Table 16. Contents of selected minor elements in coal ashes of Carboniferous relics at Merklín (MeR), Lísek (LiR) and Malé Přílepy (MP) (Bolsovian)

	MeR	LiR	MP
Ag ppm	0.8	0.8	0.8
As ppm		34.7	
Be ppm	50.6	23.3	10.5
Bi ppm	0.6	0.2	0.3
Cd ppm	0.8	0.8	0.8
Co ppm	71	75.0	19
Cr ppm	187	43.0	213
Cs ppm	104	242	49
Cu ppm	193	293	121
Hg ppm	0.005		0.005
Ir ppb	1.8	0.6	
Mo ppm	5	19.0	11
Ni ppm	91	152	107
Pb ppm	120	81.0	73
Pd ppb	10.6	11.5	
Pt ppb	12.0	24.1	
Rb ppm	241	246	196
Rh ppb	1.0	0.2	
Ru ppb	1.0	1.0	
V ppm	344	454	354
Zn ppm	137	118	118

Neogene covered much larger areas than can be seen at present.

For these reasons it is a problem to draw inferences about the source areas of elements identified in numerous samples of coals and their ashes. Although some Pb-Zn deposits with high Ag in galena lie in the close vicinity of coal-bearing Carboniferous relics near Vranov and Merklín, the contents of the above-mentioned elements in the Nýřany and/or Radnice coal seams can hardly be considered high. Similarly, the low contents of Pb and Zn found in the coals of the České Budějovice relic of the BG are difficult to relate to a base metal deposit in the close vicinity that was already being mined in medieval times. Perhaps only enhanced contents of Ag in ash from the local coal could be connected with this deposit. Such examples and other inconsistencies led us to the conclusion that it was not feasible to make credible predictions about the origins of trace elements in the coals of the Bohemian basins.

5. Discussion and conclusions

The inorganic components play an important role in determining the chemistry of coal since they are the major source of trace elements. Sulfides in our bituminous coals and anthracites are the source of As, Cu, Ni, Pb and Zn, whereas clay minerals absorb, for instance, Ga, Sc, Sr and Rb. In the case of a number of elements (As, Be, Co, Ge, Ni, Sb, Sr, U, V and Zr) it is often a problem to establish unambiguously their affinity with the inorganic or organic component of the coal or even with a specific mineral.

Statistical treatment of data from more than fifty thousand chemical and technological analyses of coal and coal ashes from the Upper Paleozoic basins of the CR have contributed to a better knowledge of the quality of coals, with regard to ash and sulfur contents and the distribution of trace elements. Because of the diversity of samples and analyses included in the database (older and newly analyzed samples, various analytical methods, etc.) and the

Table 17. Basic chemical and technological characteristics and contents of selected major and minor elements in coal ashes of Carboniferous relics near Vranov (VR) and Mirošov (MiR) (Asturian)

	VR	MiR
W_f^r %	3.7	
C^{daf} %	76.9	78.6
H^{daf} %	5.0	5.2
N^{daf} %	1.5	1.5
O^{daf} %	16.1	9.4
V^{daf} %	35.3	39.8
R_o %	0.7	
S_t^d %	1.1	5.2
S_p^d %	0.4	
S_{SO4} %	0.2	
S_0^d %	0.5	
Q_s^{daf} $MJ.kg^{-1}$	29.5	
A^d %	16.8	11.3
Ag ppm	0.8	1.8
As ppm	48.3	
Be ppm	49.0	17.6
Bi ppm	0.9	5.3
Cd ppm	< 0.8	
Co ppm	296	22
Cr ppm	153	145
Cs ppm	20	
Cu ppm	593	113
Hg ppm	0.011	< 0.005
Ir ppb	0.2	
Mo ppm	26.0	22
Ni ppm	684	65
Pb ppm	72.0	286
Pd ppb	4.5	
Pt ppb	11.5	
Rb ppm	24.0	60
Rh ppb	1.0	10
Ru ppb	0.5	< 10
V ppm	775	350
Zn ppm	409	109

Table 18. Contents of selected minor elements in coal ashes of Carboniferous relic at Brandov (Bolsovian). Compiled from earlier data

	numb. samples	arithm. mean
Ag ppm	5	3.0
As ppm	5	1900
Be ppm	5	40.0
Co ppm	5	240
Cu ppm	5	1500
Ga ppm	5	260
Ge ppm	5	57.0
Mo ppm	5	30.0
Ni ppm	5	270
Pb ppm	5	90.0
Sn ppm	5	20.0
V ppm	5	400
Zn ppm	5	800

often incomplete nature of the analyses, there is great variation in the pattern of distribution of individual elements and their concentrations. Based on the Table 21, the most abundant coal in the Czech basins ranks among high volatile dirty coal (R_o 0.7 %, A^d 36.3 %) with total sulfur (S_t^d) equal to 1.7 %.

