganic associations of Cl in this fragment can also be distinguished. However, Br also reveals a strong affinity to some inorganic matter (see below). The summarized observations suggest that these elements could have a dominant organic occurrence and association in water-soluble (mainly ionic) and water-insoluble (ionic and covalent) element–organic combinations. The latter combination is more characteristic of high-rank coals (Table 8). The exact organic location of Cl and Br is not certain, but they are probably bound preferentially in carboxyl (dominantly for Cl) and nitrogen (mainly for Br) functional groups, according to their association and correlation trends.

3.6.2. Chlorine and bromine as impurities in the mineral matter

Chlorine and Br may occur isomorphously or in defect sites of crystal structures. They could be also present as ion-exchanged and adsorbed elements of the mineral matrix, or adsorbed onto mineral surfaces. Oakey et al. [33] state that trace Cl amounts are present in association with the aluminosilicate (clay) minerals. A significant positive correlation between Cl and Ca indicating the possible substitution of Cl in carbonate mineral structures [37]was also found. Small Br amounts could be associated with Fe oxides and clays [7].

Coals with very high Cl contents are enriched in kaolinite, illite, mica and phosphates (Table 6). The occurrence of Cl as an impurity in the mineral matter may be the case for the aforesaid minerals. For example, Cl was detected by microprobe analyses as an impurity (Fig. 3d) in minerals such as clay minerals and mica (≤ 2.0 wt%), feldspars (≤ 2.3 wt%), polyhalite (1.4–2.0 wt%), gypsum (≤ 0.4 wt%), siderite (≤ 0.2 wt%), and trace in other carbonates, sulphates and phosphates in Bulgarian and Ukrainian coals. Certain replacements of OH group by Cl in apatite can occur. Nevertheless, some Cl may be present occasionally as fine, discrete phases (mainly chlorides below 1 μm in size) in the aforesaid host mineral matrices (see below).

Coals with very high Br contents are enriched in illite, brucite, phosphates, and Fe sulphides-sulphates (Table 7). The occurrence of Br as an impurity in the mineral matter is probably similar to that of Cl. Fig. 4 shows that Br distribution is parallel to typical inorganic elements such as Si, Al, Fe, and K. These results emphasize a characteristic Br association with illite and to a lesser extent with mica, kaolinite

