

Relationships between chemical and mineral composition of coal and their potential applications as genetic indicators.

Part 1. Chemical characteristics

Stanislav V. Vassilev^{1,2}, Christina G. Vassileva¹, David Baxter²,
Lars K. Andersen²

¹ Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 107, Sofia 1113, Bulgaria

² Institute for Energy, Joint Research Centre, European Commission, P.O. Box 2, NL-1755 ZG Petten, The Netherlands
e-mail: vassilev_stan@yahoo.com

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Abstract. The relationships between the chemical and mineral composition of 37 coal samples from Australia, Bulgaria, USA, Japan, Canada, South Africa, China, Spain, and Ukraine, which differ considerably in their geology, rank, age, ash yield, chemistry and mineralogy, have been investigated. For that purpose complete data from chemical (proximate, ultimate and ash analyses) and mineral composition (major and minor minerals) of these samples have been used. The study explains initially some general considerations of the inorganic matter in coal. Then, the work provides and elucidates the statistically significant positive or negative correlations of chemical characteristics of the coals studied. Further, different geochemical indicators for some genetic interpretations of coal formation are also provided and described. The correlations of minerals in coals, as well as the potential applications of relationships among chemical and mineral composition are described in Part 2 of the present work.

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INTRODUCTION

Each coal deposit has specific plant precursors and individual regional, depositional and palaeoenvironmental conditions, which can cause enrichment or depletion of different elements, phases or minerals. The phase and chemical composition of a given coal is a unique fundamental code that characterizes such fuel, whereas the mineral composition and association between mineral matter and organic matter is the genetic code of coal. This composition can be interpreted to infer type, properties, quality, and genesis of coal (Vassilev and Vassileva, 2009). For example, it is well known that the minerals in coal are particularly illuminating in considering interpretations of coal formation (Mackowsky, 1968). Their occurrence, abundance, and distribution in coal can be applied for partial reconstruction of the conditions of formation and processes occurring during material deposition,

coalification, and epigenesis (Vassilev and Vassileva, 2009). Moreover, the chemical and mineral composition of coal has a strong impact on processing, application, and environmental and technological concerns related to this fuel (Vassilev et al., 2009).

Different chemical, petrographic and mineralogical parameters have been used for characterization of coal. For example, data from: (1) proximate analysis, namely fixed carbon (FC), volatile matter (VM), ash yield (A), and moisture (M); (2) ultimate analysis (C, O, H, S, N) plus determination of calorific value (CV); (3) ash analysis for major oxides (SiO₂, Al₂O₃, Fe₂O₃, CaO, SO₃, MgO, K₂O, TiO₂, Na₂O); (4) petrographic analysis (different ingredients); (5) mineralogical analysis (various minerals and inorganic phases); and occasionally (5) trace element analysis of coal, low-temperature ash (LTA) or high-temperature ash (HTA) are applied traditionally to characterize and specify a given coal. Detailed and/or

summarised data on bulk composition, as well as some comparative similarities or differences in common characteristics for various coals have been reported (Francis, 1961; Yudovich, 1978; Berkowitz, 1979; Bouska, 1981; Finkelman, 1981; Stach et al., 1982; Krejci-Graf, 1983; Valkovic, 1983; Ward, 1984; Raask, 1985; Kler et al., 1987; Korobetskii and Shpirt, 1988; Swaine, 1990; Diessel, 1992; Taylor et al., 1998; Querol et al., 2001a; Goodarzi, 2002; Yudovich and Ketris, 2002, 2005, 2006; Shao et al., 2003; Lopez and Ward, 2008; Belkin et al., 2009). A number of correlations among the coal characteristics have also been identified and described in the above listed references plus some other investigations (Vassilev et al., 1996, 1997; Alastuey et al., 2001; Querol et al., 2001b; Ward, 2002; Zhuang et al., 2003, 2007; Dai et al., 2005; Wang et al., 2008; Vassilev and Vassileva, 2009). For instance, some fundamental and well-known relationships for the common characteristics of coal based on these studies include:

- positive correlations between FC, C, H, CV, and vitrinite reflectance; as well as for the couples S–Fe, Al–Si, Si–Al, Si–quartz, Al–kaolinite, Fe–pyrite, Fe–siderite, K–illite, and Ca–calcite;
- negative correlations between couples such as C–O, C–H, C–M, C–VM, H–O, H–VM, and VM–CV;
- lack of strong correlations for N and occasionally S and H with other characteristics;
- increasing values of FC, C, K, Si, CV, vitrinite reflectance, and true density; as well as C/O, C/H, and FC/VM ratios throughout the coal rank advance;
- decreasing values of the parameters listed in the previous item and increasing values of H, O, VM, M, Ca, Mg, S, H/C, O/C and reactivity with decreasing degree of coalification;
- relations between sequential extraction, density fractionation, ash yield, contents of particular major elements (Al, C, Ca, Fe, S, P), trace elements or minerals, and occasionally bulk chemical and mineral composition;
- establishment of simple or more complex coal classifications based on values of FC, VM, CV, M, C–H, VM–vitrinite reflectance, H/C–O/C, O–H–C, FC–VM–CV, C–H–VM–CV, M–VM–C–CV–vitrinite reflectance, petrographic ingredients, and combined chemical and mineral characteristics.

Despite the extensive investigations, the relationships between the chemical and mineral composition of various coals are still not understood in detail, and additional studies are required to extend the knowledge for inorganic matter. Complete data for chemical composition (18 traditional characteristics from proximate, ultimate and ash analyses) and mineral composition (39 major and minor minerals) plus ash-fusion temperatures of 37 random coal types worldwide have been reported recently for classification purposes of inorganic matter in coal (Vassilev and Vassileva, 2009; Vassilev et al., 2009). Interesting correlations and associations between the ash-forming elements were found in this complex system (Vassilev and Vassileva, 2009) and an attempt for their more detailed explanation is required. Furthermore, correlation analyses for such a suite of chemical and mineral data (totally 53 characteristics) for various coals, as well as their combined interpretations are still missing in the

literature. The goal of the present work is to use further these data for:

- (1) elucidating some general considerations of inorganic matter in coal;
- (2) determining and explaining the relationships, namely statistically significant positive or negative correlations for chemical characteristics;
- (3) providing and clarifying the significant relationships for mineral classes, groups, and species;
- (4) indicating certain similarities and differences between the composition of coals;
- (5) identifying and characterizing some important relationships between the composition, coal rank, and ash-fusion characteristics;

(6) proposing potential applications of relationships, namely: a) suggesting certain definitive mineralogical and geochemical indicators applicable for some genetic interpretations of coal formation; b) introducing some new indicators and features of coal that can be used as criteria for elucidating the coal properties and for predicting potential technological and environmental problems related to the use of this fuel.

Basic and advanced references are also extensively used to support the authors' own data. Part 1 of this study includes the above-listed items 1 and 2.

MATERIAL AND METHODS

Thirty-seven random coal samples originated from basins or deposits of Australia (8), Bulgaria (7), USA (7), Japan (6), Canada (3), South Africa (3), China (1), Spain (1), and Ukraine (1) were used for the present study (Table 1). They comprise homogenised composite samples with well-known coal sources and from actual feed fuels used in large thermo-electric power stations. These samples have been previously described for some investigations of ash fusibility (Vassilev et al., 1995), coal rank (Vassilev et al., 1996), ash yield (Vassilev et al., 1997), occurrence of Cl and Br (Vassilev et al., 2000), chemical and mineral classification of the inorganic matter (Vassilev and Vassileva, 2009; Vassilev et al., 2009), and bulk mineralogy and geochemistry (Vassilev and Vassileva, 1996, 1997, 2009; Vassilev et al., 2000, 2003). Despite the limited total number of coal samples, they represent: (1) widely dispersed geographic regions (North America, Europe, Asia, Australia, Africa); (2) different coal rank (lignites, sub-bituminous, bituminous coals, and semi-anthracites); (3) varied age (Carboniferous, Permian, Jurassic, Cretaceous, Tertiary); (4) a great range of ash yield (5–49%); and (5) all inorganic chemical and mineral types identified for coals (Tables 1–4 and Fig. 1). These properties make the set of samples suitable for some comparative characterizations.

The approaches and methods for characterization of inorganic and mineral matter in coal have been summarized earlier (Vassilev and Tascon, 2003). The standard proximate and ultimate coal analyses, as well as chemical analyses and ash-fusion tests of HTA were described in the above listed publications related to these samples. The detailed identification of minerals in most of the coal samples, their LTAs and HTAs, and coal fractions (after

Table 1

Numeration, geographic locality, rank, ash yield, age, mineral and inorganic chemical types and subtypes of the coal samples studied

Number and locality	Rank and ash yield ^a	Age	Chemical type – subtype ^b	Mineral type – subtype ^c
<i>Northern Hemisphere</i>				
<i>North America</i>				
5. Beluga (USA)	Sub-bituminous, medium ash	Tertiary	CS-MA	Si-HD
6. Black Thunder (USA)	Sub-bituminous, low ash	Tertiary	CS-LA	SS-LD
9. Coal Mountain (Canada)	Bituminous, medium ash	Jurassic-Cretaceous	CS-LA	SC-LD
10. Coal Valley (Canada)	Bituminous, low ash	Jurassic-Cretaceous	CS-MA	Si-HD
11. Colowyo (USA)	Sub-bituminous, low ash	Jurassic-Cretaceous	CS-LA	Si-MD
18. Fording River (Canada)	Bituminous, medium ash	Jurassic-Cretaceous	S-HA	Si-MD
20. Illinois (USA)	Bituminous, medium ash	Carboniferous	FCS-LA	SS-MD
24. Montana (USA)	Sub-bituminous, medium ash	Cretaceous-Tertiary	CS-LA	SS-MD
29. Plateau (USA)	Bituminous, low ash	Carboniferous	S-MA	Si-MD
34. Usibelli (USA)	Lignite, low ash	Tertiary	CS-LA	SS-MD
<i>Europe</i>				
3. Asturias (Spain)	Bituminous – semi-anthracite, high ash	Carboniferous	S-MA	Si-MD
4. Balkan (Bulgaria)	Bituminous, high ash	Cretaceous	S-MA	SS-MD
8. Bobov Dol (Bulgaria)	Sub-bituminous, high ash	Tertiary	S-MA	Si-MD
13. Donbas (Ukraine)	Bituminous – semi-anthracite, medium ash	Carboniferous	FS-MA	SS-LD
15. Elhovo (Bulgaria)	Lignite, high ash	Tertiary	FCS-LA	SSC-LD
22. Maritza East (Bulgaria)	Lignite, high ash	Tertiary	CS-MA	SS-MD
23. Maritza West (Bulgaria)	Lignite, high ash	Tertiary	FCS-LA	SSC-LD
28. Pernik (Bulgaria)	Sub-bituminous, high ash	Tertiary	S-HA	Si-MD
30. Sofia (Bulgaria)	Lignite, high ash	Tertiary	CS-LA	SSC-LD
<i>Asia</i>				
1. Akabira (Japan)	Sub-bituminous, high ash	Cretaceous-Tertiary	S-MA	Si-MD
2. Ashibetsu (Japan)	Bituminous, high ash	Tertiary	S-MA	Si-MD
12. Datong (China)	Bituminous, medium ash	Permian	S-MA	Si-MD
19. Horonai (Japan)	Sub-bituminous, high ash	Tertiary	S-HA	Si-HD
31. Sunagawa (Japan)	Sub-bituminous, high ash	Cretaceous-Tertiary	S-MA	Si-MD
32. Taiheiyo (Japan)	Sub-bituminous, high ash	Cretaceous-Tertiary	S-MA	Si-HD
33. Takashima (Japan)	Bituminous, low ash	Cretaceous-Tertiary	CS-LA	SS-MD
<i>Southern Hemisphere</i>				
<i>Australia</i>				
7. Blair Athol (Australia)	Bituminous, medium ash	Permian	S-HA	Si-HD
14. Ebenezer (Australia)	Bituminous, medium ash	Jurassic	S-MA	Si-MD
16. Entham (Australia)	Bituminous, medium ash	Permian	S-MA	SS-MD
21. Lithgow (Australia)	Bituminous, high ash	Permian	S-HA	Si-MD
25. Moura (Australia)	Bituminous, medium ash	Permian	CS-MA	Si-MD
27. Newlands (Australia)	Bituminous, medium ash	Permian	S-HA	Si-MD
35. Wallarah (Australia)	Bituminous, medium ash	Permian	S-HA	Si-HD
36. Wambo (Australia)	Bituminous, medium ash	Permian	S-MA	Si-MD
<i>Africa</i>				
17. Ermelo (South Africa)	Bituminous, medium ash	Permian	CS-MA	SC-MD
26. Natal (South Africa)	Bituminous – semi-anthracite, medium ash	Permian	S-MA	SS-MD
37. Witbank (South Africa)	Bituminous, medium ash	Permian	CS-MA	Si-MD

^a Rank is mostly based on C content, dry ash-free basis (daf), while ash has low (<10%), medium (10–20%) and high (>20%) yields (Vassilev et al., 1996, 1997).

