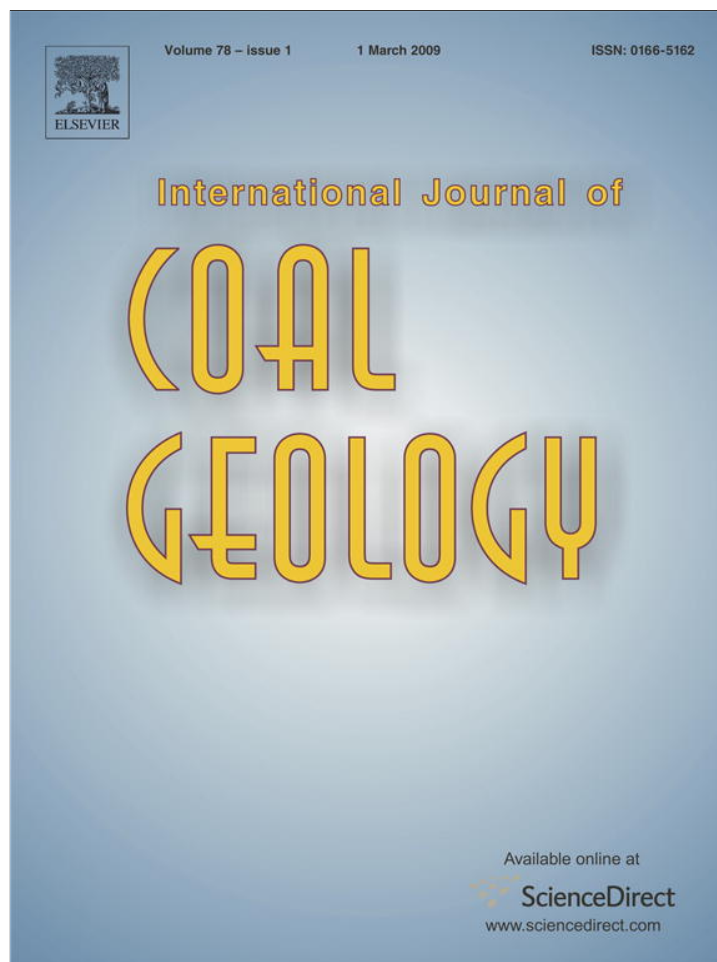


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Isotopic composition of lead in Czech coals

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ABSTRACT

The content and isotopic compositions of lead (Pb) were studied on selected coal samples from the Czech Republic. Simultaneously, the forms of bonding of Pb in coal were studied using sequential extraction (1M ammonium acetate, 3 M HCl, 48% HF and 2 M HNO₃). Lead in most samples of bituminous and brown coal is mobilized by 3 M HCl, while sulphides are already oxidized in the studied samples at the beginning of the extraction (1 M ammonium acetate). Thus, Pb could be bonded in carbonates and oxides and also to sulphides present in the coal. Following decomposition of the sulphides, Pb is adsorbed on the remainder of the solid phase and is released only in the acidic medium of the second extraction solution (i.e. 3 M HCl). Bituminous coal contains an average of 33 mg/kg Pb, while brown coal contains an average of 8.9 mg/kg Pb. The ²⁰⁶Pb/²⁰⁷Pb ratio varies in the range 1.167–1.234 for bituminous and 1.172–1.24 for brown coal. No inverse proportionality of the Pb content and the ²⁰⁶Pb/²⁰⁷Pb ratio was observed in the studied samples and, thus, the Pb content in most samples is a result of the combination of lithogenic and ore Pb. Only several samples with high uranium contents exhibited a highly radiogenic ²⁰⁶Pb/²⁰⁷Pb ratio (>1.3). It was not possible to demonstrate any statistical dependence between the operational defined speciation of Pb, the mineralogical composition and the Pb isotopic composition.

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1. Introduction

The combustion of coal leads to a number of changes in the composition of the surface of the Earth, which are related to human activity. The amount of coal burned reached a maximum in the Czech Republic in the 1980s (e.g. [Kopáček and Veselý, 2005](#)) and this led to intensive acidic atmospheric deposition and contamination of the soil by metals.