As shown in the database of sulfur and trace element contents in coals from the Permo-Carboniferous basins in the CR, besides sulfur, the elements most analyzed were germanium and arsenic. Less studied were Ag, B, Ba, Be, Cr, Cu, Ga, Nb, Ni, Pb, Rb, Sn, Sr, U, V, Y, Zn and Zr. Rarely, elements such as Au, Bi, Br, Ce, F, Gd, Ir, La, Pd, Pt, Rh, Ru, Sc, Te and Th were also analyzed.

Sulfur is one of the most common elements occurring in coal but its concentrations may vary widely. The mean content is around 1.7 % S_t^d but the highest concentrations are mostly lower than 10 % S_t^d. The highest contents of sulfur were found in coal from the bottom of the Slaný Formation in the MRB (S_t^d 0.04-18.4 %, on average 2.1 %), from the Svatoňovice Formation in the CPISB (S_t^d 0.54–10.1 %, on average 3.5 %), from the Nýřany Member in the PB

Table 19. Basic chemical and technological characteristics and contents of selected major and minor elements in coal ashes of the Rosice-Oslavany Formation of the Boskovice Graben (Stephanian C). Compiled from earlier and recent data

	numb. samples	arithm. mean	stand. deviation	min	Q1	median	Q3	max
C^{daf} %	11	88.7	1.33	86.1	87.8	88.8	89.8	90.2
H^{daf} %	11	4.4	0.28	4.2	4.2	4.3	4.7	5.0
N^{daf} %	11	1.6	0.09	1.4	1.6	1.6	1.6	1.7
O^{daf} %	11	1.8	0.67	0.45	1.4	1.8	2.1	2.9
V^{daf} %	3012	24.0	3.46	15.0	20.5	24.0	27.0	28
R_o %	1	1.9						
S_t^d %	3018	3.8	0.44	1.9	3.4	3.8	4.0	5.2
A^d %	3152	49.4	13.71	8.3	37.5	45.0	60.0	67.5
Ag ppm	1	2.8						
As ppm	1	220						
Be ppm	1	19.8						
Bi ppm	1	0.3						
Co ppm	1	16						
Cr ppm	1	96						
Cs ppm	1	13						
Cu ppm	1	86						
Ge ppm	131	3	1.33	0.9	1.7	3.6	4.3	5.3
Hg ppm	1	0.011						
Ir ppb	1	2.9						
Mo ppm	1	48						
Ni ppm	1	55						
Pb ppm	1	27						
Pd ppb	1	2.9						
Pt ppb	1	44.1						
Rb ppm	1	107						
Rh ppb	1	0.300						
V ppm	1	75						
Zn ppm	1	140						

Table 20. Basic chemical and technological characteristics and contents of selected major and minor elements in coal ashes of the Lhotice Member of the Blanice Graben (Autunian). Compiled from earlier and recent data

	numb. samples	arithm. mean	stand. deviation	min	Q1	median	Q3	max
W_f^r %	1	6.0						
C^{daf} %	6	90.4		81.3				93.8
H^{daf} %	6	3.2		2.8				4.0
N^{daf} %	6	1.0		0.37				1.2
O^{daf} %	6	2.1		0.9				5.8
V^{daf} %	4	8.7		4.4				13.0
R_o %	1	3.5						
S_t^d %	8	2.3		0.9				3.4
S_p^d %	2	2.2		1.9				2.4
S_{SO4} %	2	0.6		0.02				0.1
A^d %	10	17.0	6.62	6.5	12.1	15.9	23.2	25.1
Ag ppm	2	58		2.3				113
As ppm	2	138		78.6				197.7
Au ppm	1	35						
Be ppm	2	7.1		6.9				7.3
Bi ppm	2	0.4		0.33				0.44
Co ppm	2	15.5		14				17
Cr ppm	2	111		99				122
Cs ppm	2	14.5		14				15
Cu ppm	2	65.5		54				77
Ir ppb	3	1.4		0.8				2.1
Mo ppm	2	33.5		33				34
Ni ppm	2	50		41				59
Pb ppm	2	31.5		19				44
Pd ppb	3	5.4		0.8				7.3
Pt ppb	3	23.4		5.4				52.1
Rb ppm	2	115		108				121
Rh ppb	3	0.57		0.3				0.8
Ru ppb	3	1.7		1.0				3.0
U ppm	1	9.5						
V ppm	2	277		268				286
Zn ppm	2	82.5		80				85