^b Chemical types (based on Vassilev and Vassileva, 2007, 2009). Abbreviations: S – sialic; CS – calisialic; FS – ferrisialic; FCS – ferricalisialic; HA – high acid; MA – medium acid; LA – low acid

^c Mineral types (based on Vassilev and Vassileva, 2009). Abbreviations: Si – silicate; SC – silicate-carbonate; SS – silicate-sulphide; SSC – silicate-sulphide-carbonate or mixed; HD – high detrital; MD – medium detrital; LD – low detrital

sieving, magnetic and density separations, and leaching procedures), was performed by transmitted light microscopy (in glycerine immersion medium), X-ray powder diffractometry, differential-thermal and thermo-gravimetric analyses, as well as scanning and transmission electron microscopy equipped with an energy dispersive X-ray analyzer. The present mineral data used are based only on the detectable major and minor minerals in bulk coal samples semi-quantified using X-ray diffractometry and this approach has been described elsewhere

(Vassilev and Vassileva, 2009). The above chemical and mineral data were subjected to the Pearson's correlation test to calculate correlation coefficient values between 53 characteristics for these coal samples. Due to the huge amount of data obtained, only the statistically significant relationships, namely positive and negative correlation coefficient values at 99% and 95% confidence levels (ash yield is the only exception), are used and interpreted in the present work. Some limited repetition will appear in discussing specific characteristics, but this is unavoidable

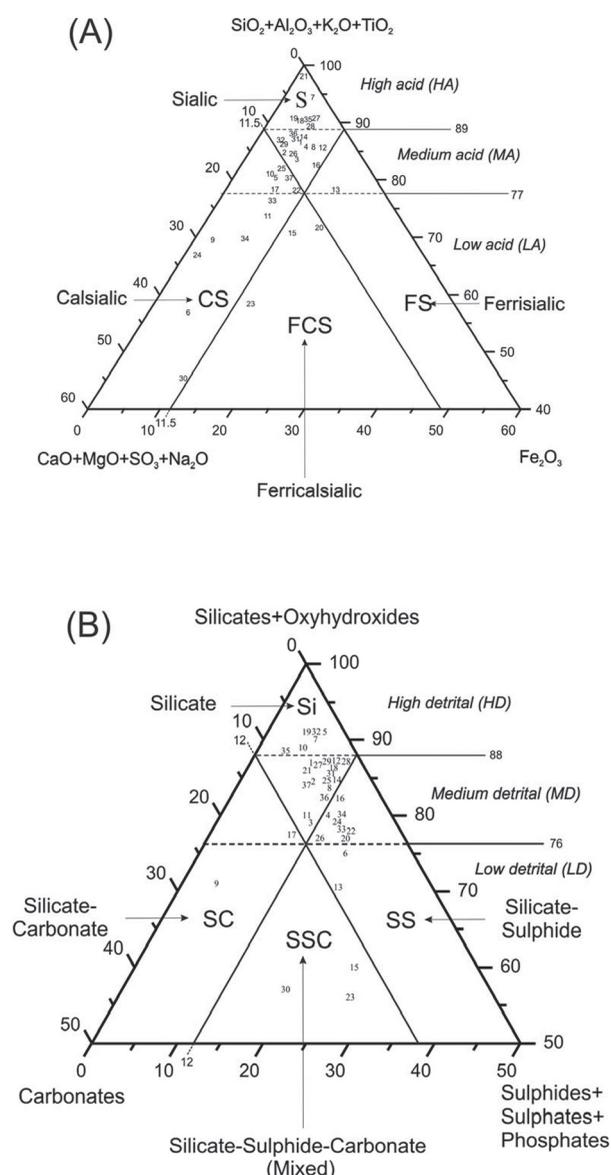


Fig. 1. (A) Chemical classification (based on Vassilev and Vassileva, 2007, 2009) of the inorganic matter in coal ashes studied, in wt. %. (B) Genetic mineral classification (based on Vassilev and Vassileva, 2009) of the inorganic matter in coals studied, in wt. %

able in order to maintain a degree of completeness and continuity in developing the approach and description.

RESULTS AND DISCUSSION

General considerations of the inorganic matter in coals

Coal, as a sedimentary rock, is a complex heterogeneous mixture of organic matter (OM) and, to a lesser extent, inorganic matter (IM), containing various solid and fluid intimately associated phases of allochthonous or autoch-

thonous origin. The organic matter comprises: (1) mostly non-crystalline constituents such as petrographic ingredients (lithotypes, microlithotype groups, and macerals); and (2) occasionally crystalline compounds, namely certain organic minerals (for example, Ca oxalates). The inorganic matter includes: (1) dominantly crystalline constituents (mineral species from different groups and classes); (2) to a lesser extent semi-crystalline components (for instance, poorly crystallized mineraloids of some silicates, phosphates, and hydroxides); and (3) occasionally amorphous compounds (for example, glass and other non-crystalline phases). The actual mineral matter (MM), as a part of IM, includes minerals and mineraloids. The fluid matter of coal comprises moisture, gas, and gas-liquid inclusions associated with both solid OM and IM (Vassilev and Vassileva, 1996; Vassilev and Tascon, 2003).

The inorganic and mineral matter of coal have been divided into different groups; however, the most popular and correct terms used for their specifications are related to the biogenic, detrital, and authigenic (syngenetic and epigenetic) groups depending on the origin, place, and time of formation of inorganic phases or minerals. The biogenic group comprises relict phases (normally <1% in coal) originating from vegetation and animal remains formed during the growing stage of plants and animals. The detrital group includes solid particles transported by water and wind, and introduced into the peat swamp. The authigenic group comprises phases formed in the peat swamp or coal seam during syngeneses (with sedimentation and coalification) and epigenesis (after the coal reached its final rank). The last two groups and their composition, abundance, and distribution in coal have the strongest influence on specifications of IM and MM in coal (Vassilev and Vassileva, 2009).

A general description of the coal samples included in this study (Table 1), as well as individual, mean and range values of their chemical (Tables 2 and 3), ash-fusion (Table 2) and mineral (Table 4) characteristics are given. The chemical composition of these samples is highly variable for both organic-forming (C, O, H, S, N) and inorganic or ash-forming elements (oxides of Si, Al, Fe, Ca, S, Mg, K, Ti, Na). The chemical classification of the inorganic matter for these coal samples is illustrated in Fig. 1(A). However, most of the elements in coal occur in both OM and IM and each element has dominant associations and affinities with these constituents because it is combined in specific phases or minerals. Therefore, the modes of phase, mineral and element occurrences, as well as their genesis, abundance, and distribution are leading parameters for detailed and advanced characterization of a given coal. Unfortunately, the bulk chemical composition alone is insufficient for the actual characterization of a given coal because these data do not provide any information about the modes of element occurrence.

The mineral classification of the inorganic matter for the coal samples studied is illustrated in Fig. 1 (B). The occurrence and abundance of minerals in these samples is also variable, but some major trends are observed. The mineral classes in coal, in decreasing order of abundance, are normally silicates, sulphides-sulphates, carbonates, oxyhydroxides, and phosphates (Table 4). This order

Table 2

Chemical composition (wt. %) and ash-fusion temperatures (°C) of the coal samples

Sample	Proximate analysis (as received)						Ultimate analysis (dry, ash-free basis)						High-temperature ash analysis (815°C)										Ash-fusion tests			
	FC	VM	A	M	C	O	H	S	N	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	MgO	K ₂ O	TiO ₂	Na ₂ O	ST	HT	FT					
1. Akabira	23.8	24.6	48.9	2.7	76.4	16.0	6.1	0.4	1.1	62.96	21.16	5.58	2.37	1.28	2.11	2.33	0.80	1.42	1180	1380	1400					
2. Ashibetsu	35.3	31.1	31.5	2.1	80.8	11.8	6.0	0.4	1.0	62.43	19.84	4.82	4.69	1.59	2.04	1.63	0.78	2.19	1180	1300	1320					
3. Asturias	51.6	17.5	29.3	1.7	86.9	6.9	3.5	1.4	1.3	52.69	25.97	7.20	3.84	1.78	2.83	3.78	0.95	0.96	1325	1430	1465					
4. Balkan	46.8	14.7	38.1	0.4	85.7	4.5	4.7	4.1	1.0	57.81	22.87	7.34	2.66	2.70	1.35	4.15	0.80	0.32	1210	1405	1425					
5. Belga	27.4	42.0	11.7	18.9	70.2	23.0	5.4	0.2	1.2	48.51	29.89	6.04	9.81	1.87	1.54	0.90	0.90	0.54	1250	1400	1420					
6. Beluga Thunder	38.4	36.4	5.0	20.2	72.5	21.4	5.0	0.4	0.7	38.54	16.34	5.70	18.40	14.42	3.98	0.70	1.18	0.70	1240	1270	1340					
7. Blair Athol	56.7	25.3	10.3	7.7	83.3	10.0	4.5	0.5	1.7	59.51	32.52	3.97	0.57	0.27	0.41	0.89	1.38	0.48	1420	>1500	>1500					
8. Bobov Dol	34.8	29.7	29.2	6.3	73.9	14.3	6.1	3.1	2.6	59.78	22.11	8.40	1.95	1.60	2.16	2.68	0.99	0.33	1210	1420	1430					
9. Coal Mountain	55.5	26.2	17.1	1.2	85.0	8.6	4.8	0.4	1.2	39.89	27.33	2.55	22.18	2.02	3.18	0.64	1.54	0.70	1240	1380	1450					
10. Coal Valley	55.4	31.4	9.9	3.3	81.6	10.4	4.8	1.1	2.1	59.42	19.99	4.80	9.15	3.39	1.15	0.64	0.82	0.63	1220	1325	1345					
11. Colowyo	48.3	37.4	5.2	9.1	77.2	15.7	5.1	0.4	1.6	46.91	24.62	8.00	8.86	4.90	1.79	0.99	1.02	2.90	1220	1295	1300					
12. Datong	56.7	27.8	12.9	2.6	82.3	11.5	4.6	0.8	0.8	63.31	19.72	9.62	2.14	1.97	0.49	1.57	0.94	0.23	1225	1425	1440					
13. Donbas	66.9	17.0	14.3	1.8	86.6	4.4	4.3	3.2	1.5	53.76	20.38	15.12	2.81	2.10	1.26	3.05	0.87	0.65	1175	1355	1370					
14. Ebenezzer	45.8	38.5	12.3	3.4	79.9	12.5	6.0	0.5	1.1	62.77	22.74	5.82	3.23	1.30	1.10	0.91	1.35	0.79	1340	1500	>1500					
15. Elhovo	22.4	29.4	39.9	8.3	64.2	18.6	5.7	9.8	1.7	48.67	19.56	13.19	6.01	7.10	2.70	1.58	0.88	0.31	1145	1280	1295					
16. Entham	53.9	28.2	10.1	7.8	85.6	7.8	4.8	0.5	1.3	51.67	29.15	10.73	3.72	1.47	1.41	0.29	1.24	0.31	1300	1470	1520					
17. Ermelo	49.6	33.8	10.0	6.6	78.8	14.8	5.0	0.3	1.1	44.11	31.76	6.71	8.74	3.21	2.88	0.83	1.33	0.44	1230	1410	1435					
18. Fording River	57.3	29.4	10.0	3.3	83.4	10.1	5.0	0.5	1.0	62.38	24.08	4.72	3.13	1.25	0.96	1.96	1.35	0.17	1230	1490	>1500					
19. Horonai	31.7	33.6	32.1	2.6	76.7	15.8	6.0	1.0	0.5	64.40	23.02	3.19	3.33	0.72	1.44	2.12	1.07	0.73	1250	1470	1480					
20. Illinois	45.9	39.1	11.2	3.8	78.2	12.0	5.8	3.3	0.7	49.66	19.05	16.44	5.62	4.11	1.05	2.04	0.93	1.10	1260	1380	1420					
21. Lithgow	48.6	28.7	20.9	1.8	83.8	9.2	4.8	0.8	1.4	68.27	25.61	0.79	0.43	0.43	0.31	2.77	1.31	0.09	>1500	>1500	>1500					
22. Maritza East	25.2	29.9	36.3	8.6	65.5	21.1	5.6	6.8	1.0	56.99	18.27	10.24	5.23	3.20	2.57	2.11	0.74	0.66	1105	1260	1270					
23. Maritza West	17.9	25.0	46.4	10.7	62.9	21.9	5.6	8.5	1.1	40.93	15.69	13.23	14.14	11.80	2.04	1.06	0.62	0.50	1135	1230	1240					
24. Montana	42.5	37.3	11.8	8.4	70.6	22.9	4.9	0.9	0.7	44.48	20.34	1.64	15.71	11.08	3.54	1.08	0.83	1.31	1150	1200	1205					
25. Moura	57.1	31.5	10.2	1.2	85.5	7.4	5.2	0.5	1.4	54.60	23.95	6.05	5.50	3.28	2.08	1.94	1.27	1.33	1290	1400	1480					
26. Natal	70.4	12.2	15.5	1.9	86.5	5.6	4.1	1.5	2.3	50.48	30.75	6.04	4.28	2.10	1.82	1.67	1.55	1.31	1525	1575	1585					
27. Newlands	56.1	27.4	14.8	1.7	84.1	9.5	4.8	0.5	1.1	52.23	35.23	6.59	2.21	0.93	0.56	0.51	1.61	0.12	1480	>1500	>1500					
28. Pernik	25.9	20.7	47.4	6.0	74.3	16.2	5.2	1.4	2.9	63.93	21.85	6.03	1.52	1.40	1.47	2.36	1.11	0.33	1200	>1500	>1500					
29. Plateau	44.9	39.9	9.2	6.0	79.7	12.1	5.7	0.9	1.6	64.99	19.09	3.73	4.79	3.23	1.32	1.10	0.96	0.79	1215	1375	1400					
30. Sofia	27.8	35.6	24.1	12.5	63.0	27.1	5.5	3.5	0.9	32.04	11.32	10.66	27.78	13.20	2.86	1.15	0.77	0.22	1120	1215	1225					
31. Sunagawa	36.2	32.0	29.4	2.4	78.3	13.2	6.3	0.9	1.3	60.65	23.42	4.97	2.73	1.62	2.00	2.30	0.90	1.41	1180	1410	1430					
32. Taiheyo	32.5	40.2	22.0	5.3	73.8	18.8	6.2	0.3	0.9	57.78	26.09	3.54	5.87	1.76	1.35	1.27	1.16	1.17	1300	1440	1500					
33. Takashima	47.8	42.4	8.1	1.7	82.2	9.6	6.1	0.9	1.2	46.60	27.27	7.13	7.36	5.54	2.03	0.95	1.49	1.62	1180	1355	1370					
34. Usibelli	35.0	44.5	8.1	12.4	64.2	29.9	5.2	0.2	0.5	46.15	20.91	6.77	12.54	8.00	2.35	1.49	1.06	0.73	1230	1320	1400					
35. Wallarah	55.1	29.8	13.8	1.3	84.1	9.6	4.9	0.4	1.0	57.85	29.60	5.22	2.53	1.00	1.11	0.90	1.31	0.49	1330	>1500	>1500					
36. Wambo	50.5	34.2	11.8	3.5	81.9	11.0	5.3	0.3	1.5	68.35	18.47	4.14	3.20	1.48	1.74	0.88	0.64	1.10	1210	1350	1370					
37. Witbank	51.8	33.6	12.1	2.5	82.3	9.6	5.3	0.8	2.0	55.10	22.06	7.90	5.13	2.64	2.99	2.22	0.78	1.18	1295	1345	1370					
Mean	44.0	30.8	19.8	5.5	78.2	13.6	5.2	1.7	1.3	54.34	23.30	6.88	6.60	3.56	1.84	1.61	1.06	0.82	1251	1388	1411					
Minimum	17.9	12.2	5.0	0.4	62.9	4.4	3.5	0.2	0.5	32.04	11.32	0.79	0.43	0.27	0.31	0.29	0.62	0.09	1105	1200	1205					
Maximum	70.4	44.5	48.9	20.2	86.9	29.9	6.3	9.8	2.9	68.35	35.23	16.44	27.78	14.42	3.98	4.15	1.61	2.90	1525	1575	1585					
Lignites	25.7	32.9	31.0	10.5	64.0	23.7	5.5	5.8	1.0	44.96	17.15	10.82	13.14	8.66	2.50	1.48	0.81	0.48	1147	1261	1286					
Sub-bituminous coals	34.2	33.4	24.3	8.2	74.4	17.7	5.6	0.9	1.4	54.79	22.88	5.31	7.06	4.07	2.14	1.67	1.00	1.09	1218	1365	1389					
Bituminous coals and semi-anthracites	52.7	29.1	15.2	3.1	83.1	9.5	5.0	1.1	1.3	56.27	24.88	6.70	4.91	2.17	1.55	1.61	1.15	0.77	1280	1404	1423					