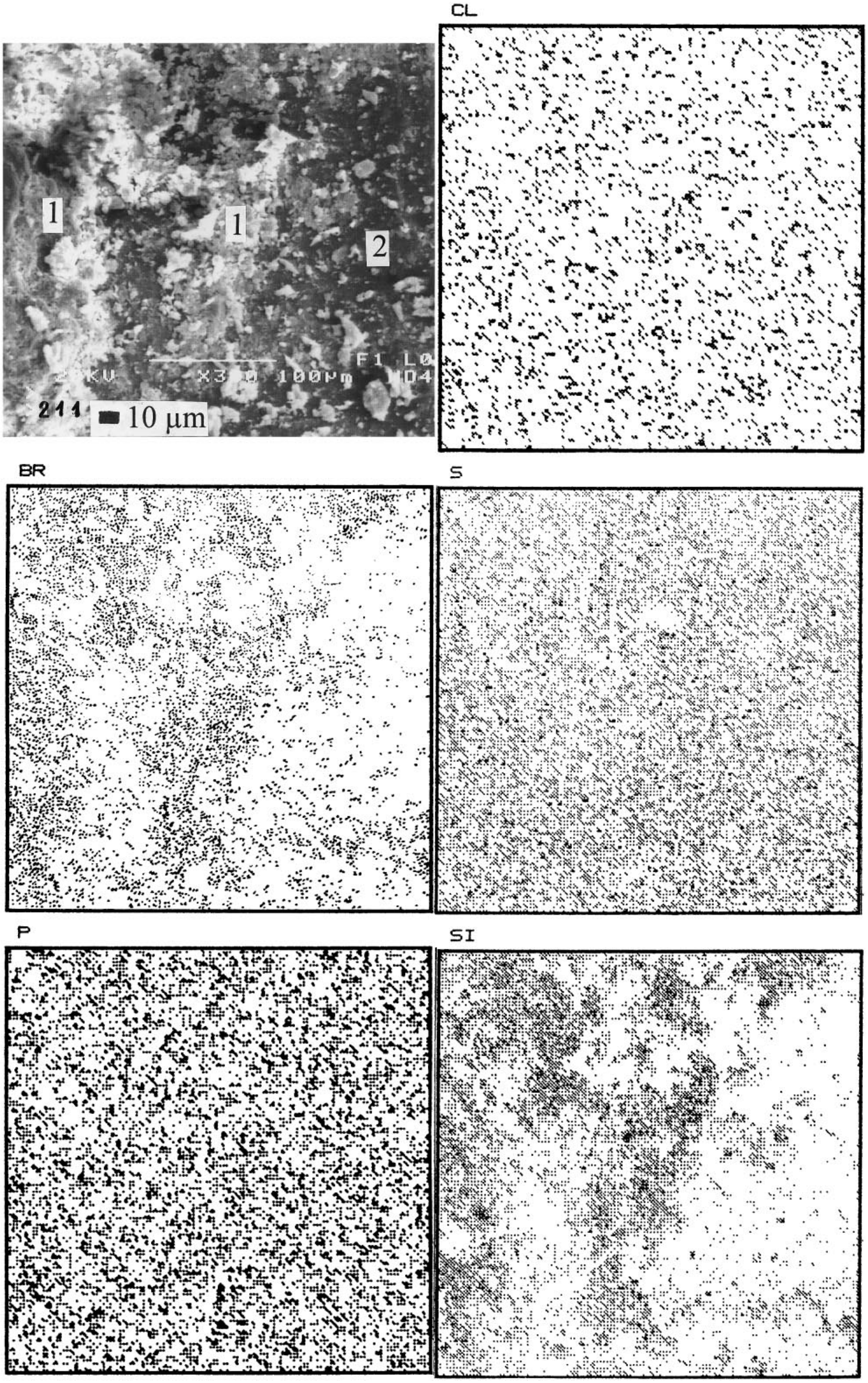

Fig. 4. SEM–EDAX dot image with an elemental distribution of Cl, Br, S, P, Si, Al, Fe, K, Mg, Ca, and Na in Bobov Dol coal. 1, clay minerals (illite and kaolinite); 2, vitrinite substance.

and Fe-bearing minerals. This observation also confirmed the significant correlations between Br, K and Fe detected by the bulk chemical data (Table 3).

It should be stated that water molecules and hydroxyl groups in clay minerals, mica, sulphates, hydroxides and phosphates, as well as exchangeable cations in clay minerals play a leading role for the inorganic occurrence and distribution of Cl and Br ions. The similar ionic radii of Cl and Br emphasize the possibility for considerable isomorphic substitutions of