(S_t^d 0.01–9.2 %, on average 1.0 %), from the Syřenov Formation in the KPB (S_t^d 0.24–10.7 %, on average 3.4 %), from the České Budějovice relic in the BG (on average S_t^d 2.3 %) and in the BOG (on average S_t^d 3.8 %). Relatively low sulfur contents were determined in both formations of the Czech part of the Upper Silesian Basin: Ostrava Formation (S_t^d 0.19–3.3 %, on average 0.9 %) and Karviná Formation (S_t^d 0.24–2.0 %, on average 0.7 %).

Sulfur is present in coals from Carboniferous relics in the surrounding of the WCBB (Table 17) where the contents of sulfur (S_t^d) vary between 0.62 to 5.2 % (the relic near Mirošov). Framboids and crystals of syngenetic pyrite were also found in anthracite from Brandov. The low sulfur coals of the CPISB have a low content of pyrite sulfur because dispersed framboids and crystals of pyrite are usually absent, but massive aggregates of various sulfides may be found occasionally. More massive forms and filling of micro-fractures by sulfides were observed only in coal of the Jívka Member in the CPISB and in the Syřenov Formation in the KPB. Anthracite from the BG (Table 20) and coal from the BOB (Table 19) contain on average 0.9–3.8 % (max. < 5.2 %) of S_t^d. This is contained mostly in pyrite and in the organic component. Crystals of pyrite and, less commonly, framboids were identified.

Apart from substantial variations in the content of germanium, it is worthy of note that the highest concentrations occur in high volatile bituminous coal that was extracted from the WCBB. This finding corresponds with results obtained from Swaine (1990) and Spears and Zheng (1999). The highest concentrations of Ge were found in coal seams of the Nýřany Member of the PB (on average 111 ppm, max. 7,110 ppm), in the Radnice Member of the KRB (on

Table 21. Basic chemical and technological characteristics and contents of selected major and minor elements in coal ashes of "an ideal coal seam" of all hard coal basins in the Czech Republic. Compiled from earlier and recent data

	numb. samples	arithm. mean	stand. deviation	min	Q1	median	Q3	max
W_f^r %	27806	9.4	7.4	0.4	2.7	8.0	16.6	28.7
C^{daf} %	14054	77.9	7.2	16.1	76.9	79.2	79.7	97.8
H^{daf} %	13777	5.5	0.2	2.8	5.4	5.5	5.6	6.4
N^{daf} %	8732	1.1	0.2	0.3	1.1	1.1	1.3	3.1
O^{daf} %	6704	13.8	3.0	0.5	12.4	13.9	15.3	25.7
V^{daf} %	27534	36.3	5.7	3.0	35.3	37.7	39.8	97.7
R_o %	11236	0.7	0.1	0.6	0.7	0.8	0.8	1.6
S_t^d %	37536	1.7	1.8	0.01	0.5	0.8	2.2	72.0
S_p^d %	6681	33.7	5.5	0.2	30.4	31.8	36.3	82.5
S_{SO4} %	7	0.03		0.01				0.1
A^d %	52418	33.4	16.9	0.88	21.6	30.8	41.3	99.99
Ag ppm	393	5.6	9.2	0.7	3.0	3.0	5.0	113
Al ppm	12	68800	59460	1833.8	17400	64100	103600	190000
As ppm	5265	43.4	99	0.4	23.0	29.0	33.0	2830
Au ppm	1	35.0						
B ppm	602	545	796	4.89	200	300	500	8000
Ba ppm	1023	342	621	0.2	2	3	679	7948
Be ppm	639	43.3	65.2	0.1	20.0	30.0	50.0	1338
Bi ppm	32	1.5	1.28	0.11	0.4	1.2	2.0	5.7
Br ppm	14	9.0	3.81	3	5.0	10.5	12.0	12.8
Cd ppm	40	1.8	3.88	0.2	0.3	0.4	1.6	22.9
Ce ppm	5	14		10				20
Cl ppm	80	746	699.4	160	200	545	837	3750
Co ppm	1175	104	206.2	0.9	50	92	92	5300
Cr ppm	972	231	319.7	2	83	112	300	4970
Cs ppm	224	44.9	31.16	1.1	30.0	40.0	50.0	300
Cu ppm	1413	239	514.1	4.9	100	150	250	12800
F ppm	28	68	58.13	10	40.0	40.0	110.0	300
Fe ppm	9	93300		3192				308000
Ga ppm	413	36.3	31.73	0.6	22.0	26.0	36.0	260
Gd ppm	1	10						
Ge ppm	6845	45.1	145.18	0.1	24.6	34.0	50.0	7110
Hg ppm	52	0.454	0.559	0.006	0.020	0.080	1.200	1.33
Ir ppb	11	2.8	5.65	0.2	0.4	0.7	2.1	19.5
K ppm	596	16000	8660	1000	10500	15700	21100	106244
La ppm	2	1000		1000				1000
Li ppm	605	146	120	1.2	90	120	180	1440
Mg ppm	8	36000		7400				101000
Mn ppm	607	96.5	592.13	0.1	0.5	1.0	2.0	6480
Mo ppm	713	19.3	24.73	1	3.0	10.0	25.0	201
Na ppm	578	17200	8900	1279	12900	16200	20300	151237
Nb ppm	410	18.8	6.88	0.7	16.0	20.0	22.0	52
Ni ppm	1919	263	511.6	3.2	29	100	620	17170
P ppm	397	41.9	252.02	0.032	3.0	5.0	10.0	3680
Pb ppm	1867	1510	2138	2.7	60	250	5000	9550
Pd ppb	12	4.8	3.49	0.7	2.4	3.9	6.6	11.2