^a ST – softening temperature; HT – hemispherical temperature; FT – fluid temperature

Table 3
Some oxide ratios of the coal samples

Sample	SiO ₂ /Al ₂ O ₃	CaO+MgO/K ₂ O+Na ₂ O	CaO/MgO	K ₂ O/Na ₂ O	DAI ^a
1. Akabira	3.0	1.2	1.1	1.6	7.8
2. Ashibetsu	3.1	1.8	2.3	0.7	6.6
3. Asturias	2.0	1.4	1.4	3.9	5.4
4. Balkan	2.5	0.9	2.0	13.0	6.1
5. Beluga	1.6	7.9	6.4	1.7	4.2
6. Black Thunder	2.4	15.4	4.6	0.9	1.4
7. Blair Athol	1.8	0.7	1.4	1.9	18.2
8. Bobov Dol	2.7	1.4	0.9	8.1	6.1
9. Coal Mountain	1.5	18.9	7.0	0.9	2.3
10. Coal Valley	3.0	8.1	8.0	1.0	4.4
11. Colowyo	1.9	2.7	4.9	0.3	3.2
12. Datong	3.2	1.5	4.4	6.8	6.0
13. Donbas	2.6	1.1	2.2	4.7	3.7
14. Ebenezer	2.8	2.5	2.9	1.2	7.7
15. Elhovo	2.5	4.6	2.2	5.1	2.4
16. Entham	1.8	8.6	2.6	0.9	4.8
17. Ermelo	1.4	9.1	3.0	1.9	3.6
18. Fording River	2.6	1.9	3.3	11.5	8.9
19. Horonai	2.8	1.7	2.3	2.9	10.5
20. Illinois	2.6	2.1	5.4	1.9	2.7
21. Lithgow	2.7	0.3	1.4	30.8	50.0
22. Maritza East	3.1	2.8	2.0	3.2	3.7
23. Maritza West	2.6	10.4	6.9	2.1	1.4
24. Montana	2.2	8.1	4.4	0.8	2.1
25. Moura	2.3	2.3	2.6	1.5	4.9
26. Natal	1.6	2.0	2.4	1.3	6.0
27. Newlands	1.5	4.4	3.9	4.3	8.7
28. Pernik	2.9	1.1	1.0	7.2	8.6
29. Plateau	3.4	3.2	3.6	1.4	6.7
30. Sofia	2.8	22.4	9.7	5.2	0.8
31. Sunagawa	2.6	1.3	1.4	1.6	7.8
32. Taiheiyo	2.2	3.0	4.3	1.1	7.0
33. Takashima	1.7	3.7	3.6	0.6	3.5
34. Usibelli	2.2	6.7	5.3	2.0	2.4
35. Wallarah	2.0	2.6	2.3	1.8	9.1
36. Wambo	3.7	2.5	1.8	0.8	8.5
37. Witbank	2.5	2.4	1.7	1.9	4.4
Mean	2.4	3.5	3.6	2.0	6.8
Minimum	1.4	0.3	0.9	0.3	0.8
Maximum	3.7	22.4	9.7	30.8	50.0
Lignites	2.6	8.0	5.3	3.1	2.1
Sub-bituminous coals	2.4	3.3	3.3	1.5	5.9
Bituminous coals and semi-anthracites	2.4	2.7	3.2	2.1	8.3

^a Detrital/authigenic index = (SiO₂+Al₂O₃+K₂O+TiO₂+Na₂O) / (Fe₂O₃+CaO+SO₃+MgO)

for the major and minor minerals is commonly quartz, kaolinite, illite + muscovite, calcite, pyrite, plagioclase, chlorite, gypsum, K feldspar, dolomite, montmorillonite, zeolites, Fe hydroxides, Fe sulphates, Fe oxides, siderite, others (Table 4). Silicates and oxyhydroxides normally have a dominant detrital origin, while carbonates, sulphides, sulphates, proportions of clay minerals (mostly kaolinite and some illite and chlorite) and phosphates (excluding some apatite and rare-earth phosphates) commonly have an authigenic origin in coal (Vassilev and Vassileva, 1996). Limited enrichment in Ca and Fe sulphates and oxyhydroxides in the coal samples could also be attributed to some weathering during sample storage. The various coals studied normally contain a similar assemblage of common minerals, but the quantitative proportions, modes of occurrence, origin, and distribution of these minerals vary among samples.

The statistically significant correlation coefficient values for the chemical variables are listed in Table 5 and some of them are illustrated in Figs 2 and 3. In contrast to coals from different coalfields in a basin or basins in an area, significant compositional similarities between coals worldwide are not common and their identification requires special attention. Such correlation data can provide valuable information for understanding some fundamental relationships and trends in coal because their occurrence is statistically confirmed. However, such correlation results should be used with caution because they could not be exclusive and future use of a larger number of coal samples worldwide would very likely lead to some changes in the system. Additionally, subsidiary investigations should always be applied together with such correlation tests. For example, a strong positive correlation between an element and phase does not always

Table 4
Mineral composition (mineral matter basis) of the coal samples, wt. %

Mineral	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	
<i>Silicates</i>																				
Quartz (Q)	83.5	82.5	79	78.5	85	69	86	82	69	88	76	82	68.5	79	55	76	76	83	89	
Cristobalite (Cr)	49	38	38	42	28	23	25	35	21	39	22	45	24	34	20	23	19	36	56	
Opal (Op)				0.5	3		1	1					0.5	1	1	1	1			
Kaolinite (Ka)	14	20	19	18	29	22	42	25	34	25	26	24	19	25	19	35	40	29	19	
Illite+muscovite (I+M)	6	7	13	9	7	5	9	8	5	6	10	3	11	5	7	7	8	8	7	
Montmorillonite (Mo)	0.5	0.5	1	1	3	3	3	3	2	3	2	1	2	4	2	1	1	2	0.5	
Chlorite (Ch)	2	2	4	3	3	4	3	3	2	5	5	3	4	3	2	4	3	3	2	
Plagioclase (Pl)	7	11	2	3	5	4	3	3	3	6	6	1	4	2	2	1	3	2	2	
K feldspar (Kf)	3	2	2	1	2	4	2	2	1	2	5	2	1	2	1	2	2	2	2	
Zeolites (Z)	2	2	2	1	3	4	1	1	1	1	1	3	2	3	1	2	1	1	0.5	
<i>Oxides and hydroxides</i>																				
Magnetite+hematite (Ma+He)	2.5	2			7	4	6	2	1.5	3	4	3.5	7	5	4	6	7	2	3	
Goethite+lepidocrocite (Go+Le)	1	2			3	4	2	1	2	2	2	2	1	2	2	2	2	1	1	
Spinel+Fe spinel (Sp+FSp)	1	2			2	2	2	1	0.5	1	2	1		3	2	3		1	1	
Corundum (Cor)	0.5								0.5							0.5				
Diaspore+boehmite+gibbsite (Di+Bo+Gi)					2	2	1			2						2			1	
<i>Carbonates</i>																				
Brucite (Bru)									0.5			0.5					0.5			
Calcite (Cc)	5.5	7	10	8	3	8	4	5.5	24.5	6	10	3	11.5	3	14.5	6.5	13	3.5	4.5	
Dolomite (Do)	3	4	4	5.5	2	5	1	3	17	3	5	1	9	2	13	3	6	2	3	
Ankerite (An)	1	1	3	1	1	1	1	1	6	1	1	1	1		1	1	5	0.5	1	
Siderite (Sid)	0.5	1	1	0.5	1			0.5	1	1	2	1	0.5		0.5	0.5	1		0.5	
Magnesite (Mag)	1	1	2	1	1	1	2	1	0.5	1	2	1	1	1		2	1	1		
<i>Sulphides</i>																				
Pyrite (Pr)	2	4	7	6.5	2	3	7	5	7	2	4	5	10	1.5	6	3	5	5	7	
Marcasite (Mc)	2	3	6	6	2	3	1	4	1	2	3	4	9	0.5	3	2	4	2	1	
Pyrrhotite (Py)	1	1	1	0.5				1			1	1	1	1	2	1	1	1		
<i>Sulphates</i>																				
Gypsum (Gp)	3.5	3.5	4	3.5	4	11	2	2.5	3	3	6	3.5	7	7	17	5	4	3	2.5	
Jarosite+melanterite (J+Me)	1	2	3	3	2	5	2	2	1	2	2	0.5	5	4	13	2	3	1	1	
Alunite (Alu)	1.5	1	1	0.5	2	2	2	0.5	1	1	1	1	2	2	2	1	1	1	0.5	
Alumite (Alu)	0.5																			
Hexahydrate (Hex)		0.5																		
Barite (Bar)	0.5	1			2	4			1	1	3	2		1	1	2		1	1	
<i>Phosphates</i>																				
Apatite (Ap)	1.5	7		1.5		3	3	3			7	7	7	3.5	2.5	4	0.5	2	7	
Vivianite (Vi)	1	1			2	2	2	2			1	1	1	2	1	1	0.5	1	1	
Goyazite (Goy)	0.5			0.5	1	1	1	1			1	1	1	1	0.5	1	1	1	1	
Total	98.5	100	100	98	101	98	102	100	99	102	100	98	99	99	99	100.5	99.5	98.5	101	