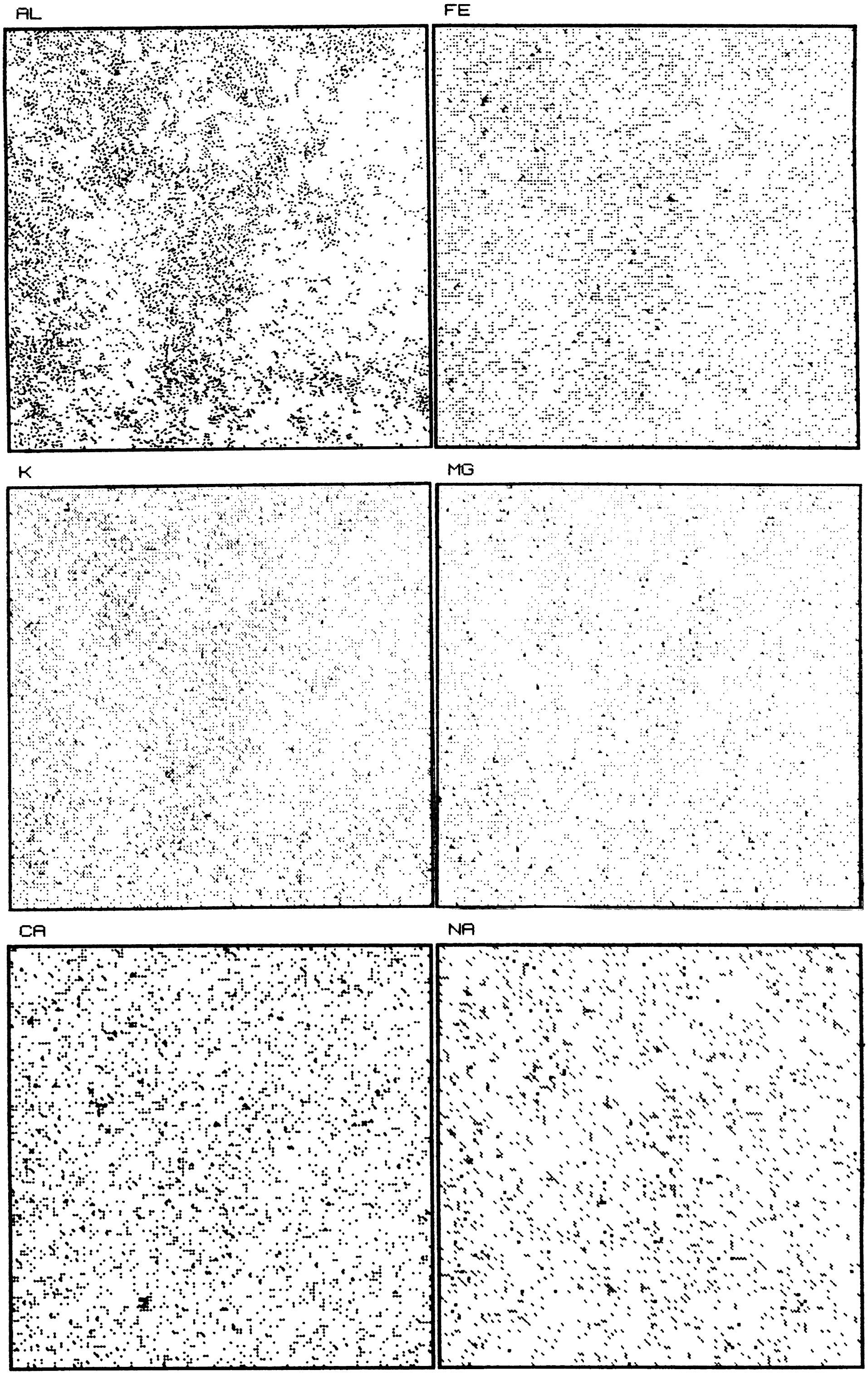

Fig. 4. (*continued*)

both elements in the aforesaid minerals. For example, a high sorption capacity of montmorillonite and mixed-layered minerals for Cl and Br was detected during purification of waste waters contaminated with these elements [43].

3.6.3. Chlorine and bromine as major components in the mineral matter

Chlorine was identified as discrete finely dispersed accessory minerals such as sylvite and to a lesser extent halite, chlorapatite and probably carnallite in some coals. The chloride minerals found are authigenic and mainly epigenetic in origin. Sylvite and halite occur as individual or clusters of cubic 3–10 μm crystals in cleats and fractures parallel to stratification bands (Fig. 3e–g). These chlorides are occasionally associated with volcanic glass (Fig. 3g) and epigenetic sulphates such as gypsum and polyhalite [30,32]. Some of the chloride crystals may also be a product of pore-water crystallization like some sulphates (see below). The present results emphasize that when there is a high enrichment of Cl in lower-rank coals a significant occurrence of this element could be as finely dispersed sylvite, halite, and complex Na–K–Ca–Mg–Fe chlorides and sulphates.

There is no direct evidence for discrete mineral forms of Br in coal until now. Proper Br minerals in coal such as bromides were not detected in this study. However, the similar ionic radii of Cl and Br suggest the possibility for extensive isomorphic substitutions in halogen mineral types. For example, it was emphasized that Br is a characteristic isomorphic impurity in sylvite [44]. It can be seen that the detected relationships between K, Cl and Br in the generated DWSR are in accordance with the aforesaid identification.