Table 21 – continued

	numb. samples	arithm. mean	stand. deviation	min	Q1	median	Q3	max
Pt ppb	12	95.6	192.01	16.9	23.0	44.4	56.6	702.4
Rb ppm	913	144	72.1	1.3	95	140	181	1150
Rh ppb	10	0.33	0.455	0.1	0.100	0.200	0.300	1.6
Ru ppb	1	3						
Sb ppm	50	83.7	386.82	0.2	0.8	1.6	4.1	2210
Sc ppm	14	38.7	18.62	7.4	25.3	35.7	54.8	66.5
Se ppm	52	1.5	2.10	0.3	0.6	1.0	1.4	13.2
Sn ppm	745	9.5	9.27	0.4	3.0	10.0	12.0	119
Sr ppm	447	396	877.7	26.7	65	146	177	6601
Te ppm	17	0.8	0.468	0.2	0.500	0.700	0.900	1.9
Ti ppm	645	357	1621.1	0.3	6	10	10	21700
Th ppm	31	21.7	26.41	3.9	5.5	5.5	33.9	115
Tl ppm	20	5.3	10.12	0.23	2.0	3.1	4.0	47.2
U ppm	93	15.1	14.49	1	5.0	13.0	13.0	90
V ppm	1846	199	162.7	1.7	100	154	200	1680
W ppm	43	78.8	131.89	0.9	13.9	53.0	88.5	838
Y ppm	413	69.5	61.51	4.1	44.0	49.0	56.0	544
Zn ppm	1244	348	496.2	2.5	94	129	720	8000
Zr ppm	419	182	105.6	0.8	93	187	229	826

average 70.0 ppm, max. 4,440 ppm) and in coal seams of the Radvanice Member of the CPISB (on average 23.1 ppm, max. 3,680 ppm). The concentration of Ge decreases with increasing coalification – e.g., coal seams from the Karviná Formation of the CPUSB contain on average 15.6 ppm Ge (max. 200 ppm), from the Žacléř Formation in the CPISB on average 43.9 ppm Ge (max. 280 ppm) and from the Svatoňovice Member on average 25.9 ppm Ge (max. 100 ppm). Anthracite from Brandov contained on average 57 ppm Ge and coal of the Boskovice Graben shows only 3.0–5.3 ppm Ge. No germanium was found in coal of the Blanice Graben (Vlášek 1958, Bouška 1966) – Fig. 8. Swaine (1990), Bouška (1981), Bouška et al. (2000), Klika et al (2003) consider Ge to be bound in the organic component, whereas Finkelman (1981) is of the opinion that Ge is confined to pyrite.