Table 4 (continued)

Mineral	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	Mean	Min	Max
<i>Silicates</i>	72	81	75	53	77	77	79	81	81.5	85.5	52	82.5	87	74	71	81.5	77	84	77.3	52	89
Quartz (Q)	29	39	37	12	24	27	26	20	38	50	11	43	33	21	25	26	45	37	31.4	11	56
Cristobalite (Cr)	1	1	1										1		2	1	1		0.4	0	5
Opal (Op)	1				2	1													0.4	0	3
Kaolinite (Ka)	24	24	17	19	30	28	27	42	29	21	22	21	26	26	22	41	16	34	25.8	14	42
Illite+muscovite (I+M)	7	5	6	8	8	8	12	8	7	7	7	7	7	7	8	6	6	5	7.3	3	13
Montmorillonite (Mo)	1		3	2	2	3	2	2	1	1	3	0.5	2	2	3	2	2	2	1.6	0	4
Chlorite (Ch)	4	2	3	3	5	5	6	2	3	3	3	2	5	3	4	2	3	3	3.3	2	6
Plagioclase (Pl)	3	5	4	5	2	2	6	2	1	1	3	5	6	8	2	1	1	3	3.5	1	11
K feldspar (Kf)	2	2	2	1	2	2	2	1	2	2	2	2	3	2	3	0.5	1	2	2.0	0.5	5
Zeolites (Z)	1	2	1	3	2	1	3	3	0.5	0.5	1	2	3	5	2	2	2	2	1.6	0	5
<i>Oxides and hydroxides</i>	3	5	3	2.5	4	7.5		8	5	1	5	2.5	3.5	3	8	7.5	3.5		3.6	0	8
Magnetite+hematite (Ma+He)	1	1	1	0.5	2	3		4	3	1	1	0.5	1	1	2	4	0.5		1.2	0	4
Goethite+lepidocrocite (Go+Le)	1	2	1	1	2	2	2	2	2	1	4	2	2	2	2	2	2		1.4	0	4
Spinel+Fe spinel (Sp+FSp)						1.5							0.5		1	2			0.1	0	1.5
Corundum (Cor)	2														2		1		0.2	0	2
Diaspore+boehmite+gibbsite (Di+Bo+Gi)		2		1		1		2								1			0.5	0	2
Brucite (Bru)					7	5	10	5	2.5	4	24	4	3.5	7	6	8.5	7	8	7.9	2.5	24.5
<i>Carbonates</i>	7	7	6.5	16.5	7										3	0.5			0.2	0	3
Calcite (Cc)	5	3	5	13	5	3	3	2	1	2	22	1	2	4	4	5	2	3	4.8	1	22
Dolomite (Do)	1	1	0.5	1	1	0.5	2	0.5	0.5	1	1	1	0.5	2	2	0.5	2	3	1.2	0	6
Ankerite (An)	1	1	1	1	1	3	3	0.5		1	1	1	1	1	2	0.5	1	2	0.7	0	3
Siderite (Sid)	1	2	1	1	1	1	2	2	1	1	1	1	1	1	2	2	2		1.1	0	2
Magnesite (Mag)				0.5		0.5										0.5			0.1	0	1
<i>Sulphides</i>	8	1	6.5	14	5	2	8	2	3	3	7	3.5	2	6	4	1	1.5	6	4.4	1	14
Pyrite (Pr)	7	1	5	12	3	2	8	1	3	2	6	3	2	4	4	1	1	6	3.6	0.5	12
Marcasite (Mc)	1		1	2	2			1		1	1	0.5		2			0.5		0.7	0	2
Pyrrhotite (Py)			0.5																0.1	0	2
<i>Sulphates</i>	5	3	9	11.5	8	5	3	3	4	6	10	5.5	2.5	7	7	2	5.5	2	5.2	2	17
Gypsum (Gp)	4	1	7	5	5	2	1	1	2	3	5	2	1	2	4	1	4	2	2.8	0	13
Jarosite+melanterite (J+Me)	1	2	2	3.5	2	1	3	1	1	1	3	0.5	1	1	1	0.5	1		1.2	0	3.5
Alumite (Alu)				1							1								0.1	0	2
Hexahydrate (Hex)					1	2		1	1	2	1	1	0.5	1	2	0.5			0.2	0	3
Barite (Ba)				2	1	2		1	1	2	1	2	0.5	1	2	0.5	0.5		0.9	0	4
<i>Phosphates</i>	3	3	0.5	1	1	3	3	3	3		2	1.5	1	2	3	0.5	3.5		1.6	0	4
Apatite (Ap)	2	1	0.5	1	1	1	0.5	0.5	1	1	1	1	1	1	1	0.5	0.5		0.7	0	2
Vivianite (Vi)	1				1	1	1	0.5	1	1	1	0.5	1	1	1	1			0.4	0	1
Goyazite (Goy)		2				1	2	2	1	1	2	2	2	2	2	2	2	100	0.5	0	2
Total	98	100	100.5	98.5	102	99.5	100	102	99	99.5	100	99.5	99.5	99	99	101	98	100	100	100	100

Table 5

Significant positive (+) and negative (-) correlation coefficient values (R2) at 99% (bold font)^a and 95% (normal font)^b confidence levels for the characteristics of 37 coal samples. The listed symbols and abbreviations follow the order according to Tables 2–4.

Symbol	Significant correlation coefficient values with:
FC	(+) C(0.84) ST(0.56) Ti(0.51) Al(0.48) FT(0.48) HT(0.46) Sid(0.46) Ka(0.45) Ch(0.37)
VM	(-) O(0.76) A(0.66) H(0.65) Alu(0.51) M(0.50) S(0.46) Gp(0.44) SO ₃ (0.38) Ap(0.35) Mg(0.31)
	(+) H(0.58) O(0.55) Go+Le(0.48) M(0.43) Bar(0.39) Kf(0.39) Z(0.34) Cor(0.33) Ca(0.32) Mo(0.31)
	(-) K(0.52) A(0.46) I+M(0.44) C(0.42) Sid(0.40) N(0.39) Pr(0.39) HT(0.35)
	(+) S(0.57) K(0.50) Alu(0.47) and insignificant with H(0.28) Q(0.28) Cc(0.21) Si(0.18) Ap(0.18) Fe(0.16) Pl(0.16) O(0.15) N(0.15) J+Me(0.12) Mg(0.09) Me(0.09)
A	Py(0.05) Hex(0.05) DAI(0.04) I+M(0.04) Ma+He(0.02)
	(-) FC(0.66) Ka(0.47) VM(0.46) Ch(0.43) Ti(0.42) C(0.35) ST(0.33) Bar(0.32) and insignificant with Op(0.30) Al(0.29) Di+Bo+Gi(0.25) Bru(0.24) Kf(0.23) Go+Le(0.18) FT(0.16) An(0.15)
	Ca(0.14) Cor(0.14) Vi(0.14) Mo(0.13) Z(0.13) Sid(0.13) M(0.12) Na(0.12) Goy(0.12) Sp+Fs+P(0.11) Mag(0.10) HT(0.09) Cr(0.08) Do(0.08) SO ₃ (0.03)
M	(+) O(0.78) SO ₃ (0.65) Bar(0.54) Ca(0.54) Kf(0.43) VM(0.43) Go+Le(0.41) Cr(0.40) Mg(0.39) Op(0.39) Di+Bo+Gi(0.38) Gp(0.37) Mag(0.37)
	(-) C(0.71) Si(0.53) FC(0.50) HT(0.47) FT(0.42) Q(0.40) K(0.38)
C	(+) FC(0.84) FT(0.64) HT(0.63) ST(0.56) Al(0.54) Sid(0.46) Ti(0.46) Si(0.41) Ka(0.33) Do(0.32)
	(-) O(0.94) M(0.71) SO ₃ (0.66) Gp(0.60) Alu(0.57) S(0.53) Ca(0.50) H(0.47) VM(0.42) Mg(0.41) Cc(0.40) Go+Le(0.36) A(0.35) Mo(0.33)
	(+) M(0.78) SO ₃ (0.65) Ca(0.57) VM(0.55) Go+Le(0.44) Gp(0.42) Mg(0.42) H(0.41) Alu(0.37) Kf(0.36) Bar(0.34) Bru(0.34) Mo(0.31)
O	(-) C(0.94) FC(0.76) HT(0.58) FT(0.56) ST(0.46) Al(0.44) Si(0.43) Sid(0.43) Ti(0.35) N(0.33) Do(0.32)
	(+) VM(0.58) Ap(0.52) Hex(0.41) O(0.41)
H	(-) FC(0.65) C(0.47) Sid(0.47) I+M(0.45) ST(0.43) Ch(0.37) Al(0.32)
	(+) Gp(0.75) Alu(0.74) Fe(0.65) A(0.57) Pr(0.54) Cc(0.52) Me(0.52) J+Me(0.36) SO ₃ (0.36)
S	(-) C(0.53) FT(0.49) FC(0.46) Al(0.44) Ti(0.44) HT(0.43) ST(0.41) Ka(0.40) Kf(0.35)
	(-) Z(0.40) VM(0.39) O(0.33) Ca(0.31)
	(+) Q(0.84) DAI(0.52) HT(0.52) FT(0.44) C(0.41) K(0.34)
Si	(-) Ca(0.83) SO ₃ (0.75) Cc(0.69) Mg(0.62) M(0.53) O(0.43) Pr(0.40) J+Me(0.37) Fe(0.35) Gp(0.34) Alu(0.33) Mag(0.31)
	(+) Ti(0.74) Ka(0.73) HT(0.70) FT(0.69) ST(0.69) C(0.54) FC(0.48) Sid(0.38) Di+Bo+Gi(0.36) Ma+He(0.31)
Al	(-) SO ₃ (0.58) Gp(0.53) O(0.44) S(0.44) Alu(0.38) Ca(0.38) Cc(0.38) Mo(0.38) Ap(0.33) Fe(0.33) Mg(0.33) Pr(0.31)
	(+) Pr(0.65) S(0.65) Gp(0.51) Mc(0.46) Alu(0.43) Cc(0.37) Cor(0.31)
Fe	(-) DAI(0.44) Q(0.38) Si(0.35) Ti(0.34) Al(0.33) ST(0.33)
	(+) SO ₃ (0.78) Cc(0.75) Mg(0.65) O(0.57) M(0.54) Bar(0.39) Mo(0.36) J+Me(0.34) VM(0.32)
Ca	(-) Si(0.83) HT(0.65) FT(0.57) Q(0.57) C(0.50) DAI(0.42) K(0.40) Al(0.38) ST(0.38) Goy(0.33) N(0.31)
	(+) Ca(0.78) O(0.65) M(0.65) Mg(0.62) Cc(0.56) Gp(0.54) J+Me(0.49) Mag(0.49) Alu(0.46) Mo(0.40) Mc(0.38) Pr(0.37) S(0.36)
SO ₃	(-) HT(0.76) Si(0.75) FT(0.72) C(0.66) Al(0.58) Q(0.55) ST(0.44) DAI(0.41) FC(0.38)
	(+) Ca(0.65) SO ₃ (0.62) Cc(0.45) Gp(0.45) O(0.42) Do(0.39) M(0.39)
Mg	(-) HT(0.63) Si(0.62) FT(0.54) DAI(0.51) ST(0.46) C(0.41) Goy(0.40) Ma+He(0.39) Al(0.33) Sid(0.32) FC(0.31)
	(+) A(0.50) Q(0.45) I+M(0.35) Pr(0.35) Si(0.34)
K	(-) VM(0.52) Go+Le(0.48) Ka(0.47) Bar(0.46) Ca(0.40) M(0.38) Z(0.34) Di+Bo+Gi(0.32) Ti(0.31)
	(+) Al(0.74) FT(0.69) ST(0.67) HT(0.66) Ka(0.66) FC(0.66) FC(0.51) C(0.46) Sid(0.31)
Ti	(-) Gp(0.45) S(0.44) A(0.42) O(0.35) Fe(0.34) Pr(0.33) Alu(0.31) K(0.31)
Na	(+) Pl(0.58) Kf(0.53) An(0.38)
	(-) Goy(0.41)
DAI	(+) ST(0.56) Si(0.52) HT(0.46) Goy(0.44) FT(0.39) Sid(0.35) Di+Bo+Gi(0.33) Q(0.31)
	(-) Mg(0.51) Fe(0.44) Ca(0.42) SO ₃ (0.41) Mo(0.35) Gp(0.33) Pr(0.33) Mc(0.31)

^a The significant R2 values at 99% confidence level are: ≥ 0.40 and ≥ -0.40 for 37 variables.