3.6.4. Chlorine and bromine as impurity components in the inorganic amorphous matter

The volcanic glass present in some coals has dominantly an aluminosilicate or titanium-rich composition with minor contents of Fe, Ca, Na, Mg, P, K, and S. Trace contents of Cl ($\leq$0.2 wt%) was also found in some volcanic aluminosilicate spheroids in the Bobov Dol coal. It seems that limited Cl and Br proportions may associate with volcanic glass, as well as with cryptocrystalline, metacolloid and gel phases characteristic of clay minerals, phosphates, silica, and hydroxides in some coals.

3.6.5. Chlorine and bromine in the fluid constituents

Chlorine ions are believed to be associated with solution in the inherent moisture in the coal pore structure [33]. Saunders [9] claimed that Cl could exist as sodium chloride solution residing within the microporous structure of the vitrinite. It may be that coal is behaving like a sponge with its internal surface coated with a layer of “brine” solution in which the chloride ions are dissolved [8]. Even more, it was stated recently that there is one major, universal mode of Cl occurrence in higher-rank coals: chloride anions in moisture anchored to the surface of micropores in macerals by organic ionic complexes, such as quaternary amine groups and alkali carboxyl complexes [10]. In this case, significant positive correlations between moisture and Cl or Br should occur. However, such relationship was not found in the present (Table 3) and other [21] studies. Further, negative correlations were detected between these components in both investigations, and Cl in the high-rank coal is almost entirely in water-insoluble forms (Table 8). The recent study shows that the actual modes of Cl and Br occurrences in coal are more complex than one simplified or universal form of combination.

Naturally, elements such as Ca, S, Mg, Na, Fe, K, C, P, and halogen elements may occur as ions dissolved in the pore water of coal. These highly mineralized solutions can form water-soluble: (1) carbonates; (2) sulphates; and later (3) chlorides (a sequence of precipitation from less soluble to high soluble phases) due to changes in physico-chemical conditions in the system. Additionally, some limited Cl and Br proportions may also occur in gas–liquid inclusions of detrital and authigenic apatite, quartz, zircon and other inorganic and organic minerals and phases. For example, Cl is one of the most important anions in gas–liquid inclusions of minerals [44]. Detrital apatite and quartz crystals, as well as volcanic glass phases with characteristic fluid inclusions were often observed in coal [30–32].

3.7. Genetic features of chlorine and bromine in coal

A generalized review of “salt coals” worldwide emphasizes that Cl enrichment in coal is normally associated with: favourable physical and chemical properties of organic matter; paralic basins; arid conditions; surrounding halogen-bearing rocks; volcanic activity; higher metamorphic progression; and epigenetic mineralization [45]. Some of these observations were confirmed in the present study.

Plants, in particular algaes and angiospermae plants, are enriched in Cl and Br. Hence, the coal-forming vegetation is a significant initial source of biogenetic Cl and Br in coal. The coalification process and metamorphic progression are related to changes in temperature, pressure, pH and Eh that lead to various mineral crystallizations, organic and inorganic phase transformations and migration of mobile components within and outside the coal seams. So, the biogenetic Cl and Br are unstable and should decrease their initial proportions under the action of aqueous solutions and acid products at higher temperature and pressure during biochemical and geochemical stages of coalification, as noted earlier [8,46]. For example, the significant negative correlation between Cl and O indicates that probable weathering can deplete some organically bound Cl. Similar observations for Cl and Br have been reported elsewhere [22,47].