Knowledge of arsenic distribution in coals (Fig. 8) is important from the ecological point of view. It is evident from our database that the lowest concentrations of As (< 109 ppm) occur mostly in coals from some seams in the CPISB, PB and RB. The highest mean contents of As were found in coal seams of the Nýřany Member (1,262 ppm) in the KRB and in anthracite from the Brandov relic (1,900 ppm). Newly collected and analyzed samples from the WCBB showed significantly lower amounts of arsenic (2.08-98 ppm). Markedly higher contents of As (19.7 to 536.4 ppm at 0.24–10.7 % S_t^d) were found in coal from Syřenov in the KPB, in anthracite from the locality near the town of Vlašim in the BG (78.6–197.7 ppm at 0.9–9.4 % S_t^d, 1.9–20.4 % S_p^d) and in coal from the BOG (220 ppm As at 1.9–5.2 % S_t^d). These data indicate that high contents of arsenic occur in coals having enhanced or high concentrations of total sulfur in its most abundant forms – pyrite and organic sulfur. Positive correlation between the content of pyrite and concentration of As has already been reported by Finkelman (1981) and Finkelman et al. (1990) and proved by Bouška (1981), Swaine (1990) and Bouška et al. (2000), although the latter three papers also mention the possibility that arsenic is bound in organic matter. In contrast, Hower et al. (1994) found enhanced contents of As in the vitrite and clarite fractions of bituminous coal from SE Kentucky that contained only a minor inorganic component. Huggings and Huffman (1996) found that As in less coalified coal occurs in the form of As^{+3}, which may react with the oxygen groups in organic matter.

Some elements like B, Be and Ge tend to form metal-organic complexes, whereas Cs, Li and Rb, like other alkaline metals, show high affinity to aluminosilicates and an ambiguous tendency to combine with organic components. Ba, Mn and Sr usually occur in carbonates, while As, Cd, Co, Cr, Cu, Hg, Mo Ni and Pb are linked to the occurrence of sulfides (Martínez-Tarazona et al. 1992). Studies focused on the bonding of individual elements within coal matter based on the separation of single fractions (Martínez-Tarazona et al. 1996, Klika et al. 2003) or progressive leaching (Finkelman et al.1990) showed that the patterns of distribution of elements between the organic and inorganic components of the coal mass are complex, a feature that is no doubt amplified by the intimate intergrowth of these fundamental components. Coals with enhanced contents of pyrite occur in the KRB where high As and enhanced concentrations of Cu were also found.

Similar parameters are shown by coals found within the Svatoňovice Member of the CPISB and in the Syřenov Formation in the KPB where contents of Cu are in excess of 1,000 ppm. These coals also contain enhanced to high concentrations of Ni, Pb (Fig. 9) and Zn. In contrast, most coal from Carboniferous relics in the environs of the WCBB and from the Žacléř Formation of the CPISB with $S_t^d < 1.1$ % are low in As but notably rich in Cu. The inorganic component of these coals consists of clay minerals (kaolinite), whereas sulfides, carbonates and quartz are less abundant. Although MARTÍNEZ-TARAZONA et al. (1992) believe that copper is bound mainly in sulfides (chalcopyrite), a bond with organic matter cannot be excluded (SWAINE 1990, BOUŠKA et al. 2000). With respect to Rb, SWAINE (1990) assumes that this element is bound in clay minerals. The majority of coals showing low sulfur and higher contents of mineral matter, clay minerals in particular, such as those from the Karviná Formation in the CPUSB, and in the PB and KRB, including some Carboniferous relics in their environs, and in seams of the Žacléř Formation in the CPISB contain 150 ppm Rb, whereas data published by Swaine (1990), 2–50 ppm Rb in the majority of coals, are much lower. Belgian coals reportedly contain as much as 110 ppm Rb, and coal from Nigeria up to 800 ppm Rb. The occurrence of other elements such as Cr, Ga, Sc, Ti, V and REE also seems to be connected with the presence of clay minerals. Extremely high concentrations of vanadium in quite different coal samples collected from coal seams of the Radnice Member in the KRB (735 ppm) and from the Syřenov Formation in the KPB (1,500 ppm, Table 9) seem to be governed by an affinity between V and clay minerals and also with its entry into the structure of muscovite (HUGGINS – HUFFMAN 1996) and organic matter (SWAINE 1990, BOUŠKA et al. 2000). High contents of carbonates, particularly calcite healing fractures in the coal from the Jívka Member in the CPISB and from the Syřenov Formation have not led to higher contents of trace elements characteristic of carbonate mineralization (e.g., Ba, Mn, Nb, Sr and Y). The presence of Pt in coal may also be ascribed to the occurrence of carbonates, quartz and Pt-sulfides (DAI et al. 2003). Concentrations of Pt in the studied samples fluctuated from < 3 ppb to 74 ppb. The maximum value was found in almost pure coal (3.9 % A^d). The high values for Ba (more than 1000 ppm) and Sr (more than 300 ppm) in the coal seams from the Ostrava and Karviná formations of the Upper Silesian Basin may indicate the occurrence and/or influence of clastics and volcaniclastics in the coal-bearing strata (GOODARZI et al. 2009).

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