^b The significant R2 values at 95% confidence level are: ≥ 0.31 and ≥ -0.31 for 37 variables.

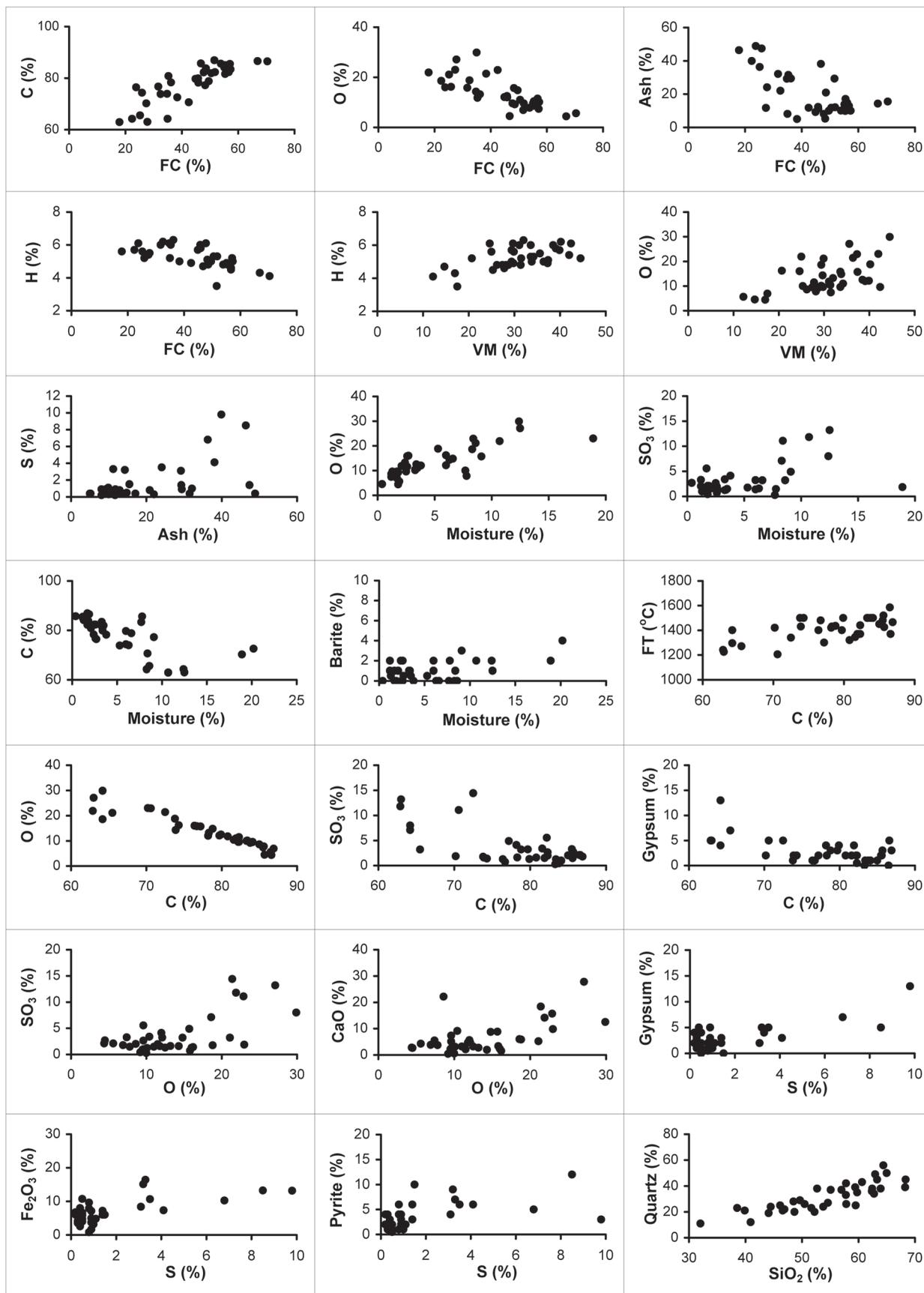


Fig. 2. Significant correlations between some characteristics of the coals studied, wt. %. The abbreviations are listed in Tables 2-4

imply that this phase is the dominant form of that element in coal (Vassilev et al., 2000; Querol et al., 2001b). Furthermore, it should be stated that the significant correlations among elements and minerals are a result of both direct and indirect genetic associations in coal. The direct genetic associations comprise: (1) mineral parageneses, namely simultaneous biogenic and detrital mineral influx or authigenic mineral formations; and (2) mineral generations such as subsequent authigenic (syngenetic, diagenetic, and epigenetic) formations of minerals at different stages during coal history. On the other hand, the indirect genetic associations include only the coexistence of mineral assemblages in this complex system. Hence, additional studies and literature data about the modes of occurrence of elements, phases or minerals in coal should always be used for the explanation of such significant correlations. For instance, there are no data for the actual macerals in the samples studied. Finally, some statistically insignificant correlations could be important, while other significant correlations could not be explained by the present knowledge of coal, or alternatively, they could simply be artefacts.

Relationships for proximate composition of coals

Fixed carbon (FC)

Fixed carbon correlates positively with C, Al, Ti, ash-fusion temperatures (AFT), kaolinite, chlorite, and siderite; and negatively with A, M, O, H, S, SO₃, Mg, and gypsum (Table 5 and Fig. 2). It is well known the FC content increases with coal rank advance (Francis, 1961; Stach et al., 1982) and the coal composition (Table 2) and correlation of FC with the above characteristics are in agreement with this. The FC values are highly dependent on C and OM concentrations in coals and normally follow the behaviour of the latter characteristics (see below).

Volatile matter (VM)

Volatile matter correlates positively with M, O, H, and some minerals mainly containing water molecules, hydroxyl and sulphate groups; and negatively with A, C, N, K, illite + muscovite, and certain typical authigenic minerals such as siderite and pyrite (Table 5 and Fig. 2). The increased VM contents are more characteristic of lower-rank coals, while the decreased values of this parameter are more typical of higher-rank coals (Table 2 and Francis, 1961; Stach et al., 1982). The high VM yield is also indicative for the enrichment in liptinite, hydrocarbons, CO, CO₂, and chemically combined water, and for the depletion in inertinite (Berkowitz, 1979). Hence, the present correlations are in agreement with the literature data; however, some contribution of the above minerals positively correlated with VM content also seems to be significant for increasing VM yields.

Moisture (M)

Moisture correlates positively with VM, O, Ca, SO₃, Mg, and minerals mainly containing water molecules,

hydroxyl and sulphate groups; and negatively with parameters typical of higher-rank coals such as FC, C, Si, K, hemispherical ash-fusion temperature (HT), fluid ash-fusion temperature (FT), and quartz (Table 5 and Fig. 2). The increased contents of this physically and chemically adsorbed water are characteristic of lower-rank coals, while the decreased values of this parameter are typical of higher-rank coals (Table 2 and Francis, 1961; Stach et al., 1982). It should be stated that the minerals positively correlated with M could precipitate following the evaporation of mineralized pore water during coal storage, in particular for lower-rank coals (see below). Hence, the above correlations show significant similarities in the behaviour of M and VM in coal.

Ash yield (A) and organic matter (OM)

The ash yield is one of the most studied parameters of coal, but unfortunately with the poorest understanding. The complex character of this parameter is the major reason for such a problem because the ash yield originates simultaneously from: (1) biogenic, detrital and authigenic IM; (2) organic matter; and (3) fluid matter during coal combustion (Vassilev et al., 1997; Vassilev and Tascon, 2003; Vassilev and Vassileva, 2009). It is well known that A is an important parameter for approximating: (1) the bulk IM; and (2) the predominant affinity of elements and compounds to IM or OM in coal.

The ash yield correlates positively with S and K, and these data indicate the strong association of the above characteristics with IM (Table 5 and Fig. 2). On the other hand, A correlates negatively with FC, VM, C, Ti, kaolinite, and chlorite and these results suggest the strong association of such variables with OM (Table 5 and Fig. 2). The increased A contents are normally more characteristic of lower-rank coals, while the decreased values of A are commonly more typical of higher-rank coals (Table 2 and Fig. 2). The highest ash yield is obtained for coals such as Akabira, Elhovo, Maritza West, and Pernik (Table 2). It can be speculated from the above correlations that ash yield is high in lower-rank coals abundant in authigenic sulphides and sulphates, and K-bearing detrital and authigenic minerals (illite, muscovite, K feldspar, zeolites, jarosite, and alunite). However, this relatively sweeping statement requires an additional and more detailed explanation. That is why, only for this parameter the statistically insignificant correlation coefficients were also included (Table 5) to support the basic trends. The correlations for ash are:

(1) positive with O, H, S, N, Si, Fe, Mg, K, detrital/authigenic index (DAI = ratio between Si + Al + K + Ti + Na oxides and Fe + Ca + S + Mg oxides) and both detrital (quartz, plagioclase, illite-muscovite, Fe oxides) and authigenic (Fe sulphides, Ca-Fe-Al-Mg sulphates, calcite, apatite) minerals, which associate preferably with IM of coal;

(2) negative with FC, VM, M, C, Al, Ca, SO₃, Ti, Na, softening ash-fusion temperature (ST), FT and other minerals, but also both detrital (kaolinite, chlorite, montmorillonite, K feldspar, spinels, Al oxyhydroxides,) and authigenic (kaolinite, opal-cristobalite, zeolites, Fe-Mg carbonates and hydroxides, barite, Fe-Al phosphates) species, which associate preferably with OM of coal.