The concentrations of Cl and Br in coal seams are modified because the circulating solutions introduce and leach such mobile elements. As a rule, the lower-rank coals are enriched in water-soluble salts (sulphates, carbonates, chlorides), organically bound, ion-exchanged and pore-water associated elements, including Cl and Br. A significant part of these unstable phases in a coal seam is modified, dissolved and washed out, whereas another part is redistributed and captured in new-formed and more stable silicate and oxyhydroxide mineral species (illite, kaolinite, chlorite, muscovite, Fe oxyhydroxides) during coalification. Thus the supply and leaching behaviour of Cl and Br during peat formation, coalification and metamorphic progression are responsible for essential changes in the final concentrations of Cl and Br in coal. During syngenesis, chlorine-containing solutions could have percolated through the seams adjacent to the salt-bearing strata [8]. However, it seems more likely that most of the Cl was introduced by saline strata waters during diagenesis [48] and in particular during epigenesis, after the establishment of coal rank [8,17,33]. Chlorine levels represent a state of equilibrium between the coal and associated ground water [8,20]. This element from ground waters, which become increasingly brackish with depth, entered coals after their formation [8]. The concentration of dissolved Cl ions may also increase with increasing depth due to evaporation of highly mineralized solutions into gases [49]. The aforesaid observations are somehow in accordance with the increased Cl concentrations in relatively higher-rank and older coals. Nevertheless, some lower-rank and younger coals influenced by epigenetic mineralization can also by highly enriched in Cl and Br. For example, a characteristic feature of the subbituminous Miocene-upper Oligocene Bobov Dol coal is the intensive and complex epigenetic mineralization (quartz, sulphides, sulphates, carbonates and chlorides) formed by infiltration of low-temperature hydrothermal solutions enriched in halogen elements [30]. The origin of solutions for this complex epigenetic mineralization is unknown, but they were probably derived from several sources.

A significant source of Cl and Br in coal seems to be the sea water, which is brine highly enriched in soluble alkali chlorides. The Cl distribution may be reflecting differences in marine influence at the time of coal formation [5,21]. Such influence can also be a result of change from continental to marine sedimentation in the area even after coal burial, according to the epigenetic mineralization in these coals. Coal basins (Bobov Dol, Balkan, Illinois, Taiheiyo, Donbass, probably some in Australia) influenced by brackish and semi-brackish water are highly enriched in Cl.

Portions of halogen and alkaline elements in brines can originate not only from sea water, but also from the weathering of surrounding halogen-bearing sediment rocks, or rocks enriched in feldspars, mica, montmorillonite and illite. The evaporites, like chlorides, are indicators of arid conditions of deposition [50]. The presence of chlorides in coal may also associate with infiltration of solutions from Permian salt deposits [49] which have been in contact with the coal seam. This case is probably characteristic of some Carbonic (USA, Ukraine) and Permian (Australia) coals.

A source of Cl in some coals seems to be also the volcanic material supply in the basins (Bobov Dol, Taiheiyo) because common fumarolic minerals in active volcanic regions are chlorides of Fe, Mn, Mg and Al [44], and especially ammonium chloride [50].

The main sources of Br is similar to Cl and seems to be the plant material, weathering during exogenetic processes, sea water, volcanic activity and diagenetic–epigenetic solutions. Paralic coals are more enriched in Br than limnic coals [5]. For instance, the Donbass, Bobov Dol and Balkan coals (highly enriched in Br) were influenced by sea water. In addition, an epigenetic Br enrichment in subbituminous coals associated with Br-bearing brines has been also emphasized [5]. For example, the most enriched in Br Bulgarian coals were also influenced by an intensive epigenetic mineralization (Bobov Dol, Balkan) or, in particular, by the occurrence of some volcanic materials supplied from surrounding rocks or directly from volcanic fly ash (Bobov Dol, Pernik).

The pore-size distribution in coal should have significant influence for Cl and Br concentrations. An extensive presence of macropores (coals with $C^{daf} < 75\%$) and development of more mesopores (coals with C^{daf} 75–84%) and micropores (coals with C^{daf} 85–91%) occur [51] during coal-rank progress as a result of organic matter densification, lithification and microstructural rearrangement. It was stated that Cl and Br anions are preferentially located in the micropores rather than in the meso- and macro-pores of coal [10,20]. However, a sharp decline in Cl above 86% C^{daf} which corresponds to the highly increased microporosity (<1.2 nm) accompanied by the well-known decrease in oxy-containing functional groups (as carboxylates) and increase in aromaticity was illustrated in Refs. [17,26]. There are distinct physical and chemical limitations of water solutions to penetrate into the microporosity of carbonaceous materials [52]. Hence, it seems that Cl and Br anions could be preferentially captured and fixed in the mesoporosity (1.2–30 nm) and the most favourable conditions for Cl and Br anionic modes of formation in coal should be during subbituminous and bituminous stages of coalification. In these coals the dominant total porosity is mesoporosity and Cl and Br anions in brines can penetrate successfully in the pores. In contrast, the dominant macroporosity (>30 nm) in lower-rank coals could be favourable environment for a leaching behaviour of mobile elements by percolating water solutions, while the dominant microporosity in high-rank coals could depress the penetration of such solutions.