Lead (Pb) is a nonessential toxic metal whose biogeochemical cycle has been very substantially affected by human activities ([Komárek et al., 2008](#)). Important sources of this metal in the natural environment include combustion of coal ([Swaine, 1990](#); [Mastalerz and Drobnik, 2007](#)), especially in the production of heat and electrical energy.

Coal in the Czech Republic contains Pb in the range 0.6–70 mg/kg ([Bouška, 1981](#); [Bouška and Pešek, 1999](#)), and a similar range is given by [Swaine \(1990\)](#) for most compared samples of coal (2–80 mg/kg) and soil (2–100 mg/kg). However, Pb contents in some samples reach up to 900 mg/kg ([Swaine, 1990](#)). Lead can be present in coal in the form of its own minerals such as galena (PbS) or clausthalite (PbSe) or as an admixture of Ba minerals, in the pyrite crystalline structure

substituting for Fe, or can be bonded to organic matter ([Swaine, 1990](#); [Finkelman, 1994](#)).

Determination of the bonding of trace minerals in coal is important from the standpoint of understanding a number of aspects of the formation of coal seams, including their inorganic components. The technical and environmental aspects of forms of inorganic substances contained in coal are just as important ([Vassilev and Tascón, 2003](#)). Qualitative and quantitative study of the speciation of substances in coal is performed by physical and chemical methods, which should be combined because of the diversity of forms and capabilities of the individual techniques ([Laban and Atkin, 1999](#); [Vassilev and Tascón, 2003](#); [Font et al., 2005](#)).

Lead has four stable isotopes, of which ²⁰⁴Pb is the primordial isotope and ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb are the products of radioactive decomposition of ²³⁸U, ²³⁵U, and ²³²Th ([Long, 1999](#)). The isotopic composition of ore bodies was formed in connection with the original isotopic composition of their sources, i.e. the contents of parent isotopes ²³⁸U, ²³⁵U, and ²³²Th; the content of radiogenic ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb, and the time when they were separated from the parent source. The isotopic composition of lead in an exogenous environment is the result of mixing of lead from its most important reservoirs, consisting particularly in lithogenic lead present in normal rock-forming minerals, lead in its compounds produced from ores and lead contained in fossil fuels. In environmental studies, the isotopic composition of lead is given especially as the ²⁰⁶Pb/²⁰⁷Pb ratio in relation to differences observed in individual reservoirs ([Komárek et al.,](#)

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2008) and the possibility of measuring this ratio using the available technology, especially quadrupole-based inductively coupled plasma mass spectrometry (ICP QMS). The isotopic ratios of lead $^{206}\text{Pb}/^{207}\text{Pb}$ can be used to determine the amount of natural and anthropogenic Pb (e.g. Monna et al., 1997; Ettler et al., 2004). Considerable attention has been devoted to the isotopic ratios of Pb in study of recent processes (e.g. Roy and Négrel, 2001; Monna et al., 2006) and also in study of the historical record contained in the geochemical archives of peat, tree rings, sediments, and glaciers (e.g. Farmer et al., 1996; Weiss et al., 1999; Watmough et al., 1999; Mihaljevič et al., 2006; Mihaljevič et al., 2008). In order to identify the individual sources of Pb, it is necessary to also know the isotopic composition of the coal employed. In contrast to ores, the isotopic fingerprint of Pb in coal was formed not only by separation of Pb from its parent isotopes by precipitation on organic matter, as its own minerals or their admixtures, but also suitable conditions also exist in coal-bearing media for the precipitation of U compounds that undergo subsequent decay and thus change the isotope fingerprint of the already accumulated Pb (Chow and Earl, 1972).

It is the purpose of this work to determine the probable source of Pb in selected samples of coal from the Bohemian Massif on the basis of its isotopic composition and to compare the isotopic composition with the elemental mode of Pb determined using extraction techniques and the mineralogical composition of coal determined by X-ray diffraction analysis.

2. Geological setting

The coal-bearing sequences of the continental and marine basins cover wide areas of the territory of the Czech Republic (Fig. 1), and differ in their tectono-metamorphic history. An extensive Late Paleozoic bituminous coal-bearing unit occurs in the Upper-Silesian Basin situated in the eastern margin of the Bohemian Massif as a fore-deep of the easternmost part of the European Variscides. Paralic and cyclic sedimentation prevailed in the Early Namurian and changed to typical continental sedimentation (Middle and Late Namurian and Langsetian) (Opluštil and Cleal, 2007).