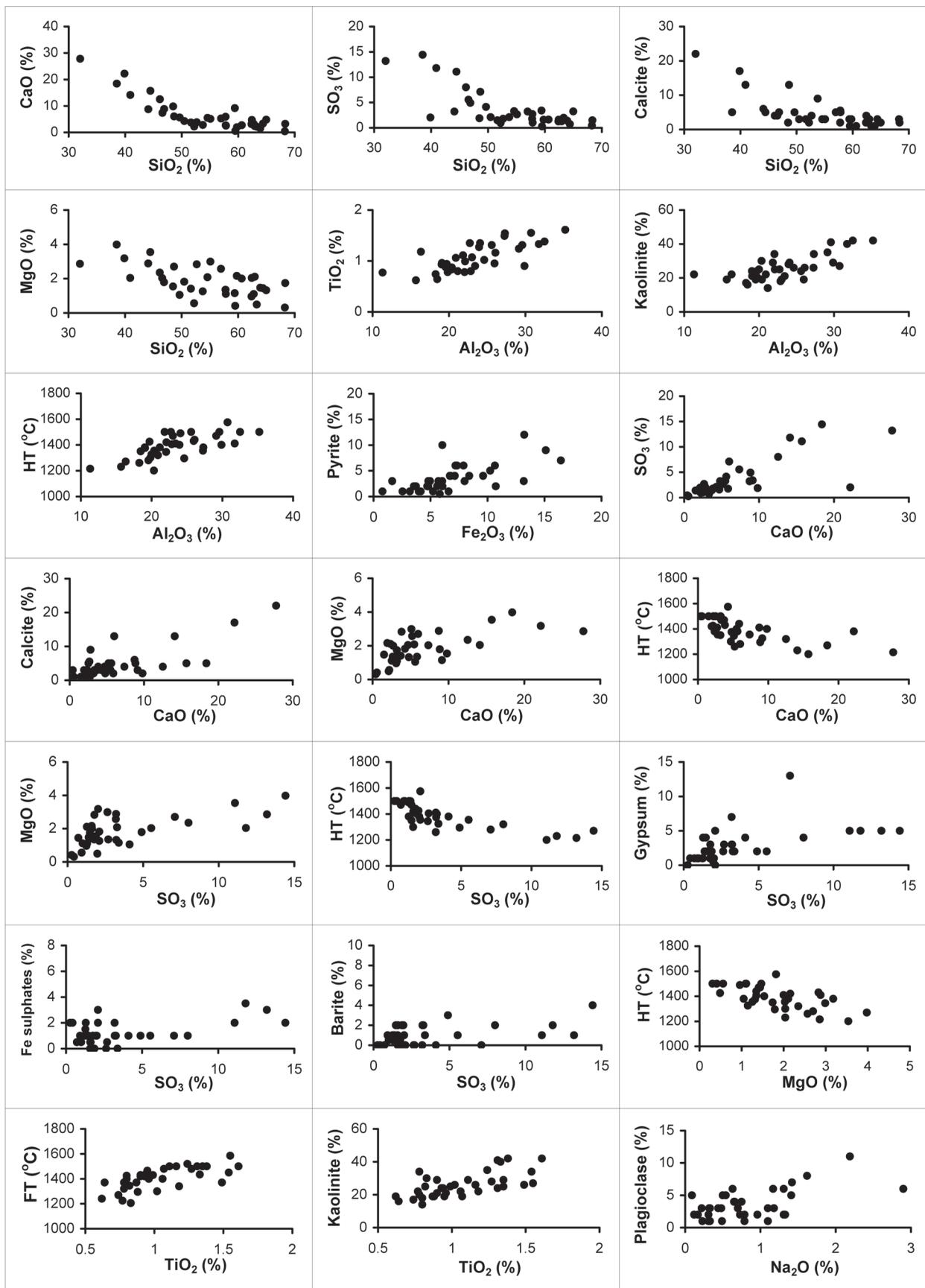


Fig. 3. Significant correlations between some characteristics of the coals studied, wt. %. The abbreviations are listed in Tables 2-4

These results reveal that the bulk ash yield itself is a poor informative characteristic of coal if the origin, composition, and abundance of the coal constituents are not considered. Therefore, the literature data about the correlation of ash yield are relatively contradictory (Vassilev et al., 1997 and the references therein). Briefly, they show that elements positively correlated with A are commonly K, Al, and Si, and in some cases Fe, Ca, Na, and Ti. Trends negative to A reveal normally S, Ca, Mg, and occasionally Na. It is suggested that elements positively correlated with A are “imported” (detrital), whereas elements negatively correlated with A are authigenic (Krejci-Graf, 1983). It is also generally accepted that Si and Al components in coal are major constituents of the detrital ash (Yudovich, 1978). Indeed, the high ash yield is normally a mark of relatively abundant supply of detrital materials in swamp. For instance, it was stated that the authigenic minerals dominate most low-ash (8-10%) coals, whereas the proportion of detrital minerals increases (Finkelman, 1988) and the concentration of organically bound elements decreases (Nicholls, 1968) with increasing ash yield. However, these observations seem to be valid mainly for higher-rank coals because cases for high-ash (24–49%) lignites, which are abundant in moisture, authigenic mineralization (calcite, pyrite and gypsum) and organically bound Ca and S are common (Vassilev et al., 1997, 2005; Vassileva and Vassilev, 2005). The latter observation is also in agreement with the statement that some low-ash (<10%) coals contain mainly authigenic and biogenic inorganic matter, whereas those with higher ash yield (>10%) show simultaneous enrichment in detrital and authigenic inorganics (Eskenazy, 1970). Hence, the composition of some low-rank coals distort the well-known main trends for common constituents in coal such as Si, Al, Fe, Ca, Mg, K, Na, quartz, pyrite, calcite, and some other minerals. This is due to the occurrence of sub-trends based on the predominant detrital or authigenic IM in the system and these associations have been described and illustrated earlier (Vassilev et al., 1996, 1997). Such sub-trends are also obvious from the above listed correlations.

These data for ash yield are an excellent example for the leading role of coal genesis during fuel characterization. They show that the ash yield should always be interpreted together with the genetic IM groups in coal, in particular detrital and authigenic constituents. Such interpretations have a great importance for inorganic elements (particularly Ca, Mg, K, Na, Si, Ti, and P) because their modes of occurrence are strongly related to mixed biogenic, detrital, and authigenic origin in coal (see below). Therefore, the use of the entire correlations and additional data in such cases can give more detail and valuable information about the relationships of each component in the system.

Relationships for ultimate composition of coals

Carbon (C)

Carbon correlates positively with FC, Si, Al, Ti, AFT, kaolinite, dolomite, and siderite; and negatively with VM, A, M, O, H, S, Ca, SO₃, Mg, montmorillonite, Fe

hydroxides, calcite, and gypsum (Table 5 and Fig. 2). Reasonably, most of the above correlations are identical to those for FC and many of them are well known in the literature (Francis, 1961; Berkowitz, 1979; Stach et al., 1982; Vassilev et al., 1996). The high concentrations of C are normally characteristic of vitrinite macerals (Francis, 1961; Berkowitz, 1979; Stach et al., 1982; Ward et al., 2008). It is also well known that the C content in coal increases steadily with increasing coal rank (Table 2 and Francis, 1961; Berkowitz, 1979; Stach et al., 1982; Li et al., 2010). The measurement of C concentration in coal is still the leading and most accurate parameter among other chemical characteristics for evaluation of coal rank advance despite some limitations (Francis, 1961; Berkowitz, 1979; Stach et al., 1982; Ward, 1984; Kler et al., 1987; Vassilev et al., 1996; Taylor et al., 1998; Li et al., 2010). However, restrictions also occur during the application of vitrinite reflectance for that purpose (Li et al., 2010). Therefore, the C contents are used everywhere below and in Part 2 when considering coal rank.

Oxygen (O)

Oxygen correlates positively with VM, M, H, Ca, SO₃, Mg, and minerals containing water molecules, hydroxyl and sulphate groups; and negatively with FC, C, N, Si, Al, Ti, AFT, siderite, and dolomite (Table 5 and Fig. 2). It is well known that the increased contents of O are characteristic of lower-rank coals, while the decreased values of this element are typical of higher-rank coals (Table 2 and Francis, 1961; Stach et al., 1982; Li et al., 2010). The highest O content is exhibited by coals such as Beluga, Montana, Sofia, and Usibelli (Table 2). The increased O concentrations are also in accordance with greater contents of moisture and hydrated minerals or a result of advanced coal weathering. On the other hand, a loss of O occurs in the later stages of metamorphic development of coal due to the well-known decrease in oxy-containing functional groups (such as carboxylates) and increase in aromaticity (Berkowitz, 1979; Stach et al., 1982). This is evidenced by the negative correlations of O with the above characteristics, which are typical of higher-rank coals. Additionally, the vitrinite macerals in some high-rank coals have unusually low percentages of O and organic S replaces some of the organic O in the vitrinite structure (Ward et al., 2008). Hence, the above correlations show significant similarities in the behaviour of O, M, and VM in coal.

Hydrogen (H)

Hydrogen correlates positively with VM, O, and apatite; and negatively with FC, C, Al, ST, illite + muscovite, chlorite, and siderite (Table 5 and Fig. 2). The increased contents of H are normally more characteristic of lower-rank coals, while the decreased values of this element are commonly more typical of higher-rank coals (Table 2). The highest H content is found in Japanese, Bobov Dol and Ebenezer coals (Table 2). The H concentrations increase with increasing liptinite (alginite, resinite, sporinite, cutinite) and degree of bituminization, as well as of residual moisture, hydrated minerals, and

methane in coals (Berkowitz, 1979; Kler et al., 1987). For example, liptinites have the highest H content among all macerals (Ting, 1978). The enhanced H concentrations are also a characteristic feature of sapropelic coals (Berkowitz, 1979). The strong positive correlation of H with apatite is unclear, but it may indicate a preferable hydroxylapatite occurrence in coal. On the other hand, the low H concentrations are in accordance with higher-rank coals due to volatilization of methane and other gaseous and liquid carbohydrates because a loss of H occurs during coal rank advance (Kler et al., 1987) and particularly in the later stages of metamorphic development (Berkowitz, 1979). This is evidenced by the negative correlations of H with some characteristics typical of higher-rank coals. The low H and high FC and C contents are also related to the increased concentrations of inertinite (like Gondwana coals) due to the fusinization (Stach et al., 1982). Coals which contain a high proportion of inertinite macerals (particularly semifusinite and inertodetrinite) apparently reflect a certain amount of in-situ oxidation of the peat bed during the course of its accumulation (Ward, 1989). Hence, the above correlations show some significant similarities in the behaviour of H, VM, O, and M in coal.

Sulphur (S)

Sulphur correlates positively with A, Fe, SO₃, typical authigenic minerals (calcite, pyrite, marcasite, gypsum, Fe-Al sulphates); and negatively with FC, C, Al, Ti, AFT, kaolinite, and K feldspar (Table 5 and Fig. 2). The increased contents of S are more characteristic of lignites, while the decreased values of this element are more typical of higher-rank coals with some exceptions (Table 2). The highest S content is exhibited by Bulgarian (Balkan, Bobov Dol, Elhovo, Maritza East, Maritza West, Sofia), Donbas and Illinois coals (Table 2). The above correlations with sulphides and sulphates were expected, while the unusual strong correlation of S with calcite is probably related to the abundance of this mineral in some high-S coals such as Asturias, Balkan, Donbas, Elhovo, Maritza West, Natal, and Sofia (Tables 2 and 4).

Sulphur is also one of the most studied parameters of coal. Briefly, it is well known that the enrichment in S is commonly observed for coal seams formed under marine or estuarine conditions (Chakrabarti, 1978; Cohen et al., 1984; Goodarzi, 1987; Querol et al., 1992, 2001a; Spears et al., 1999; Zhuang et al., 2003, 2007; Shao et al., 2003) or covered by marine sediments (Yudovich, 1978; Shimoyama, 1984). High-S coals are known to derive most of their S from reduction of sulphate ions to H₂S in sea or brackish water in the coal beds by microbial processes (Calkins, 1994). For example, a penetration of sea water in the peat bog was a major source of sulphate ion in the Donbas basin (Dobrogorskii, 1981). However, another study (Querol et al., 1991) shows that the distribution of S in some Spanish coals was modified by massive leaching of sulphates from continental source-lands toward the sedimentary basin. As a result of that, the coal seams from the fresh-water delta plain have higher S contents than the coal seams from the brackish-water swamp belt. It is also well known that the enrichment of S in coal

is connected with limestone, marl and sulphate-bearing rocks in the surroundings (Kler et al., 1987). For instance, most of the Bulgarian fresh-water coal deposits enriched in S show an association with limestones and limestone argillites in the basement or surrounding sediments. It was also noted that the high concentration of S is characteristic of coals in arid regions (Dobrogorskii, 1981). For example, the Carboniferous coals enriched in S (like Asturias and Donbas) were formed in cold and arid depositional conditions, while the Permian coals depleted in S (like Gondwana coals) were formed in a distinctly warm and humid climate under oxidizing conditions (Stach et al., 1982). On the other hand, low S concentrations normally characterise coals formed under freshwater conditions (Chakrabarti, 1978; Cohen et al., 1984). The coal deposits laid down in raised bogs of inland areas are usually low both in S and ash (Raask, 1985). For instance, the freshwater Australian coals with Permian age are low-ash fuels and contain mostly <0.6% S (Kershaw and Taylor, 1992), which is predominantly organic (Brown and Swaine, 1964) and less than 0.4% pyrite (Swaine, 1983). Fresh-water coals normally contain high organic S (Casagrande et al., 1977) and low pyrite (Cohen et al., 1984). In contrast, coals formed under brackish conditions or in sulphate-rich lakes have relatively low values of organic S (Casagrande et al., 1977; Ward, 2002). Similar major trends for S were also found for the Permian (marine) and Triassic (fresh-water) coals in China (Zhuang et al., 2003, 2007). However, a case for marine Permian coals, which are abundant in organic S (5-12% total S, of which >90% is organic S) and have high ash yields (13-50%) has been also reported for Chinese coals (Shao et al., 2003). It was also found that the vitrinite macerals in coals have significantly higher proportions of both bulk and organic S than the inertinite macerals (Shao et al., 2003; Ward et al., 2008).