4. Conclusions

The present results emphasize that despite of similar chemical and geochemical properties of Cl and Br there are some distinct differences in the association, behaviour and mode of occurrence of both elements according to their relationships with the chemical and mineral composition, rank, age, ash yield and geographic location of coals. In summary, some conclusions can be made:

- There is no correlation between Cl and Br contents in the coals and coal ashes studied. Significant positive correlations between Cl and FC, C, Ti and between Br and N, Fe and K were found. Significant negative correlations between Cl and ash yield, O and between Br and VM were also detected.
- The chlorine concentration gradually increases with

increase of coal rank, whereas Br contents depend on the coal rank to a lesser extent.

- Coals of Permian and Carbonic ages are normally more enriched in Cl than younger coals, while coals of Tertiary age are commonly more abundant in Br than older coals.
- The geographic location of coal deposits affects the Cl and Br contents strongly. The most enriched in Cl are coals from Australia and Japan, whereas the most abundant in Br are coals from Ukraine and Bulgaria.
- There is a negative correlation of ash with Cl, while Br shows a relatively weak positive correlation with ash.
- Coals with very high concentrations of Cl are enriched in kaolinite, illite, mica and phosphates, whereas coals abundant in Br are enriched in illite, rutile, brucite and phosphates.
- Substantial Cl parts in coal are related to the presence of water-soluble salts and organic materials, while the occurrence of Br is connected with strongly bound organic and inorganic water-insoluble forms.
- Chlorine and Br in coal may occur, in decreasing order of significance, as organic compounds, as impurity components in the crystalline and amorphous inorganic constituents, in the fluid constituents and as discrete minerals.
- Chlorine and Br could have an organic occurrence and association in water-soluble (mainly ionic) and water-insoluble (ionic and covalent) organic combinations. They are probably bound preferentially in carboxyl (dominantly for Cl) and nitrogen (mainly for Br) functional groups.
- Chlorine is an impurity in minerals and inorganic phases such as clay minerals, mica, feldspars, polyhalite, gypsum, siderite, volcanic glass, phosphates and other carbonates and sulphates. A characteristic Br association with illite and to a lesser extent with mica, kaolinite and Fe-bearing minerals was also found. Water molecules and hydroxyl groups in clay minerals, mica, sulphates, hydroxides and phosphates, as well as exchangeable cations in clay minerals play a leading role for the inorganic occurrence and distribution of Cl and Br ions. Discrete Cl minerals such as sylvite, halite, chlorapatite and probably carnallite were identified, whereas proper Br minerals were not found. The similar ionic radii of Cl and Br suggest the possibility of extensive isomorphic substitutions of both elements in the various aforesaid minerals.
- Significant amounts of Cl anions may associate with solutions in the inherent moisture of coal pore structures. It seems that these solutions could be preferentially captured and fixed in the mesoporosity of coal. Limited Cl and Br proportions may also occur in gas–liquid inclusions of volcanic glass, apatite, quartz, zircon and other phases.
- Chlorine and Br enrichments in coal are normally associated with favourable coal-forming vegetation, marine influence, arid and stable conditions of deposition, volcanic activity, diagenetic and epigenetic solutions enriched in halogen elements, metamorphic progression accompanied by optimum pore-size distribution in coal.

Acknowledgements

Financial support for this work was provided by the National Science Fund in Bulgaria. The authors sincerely thank Dr Kunihiro Kitano and Dr Shohei Takeda from the HNIRI (Sapporo, Japan) for providing well-characterized coal samples worldwide used in the present study. The authors are also grateful to Prof Colette Braekman-Danheux from the ULB (Brussels, Belgium) for the support and to Mrs Evgenia Karaivanova from LGI (Sofia, Bulgaria) for the assistance.

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