The bituminous coal-bearing units of the Intra Sudetic Basin with siliciclastic sedimentation began in the Late Namurian and lasted in the Stephanian B. The Intra Sudetic Basin exhibits a complex tectonosedimentary history. Except for the Viséan Stage, the succession consists purely of continental deposits (Opluštil and Cleal, 2007).

In continental basins of central and western Bohemia, the sedimentation started in the Westphalian and, with several hiatuses, lasted until the end of the Carboniferous (Opluštil, 2005). Several sub-basins exhibit very similar sedimentary records and share the same lithostratigraphical subdivision. The most important coal seams are

concentrated in the lowermost part the coal-bearing unit (Duckmantian and Bolsovian). These Late Paleozoic basins are located on the weakly metamorphosed Neoproterozoic basement.

The deposition of the Tertiary (Eocene to Pliocene) basin-filling clastics, coals, and volcanoclastics of the Most and Sokolov Basins in northern Bohemia is connected with the formation of the NE-trending Eger-rift zone (e.g. Rajchl and Uličný, 2005). In general, only one brown coal seam situated near the base of the basin with a thickness of about 20 m is extensively mined in open-pit mines. Occasional brown-coal seams of the limnic České Budějovice Basin are of Miocene age.

3. Methodology

3.1. Coal samples

Coal samples and one sample of carbonaceous shale were taken from the deposit collection of the Faculty of Sciences of Charles University and from the collections of the Brown Coal Research Institute in Most. Coal samples from the Bílina open-pit mine were taken from the seam on May 19, 2005. Fig. 1 depicts a scheme of the individual sampling sites. A total of 22 samples of bituminous coal and 26 samples of brown coal were studied. Sample codes with the name of the mine, the coal seam, and the locality are given in Table 1. The samples were pulverized in an agate mill (Retsch, Germany) and dried to constant weight at laboratory temperature.

3.2. Chemical analysis

The content of U and Pb and the Pb isotopic composition were determined following mineralization of coal by the dry method. The coal was mineralized in a Linn (Germany) programmable furnace by the dry ashing of 1 g of sample with a temperature increase of $1\text{ }^{\circ}\text{C min}^{-1}$ to a maximum temperature of $450\text{ }^{\circ}\text{C}$. The total mineralization time was 10 h. The ash content was determined gravimetrically. The sample was subsequently dampened with deionized water (DIW; Milli-Q Academic System, Millipore USA) and dissolved in 5 ml of concentrated HF and 0.5 ml of concentrated HClO_4 . The mixture of acids was evaporated to near dryness and this step was repeated once. The residue was dissolved in 2 ml of concentrated HNO_3 , transferred to a 100-ml volumetric flask, filled to the mark with DIW and transferred to a 100 ml HDPE bottle (Azlon, UK). The stock solution was diluted to 2% (v/v) HNO_3 for determination of Pb, U and the Pb isotopic composition. Analytical grade acid (Merck, Germany) was used to prepare the solutions.

The sequential leaching procedure was performed on 5 g of sample with 25 ml of the following solutions: (1) 1 M ammonium acetate (NH_4OAc), (2) 3 M hydrochloric acid (HCl), (3) 48% hydrofluoric acid (HF),

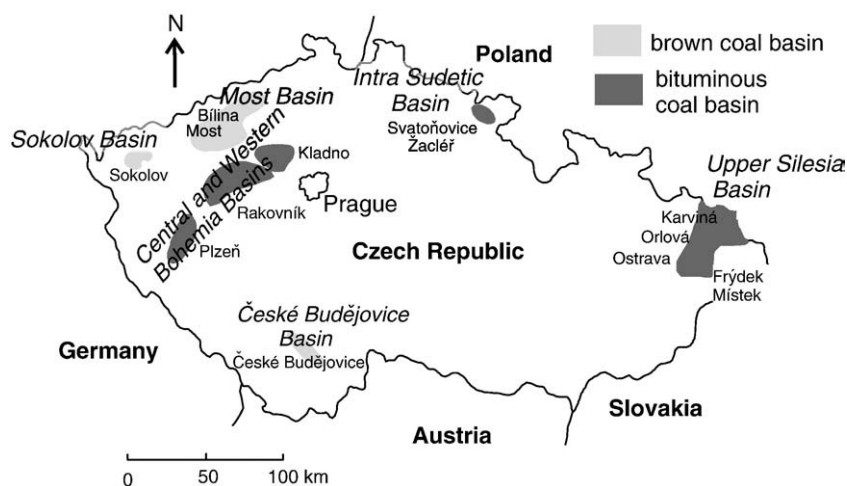


Fig. 1. Scheme of sampling sites for the studied coal samples in major Bohemian coal basins.