The above listed correlations fit relatively well with most of the literature and own data (see also Section 3.4.8). Hence, S shows quite independent behaviour in comparison with other characteristics detected by proximate and ultimate analyses, excluding only the positive correlation with ash yield and related to the authigenic IM.

Nitrogen (N)

The N content is the only characteristic (from 53 variables) without any significant positive correlation with other parameters. Less well defined positive relationships for N were also identified elsewhere (Li et al., 2010). However, N correlates negatively with VM, O, Ca, and zeolites (Table 5). It seems that the increased contents of N are normally more characteristic of higher-rank coals, while the decreased values of this element are commonly more typical of lignites (Table 2). The highest N content is found in coals such as Bobov Dol, Coal Valley, Natal, Pernik, and Witbank (Table 2). The reference data show that coal deposits laid down in marine areas are usually rich in N, S and ash (Williams and Keith, 1963). The high N values indicate brackish coals (Stach et al., 1982), enrichment in vitrinite (Berkowitz, 1979), and probably nitrate mineral species or NH₄-rich clay and mica minerals. For example, the vitrinite macerals in different coals

have significantly higher proportions of N (approximately twice) than the inertinite macerals (Ward et al., 2008; Li et al., 2010). Additionally, the proportion of N increases as the rank of the coal increases up to about 85% of C and then an apparent decrease in N over 85% of C is observed in vitrinites (Ward et al., 2008), similar to Cl and Br in coal (Skipsey, 1974; Vassilev et al., 2000). However, the present data for coals (with 62.9–86.9 % C, dry ash-free basis) do not support the significance of the above correlation. On the other hand, the low contents of N mark a decrease in vitrinite and an increase in exinite and inertinite (Berkowitz, 1979). Hence, N (like S) shows relatively quite independent behaviour in comparison with other chemical characteristics.

Relationships for chemical composition of coal ashes

SiO₂

SiO₂ correlates positively with C, K, quartz, DAI, HT, and FT; and negatively with moisture and typical authigenic minerals (calcite, pyrite, gypsum, magnesite, Fe-Al sulphates) and their constituent elements such as O, S, Fe, Ca, and Mg (Table 5 and Figs. 2 and 3). The increased contents of Si are more characteristic of higher-rank coals, while the decreased values of this element are more typical of lignites (Table 2). The highest Si content is exhibited by coals such as Horonai, Lithgow, Pernik, Plateau, and Wambo (Table 2). The abundance of Si in coal is related mainly to: (1) supply of detrital silica minerals (mostly quartz) and other silicates from source area, many of which are relatively stable during coalification; (2) weathering of detrital alkaline silicates (feldspars, mica) associated with coal or non-coaly strata; (3) biogenic Si origin (for some coals); or (4) solutions enriched in Si from different sources. The last process is especially important for some Australian coals because the ash contents are low and chalcedony was detected as infillings of cell lumens in them (Kemezys and Taylor, 1964). Similar uncommon observations with subsequent formation of authigenic and low-temperature opal, chalcedony, cristobalite, and quartz were also found for some other coals (Garcia-Valles et al., 1993; Vassilev et al., 1994, 2005; Dai et al., 2004). Additionally, the biogenic nature of some Si in coal has been emphasized (Ward, 2002; Lopez-Buendia et al., 2007). On the other hand, the low values of Si are normally a mark for relatively limited supply of detrital materials in swamp. The above negative correlations confirmed the lack of any link between Si and authigenic minerals in coal. Hence, the listed correlations for Si are in good agreement with most of the literature and own data (see also Section 3.4.10 and Part 2).

Al₂O₃

Al₂O₃ correlates positively with FC, C, Ti, AFT, kaolinite, siderite, Fe oxides, and Al hydroxides; and negatively with typical authigenic minerals (calcite, pyrite, gypsum), montmorillonite, apatite and their constituent elements such as O, S, Fe, Ca, and Mg (Table 5 and Fig. 3). The above listed positive correlations are in accordance

with the coal rank advance. For example, the increased contents of Al are characteristic of the highest-rank coals, while the decreased values of this element are typical of lignites (Table 2). The maximum Al content is present in Gondwana coals such as Blair Athol, Ermelo, Natal, and Newlands (Table 2). The abundance of Al in coal is related mainly to: (1) supply of detrital aluminosilicates and Al oxyhydroxides from source area; (2) authigenic clay minerals (especially kaolinite), zeolites, alunite, and goyazite; (3) stable Al products resulted from weathering of alkaline aluminosilicates; or (4) biogenic Al origin. Some Al may have biogenic nature because lycopods selectively absorb Al (Francis, 1961; Berkowitz, 1979; Li et al., 2007, 2010). On the other hand, the low values of Al are a mark for relatively limited supply of detrital materials in peat and their low level of weathering in source areas and coal seams. The above negative correlations confirmed the lack of any link between Al (similar to Si) and the most typical authigenic minerals in coal. Hence, the listed correlations for Al fit relatively well with most of the literature and own data.

It was also noted that the high values of SiO₂ + Al₂O₃ and ash contents (like some Japanese coals in Table 2) are normally more characteristic of coals resulting from mountain peat-forming type, while the high concentration of CaO + MgO + Fe₂O₃ and low ash yield (like some North American coals in Table 2) are more typical of coals resulting from lowland peat-forming type (Yudovich, 1978). On the other hand, the Australian coals studied are low-ash fuels and enriched in the former oxides, which are typical of stable conditions of deposition (Shibaoka, 1972) (see also Section 3.4.10 and Part 2).

Fe₂O₃

Fe₂O₃ correlates positively with S and authigenic minerals (pyrite, marcasite, calcite, gypsum); and negatively with Si, Al, Ti, DAI, ST, and quartz (Table 5 and Figs. 2 and 3). The increased contents of Fe are characteristic of lignites and some high-rank coals, while the decreased values of this element are typical of sub-bituminous coals (Table 2). The highest Fe content is found in coals such as Donbas, Elhovo, Illinois, and Maritza West (Table 2). The abundance of Fe in coal is related mainly to the occurrence of Fe-bearing minerals such as: (1) authigenic Fe sulphides; (2) authigenic Fe carbonates; (3) Fe sulphates and oxyhydroxides resulted from weathering of Fe sulphides and carbonates; or (4) detrital Fe-containing montmorillonite, chlorite, oxyhydroxides, and spinel. Some organic Fe occurrence in coal has also been inferred (Li et al., 2007, 2010). The positive correlation of Fe with Fe-bearing minerals is obvious, whereas the correlation of Fe with calcite and gypsum is probably connected with the common mineral assemblage in coal, namely Fe sulphides – calcite and their weathering products (see also Section 3.3.4 and Part 2).

CaO

CaO correlates positively with VM, M, O, SO₃, Mg, montmorillonite, and authigenic minerals (calcite, Fe sulphates, barite); and negatively with C, N, Si, Al, K,

DAI, AFT, quartz, and goyazite (Table 5 and Figs. 2 and 3). The increased contents of Ca are characteristic of lignites, while the decreased values of this element are typical of bituminous coals (Table 2). The highest Ca content is exhibited by coals such as Black Thunder, Coal Mountain, Maritza West, Montana, Sofia, and Usibelli (Table 2). The abundance of Ca in coal is related to: (1) authigenic formation of Ca-bearing carbonates, sulphates, phosphates, and organic minerals (like Ca oxalates); (2) organically bound Ca (organometallic compounds); (3) biogenic origin from plant precursors and fossil remains because Ca is a biophilic element; (4) Ca sulphates resulted from weathering of sulphides and precipitation of water solutions; or (5) detrital Ca-containing minerals (montmorillonite, basic plagioclase, apatite). The literature data show that the high Ca concentrations are related to coals with: lower rank; intensive hydrothermal activities; enrichment in humates (Kler et al., 1987); increasing proportions of sorption ash (Yudovich, 1978), and fossil bands (Francis, 1961). The great abundance of Ca is indicative for coal deposits formed in continental sediments under freshwater conditions in an alluvial plain-fluvial environment because water is always abundant in Ca under humid landscapes (Perelman, 1989). However, other studies emphasise that paralic coals may have more Ca than limnic coals (Krejci-Graf, 1983) and the reason may be the occurrence of Ca as fossil bands in coal seams of marine origin (Francis, 1961). Hence, most of the above listed correlations for Ca are in good agreement with the literature and own data (see also Sections 3.4.8 and 3.4.10, and Part 2).

MgO

MgO correlates positively with M, O, Ca, SO₃, and authigenic minerals (calcite, dolomite, gypsum); and negatively with FC, C, Si, Al, DAI, AFT, Fe oxides, siderite, and goyazite (Table 5 and Fig. 3). The increased contents of Mg are characteristic of lignites, while the decreased values of this element are typical of bituminous coals (Table 2). The highest Mg content is found in coals such as Asturias, Black Thunder, Coal Mountain, Ermelo, Montana, Sofia, and Witbank (Table 2). The abundance of Mg (similar to Ca) is related to: (1) authigenic formation of Mg-bearing carbonates and sulphates; (2) organically bound Mg; (3) biogenic origin from plant precursors and fossil remains because Mg is a biophilic element; (4) Mg sulphates resulted from weathering of sulphides and precipitation of water solutions; or (5) occurrence of detrital (montmorillonite, chlorite, spinels) and some other authigenic (brucite) Mg-bearing minerals. The high concentration of Mg is an indicator of salinity (Krejci-Graf, 1983), namely for saline lakes (Perelman, 1989) or coal deposits associated with marine transgression (Mackowsky, 1968; Dixon et al., 1970; Stach et al., 1982). The occurrence of Mg as fossil bands in coal seams of marine origin was also emphasised (Francis, 1961). Furthermore, the abundance of Mg is also characteristic of organic matter enriched in algal remains (Garcia-Valles et al., 1993) and fusinite (Lyons et al., 1990). Hence, the above listed correlations for Mg fit relatively well with most of the literature and

own data and they also demonstrate a similar behaviour between Ca and Mg in coal (see also Sections 3.4.4 and 3.4.10, and Part 2).

K₂O

K₂O correlates positively with ash, Si, quartz, illite + muscovite, and pyrite; and negatively with VM, M, Ca, Ti, kaolinite, zeolites, Fe-Al hydroxides, and barite (Table 5). The increased contents of K are more characteristic of higher-rank coals, while the decreased values of this element are more typical of lignites (Table 2). The highest K content is exhibited by coals such as Asturias, Balkan, Bobov Dol, Donbas, and Lithgow (Table 2). The abundance of K in coal is related to: (1) supply of detrital K-bearing silicates (illite, muscovite, K feldspars) from source area; (2) weathering of detrital alkaline silicates associated with coal or non-coaly strata; (3) authigenic formation of K-containing sulphates (jarosite, alunite), chlorides, and silicates (illite, muscovite); (4) organically bound K including also plant debris because K is a biophilic element; or (5) K sulphates resulted from weathering of sulphides and precipitation of water solutions. The major source of K in coal is probably detrital materials originated from acid intrusive and volcanic rocks in the supply area or volcanic ash falls abundant in sanidine (Kemezys and Taylor, 1964; Yudovich, 1978). It was noted that the high contents of K are typical of limnic coals (Kessler et al., 1967). It should be stated that a characteristic feature of K is the occurrence of this element within stable minerals during coalification and especially metamorphic progression of coal (similar to Si, Al and Ti). It can also be seen that K commonly follows the behaviour of Si. Hence, most of the above listed correlations for K are in good agreement with the literature and own data (see also Sections 3.4.1 and 3.4.10, and Part 2).

Na₂O

Na₂O correlates positively with detrital minerals (plagioclase, K feldspar) and ankerite; and negatively with goyazite (Table 5 and Fig. 3). The increased contents of Na are more characteristic of sub-bituminous coals, while the decreased values of this element are more typical of lignites (Table 2). The highest Na content is found in coals such as Ashibetsu, Colowyo, and Takashima (Table 2). The abundance of Na in coal is related to: (1) supply of detrital Na-bearing silicates (acid plagioclase, montmorillonite) from source area; (2) weathering of detrital alkaline silicates associated with coal or non-coaly strata; (3) authigenic formation of Na-containing silicates (zeolites, others), sulphates, and chlorides; (4) organically bound Na including also plant precursors; or (5) Na sulphates resulted from weathering of sulphides and precipitation of water solutions. The high concentrations of Na are indicative for coals formed in brines (Kler et al., 1987; Goodarzi, 1995). The enrichment in Na may also be a result of marine influence because an exchange of Na⁺ from seawater with the alkaline-earth elements (particularly Ca²⁺) may occur in coal (Lyons et al., 1989). Hence, the above correlations and data show that there is some similar behaviour between K and Na in

coal related to their association with feldspars, sulphates, chlorides, and biogenic precursors. However, Na correlates positively with Mg, Ca and S, while K normally follows closer behaviour to Si (Vassilev and Vassileva, 2009 and see also Sections 3.4.6 and 3.4.10, and Part 2).

SO₃

SO₃ shows correlations similar to those of S and the discussion for the latter parameter is valid to a great extent for SO₃. For example, SO₃ correlates positively with M, O, S, Ca, Mg, montmorillonite, and authigenic minerals (pyrite, marcasite, gypsum, calcite, Fe-Al sulphates, barite); and negatively with FC, C, Si, Al, DAI, AFT, and quartz (Table 5 and Figs. 2 and 3). It should be noted that some S is volatile during production of HTA. The increased concentrations of SO₃ are characteristic of lignites, while the decreased values of this oxide are typical of bituminous coals (Table 2). The highest SO₃ content is exhibited by coals such as Black Thunder, Maritza West, Montana, and Sofia (Table 2). The abundance of S and SO₃ in coal is related to: (1) authigenic formation of sulphides, sulphates, and occasionally elemental S; (2) organically bound S; or (3) mineralized water in coals (particularly in lignites), which is commonly enriched in sulphate ion. Hence, the above listed correlations for SO₃ and S are in agreement with most of the literature and own data (see also Section 3.3.4 and Part 2).

TiO₂

TiO₂ correlates positively with FC, C, Al, AFT, kaolinite, and siderite; and negatively with ash, O, S, Fe, K, and authigenic pyrite and gypsum (Table 5 and Fig. 3). The increased contents of Ti are characteristic of bituminous coals, while the decreased values of this element are typical of lignites (Table 2). The highest Ti content is found in coals such as Coal Mountain, Natal, Newlands, and Takashima (Table 2). The abundance of Ti in coal is related to: (1) organically bound Ti; (2) detrital supply or authigenic formation of Ti-containing clay and mica minerals; or (3) detrital material enriched in accessory and stable Ti-bearing minerals such as rutile, anatase, brookite, ilmenite, and titanite (sphene). The literature data show that the high Ti concentrations are in accordance with the low ash yields (Krejci-Graf, 1983) and the negative correlation between Ti and ash confirmed that. It is also well known that a significant proportion of this element may be organically bound (Brown and Swaine, 1964; Finkelman, 1988; Li et al., 2010) and that Ti is generally most concentrated in vitrinite in comparison with cutinite and fusinite (Lyons et al., 1990). However, the affinity of Ti to clay minerals and aluminosilicates (Fig. 3 and Finkelman, 1981; Lyons et al., 1989; Querol et al., 2001a, 2001b; Ward, 2002) and its occurrence in discrete minerals in coal was also identified (Finkelman, 1988; Vassilev and Vassileva, 1996; Querol et al., 2001a). Additionally, a characteristic feature of ash that falls from volcanic eruptions is the abundance of accessory Ti-bearing minerals such as sphene, anatase, and ilmenite (Finkelman, 1988). The detrital Ti-bearing minerals are very stable species and they may be concentrated in

coal (like Si, Al and K) at the expense of unstable minerals during coal formation, metamorphic progression, and weathering (Vassilev et al., 1996). It seems that this is the dominant reason for the relatively increased Ti concentrations in some coals (for example, Gondwana coals). The low concentration of Ti is probably related to the limited supply of Ti in peats and the high authigenic nature of inorganic matter. The preferable association of Ti with marine or freshwater environments is not evaluated in detail, but it was noted that Ti decreases with increasing marine influence in German coals (Krejci-Graf, 1983). It should be stated that Ti commonly follows the behaviour of Al. Most of the above listed correlations for Ti are in accordance with the literature and own data (see also Sections 3.4.2 and 3.4.10).

In summary, the above results from chemical and correlation analyses show some important associations among characteristics such as: VM–M–O–H; FC–C–Si–Al–Ti; S–SO₃–Fe–Ca; Si–K; Al–Ti; Fe–S; and Ca–Mg–SO₃. The data also reveal that most of the significant positive correlations found for inorganic elements (Si, Al, Fe, Ca, S, Mg, K, and Na) are in accordance with their discrete (proper) minerals identified in coal (Figs. 2 and 3). However, some organic occurrence of ash-forming elements (in particular for Ca, Na, S, and Ti) in coal is also significant.

Oxide ratios

Some oxide ratios have been used in the literature as geochemical indicators of coal formation. For instance, coals with high SiO₂/Al₂O₃ ratio (such as Akabira, Ashibetsu, Coal Valley, Datong, Maritza East, Plateau, and Wambo in Table 3) are presumed to have formed under unstable conditions of deposition, when subsidence in the basin was relatively rapid and irregular, and there was a high degree of tectonic movement (Shibaoka, 1972). Additionally, such high ratio and high-ash yields (such as Akabira, Ashibetsu, and Maritza East in Tables 2 and 3) are informative for coals resulting from mountain peat-forming type (Yudovich, 1978). In contrast, the low Si/Al ratio and ash contents <12 % are informative for coals resulting from lowland peat-forming type (Yudovich, 1978). For example, different coals (such as most Gondwana coals plus Beluga, Coal Mountain, and Takashima in Tables 2 and 3) have low Si/Al ratio and ash contents, and indicate stable conditions of deposition with low degree of tectonic movement and slow and constant subsidence in the basin (Shibaoka, 1972). The Si/Al ratio also depends on whether chemical decomposition (leaching) or mechanical erosion of the rocks predominates in the hinterland (Shibaoka, 1972). For instance, it was emphasised that Al and Si were relatively enriched in coal by leaching of Na, K, Mg, Ca, P, S, Mn, and Fe during coalification (Krejci-Graf, 1983). In the case of low Si/Al ratio (like Gondwana coals), the chemical leaching predominates over mechanical erosion (Shibaoka, 1972). The reason for that is the more intensive leaching of Si than Al during mineral decomposition in the peat swamp (Yudovich, 1978) and Al contents may relatively increase at the expense of Si contents. The low Si/Al ratio may also indicate that the detrital material comprises products of weathering rings because these materials are

enriched in Al and Ti, and depleted in water-soluble elements (Yudovich, 1978). It was also found that this ratio decreases with increasing marine influence in some German and Turkish coals (Krejci-Graf, 1983). Despite the above indicative observations, it should be stated that coals with highly variable chemical and especially mineral composition show similar or identical Si/Al values (Tables 2–4 and Vassilev and Vassileva, 2009). Hence, the occurrence of Al- and Si-bearing minerals is the key factor for determining the behaviour of both elements in coal.

The high values of $\text{CaO} + \text{MgO}/\text{K}_2\text{O} + \text{Na}_2\text{O}$ (such as Black Thunder, Coal Mountain, Maritza West, and Sofia in Table 3) and CaO/MgO ratios (such as Beluga, Coal Mountain, Coal Valley, Maritza West, and Sofia in Table 3) are indicative for coal deposits formed in continental sediments under freshwater conditions (Perelman, 1989). In contrast, the low $\text{Ca} + \text{Mg}/\text{K} + \text{Na}$ (such as Balkan, Blair Athol, and Lithgow in Table 3) and Ca/Mg (such as Akabira, Asturias, Blair Athol, Bobov Dol, Lithgow, Pernik, and Sunagawa in Table 3) ratios are informative for coal deposits associated with marine or brackish influences, saline lakes or organic matter enriched in algal remains. Despite low Ca/Mg ratio in most Australian coals indicating some marine influence, the low amount of pyrite and S, and high contents of kaolinite, Al and Si, as well as other indications described above support strongly a non-marine environment for these coals. On the other hand, most Japanese coals also have low Ca/Mg ratio, but these coals are enriched in Mg-bearing minerals (dolomite and hexahydrite) and have high-ash yields. The increased Mg concentrations in some carbonate minerals are characteristic indicators of coal beds that have been subjected to marine transgressions (Mackowsky, 1968; Dixon et al., 1970; Stach et al., 1982). Geological observations indicate that many dolomites have been formed from limestones by the action of Mg-bearing waters and in many instances sea water has evidently been responsible (Berry and Mason, 1961). For example, the influence of sea water during formation of most Palaeogene Japanese coal deposits (Shimoyama et al., 1990) is a reason for dolomitization of these coals.

The high $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio (such as Balkan, Bobov Dol, Datong, Fording River, Lithgow, and Pernik in Table 3) is informative for a relative enrichment of illite, K feldspar, sylvite, or K sulphates at the expense of montmorillonite, acid plagioclases, halite, or Na sulphates. The increased proportions of K in comparison with Na may also be due to intensive sorption of the large K cation by clay minerals (Dobrogorskii, 1981) and its high stability in K-bearing aluminosilicates during weathering (Kler et al., 1987) or metamorphic progression (Vassilev et al., 1996). It was also stated that an increased K/Na ratio was a result of rapid rate of sedimentation (Goodarzi, 1987). For instance, such sedimentation is typical of some Bulgarian coal deposits (Balkan, Bobov Dol, and Pernik) enriched in K. On the other hand, the low K/Na ratio (such as Ashibetsu, Colowyo, Montana, Takashima, and Wambo in Table 3) could also be related to the degradation of illite, resulting from the slow accumulation of sediments (Goodarzi, 1987).

The extremely high detrital/authigenic index in some coals (such as Blair Athol, Fording River, Horonai,

Lithgow, Newlands, Pernik, Wallarah, and Wambo in Table 3) may indicate their probable allochthonous origin because such seams contain greater detrital mineral matter input than autochthonous coal seams (Korobetskii and Shpirt, 1988). For example, evidences for allochthonous origin of some Gondwana coals were noted (Kershaw and Taylor, 1992). Respectively, the low values of DAI for other coals (such as Black Thunder, Maritza West, Montana, and Sofia in Table 3) indicate that most of these coal seams are probably autochthonous. It should be stated that the above reference observations for oxide ratios as geochemical indicators of coal formation are commonly in good agreement with the geology of the most Bulgarian coals studied (Vassilev and Vassileva, 1998 and the references therein).

CONCLUSIONS

According to the relationships derived from statistically significant positive or negative correlations for the chemical characteristics of 37 coals worldwide, preliminary conclusions can be drawn:

1. Important associations among chemical characteristics such as Si–K, Al–Ti, Fe–S, Ca–Mg– SO_3 , VM–M–O–H, S– SO_3 –Fe–Ca, and FC–C–Si–Al–Ti were identified. These associations are a result of their preferable affinities to organic matter, detrital or authigenic inorganic matter, as well as to phase-mineral assemblages.

2. It has been found that the ash yield is a poor informative characteristic of coal if the origin, composition, and abundance of the coal constituents are not considered. For example, elements such as O, H, S, N, Si, Fe, Mg, and K correlate positively with ash yield (inorganic matter) and both detrital and authigenic minerals in coal. On the other hand, elements and parameters such as FC, VM, M, C, Al, Ca, Ti, and Na correlate negatively with ash yield (or positively with organic matter) and other minerals that are also both detrital and authigenic in origin.

3. Inorganic or ash-forming elements such as Si, Al, Fe, Ca, S, Mg, K, and Na normally show strong association with their discrete minerals identified in coal; some organic association was also suggested for ash-forming elements such as Ca, Mg, K, Na, S, and Ti in coal;

4. Elements and particularly ratios of different elements (Si/Al, Ca/Mg, K/Na, $\text{Ca} + \text{Mg}/\text{K} + \text{Na}$, and DAI) can be used as geochemical indicators for some genetic interpretations of coal formation.

The significant correlations for minerals in these coals, some similarities or differences between the composition of coals, certain important relationships between the composition and coal rank and ash-fusion characteristics, as well as some definitive mineralogical and geochemical indicators applicable for interpretations of formation or application of coal will be described in Part 2.

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Appendix – Nomenclature

A – ash yield

AFT – ash–fusion temperatures

CV – calorific value

DAI – detrital/authigenic index = $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{TiO}_2 + \text{Na}_2\text{O}) / (\text{Fe}_2\text{O}_3 + \text{CaO} + \text{SO}_3 + \text{MgO})$

FC – fixed carbon

FT – fluid ash–fusion temperature

HT – hemispherical ash–fusion temperature

HTA – high–temperature ash (500–1000°C)

IM – inorganic matter

LTA – low–temperature ash (<200°C)

M – moisture

MM – mineral matter

OM – organic matter

R² – correlation coefficient value

ST – softening ash–fusion temperature

VM – volatile matter

% – weight %

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