Table 1
Detailed localization of studied bituminous and brown coals

Code	Mine	Seam	Locality
<i>Bituminous coals</i>			
Kladno 1	Kladno	Main Kladno (Upper Radnice) Coal	Libušín u Kladna
Kladno 2a	Kladno	Main Kladno (Upper Radnice) Coal	Libušín u Kladna
Kladno 2b	Kladno	Lower Lubná Coal	Libušín u Kladna
Kladno 3	Kladno	Lower Lubná Coal	Libušín u Kladna
Kladno 4	Kladno	Lower Lubná Coal	Libušín u Kladna
Kladno 5	Tuchovice	Lower Lubná Coal	Tuchlovice
Rakovník 6	Richard	Kounov Coal	Kroučová
Plzeň 7	Krimich	1. Nýřany Coal	Tlučná
Ostrava 8	Hlubina	Laura Coal	Ostrava
Ostrava 9	Petr Bezruč	Petr Coal	Ostrava
Ostrava 10	Hlubina	Flora Coal	Ostrava
Ostrava 11	Hlubina	23	Ostrava
Karviná 12	Lazy (Zápotocký)	38	Orlová
Karviná 13	Lazy (Zápotocký)	38	Orlová
Orlová 14	J. Fučík (Pokrok)		Petřvald
Orlová 15	J. Fučík (Pokrok)	11	Petřvald
Frýdek Místek 16	Staříč		Frýdek Místek
Žacléř 17	Šverma		Kralovec
Svatoňovice 1*	Kateřina (Stachanov)	Baltazar Coal	Radvanice
Svatoňovice 2	šachta č. 1	Radvanice Coal	Chvaleč
Svatoňovice 3	Novátor	Rybníček Coal	Rybníček
Svatoňovice 4	úpadní šachta	Visutá Coal	Bystré
<i>Brown coals</i>			
Bílina 17	Bílina	Main Coal	Bílina
Bílina 18	Bílina	Main Coal	Bílina
Bílina 19	Bílina	Main Coal	Bílina
Bílina 20	Bílina	Main Coal	Bílina
Bílina 21	Bílina	Main Coal	Bílina
Most 22	J. Šverma–Vršany	Main Coal	Most
Most 23	J. Šverma–Vršany	Main Coal	Holešice
Most 24	J. Šverma–Vršany	Main Coal	Dřínov
Most 25	J. Šverma–Vršany	Main Coal	Dřínov
Most 26	J. Šverma–Vršany	Main Coal	Strupčice
Most 27	J. Šverma–Vršany	Main Coal	Strupčice
Most 28	ČSA	Main Coal	Albrechtice
Most 29	Hrabák–Vršany	Main Coal	Hořany
Most 30	Hrabák–Vršany	Main Coal	Hořany
Most 31	Hrabák–Vršany	Main Coal	Hořany
Most 32	Hrabák–Vršany	Main Coal	Hořany
Most 33	Merkur	Main Coal	Ahňkov
Most 34	Merkur	Main Coal	Ahňkov
Most 35	Libouš	Main Coal	Brány
Most 36	Libouš	Main Coal	Spořice
Most 37	Libouš	Main Coal	Spořice
Most 38	Libouš	Main Coal	Drouškovice
Sokolov 39	Jiří	Antonín Coal	Sokolov
Sokolov 40	Jiří	Antonín Coal	Sokolov
Sokolov 41	Družba	Antonín Coal	Sokolov
Sokolov 42	Medard	Antonín Coal	Sokolov
České Budějovice 43	Svatopluk	Mydlovary Coal	Mydlovary

*Carbonaceous shale.

(4) 2 M nitric acid (HNO₃) (Huggins et al., 2002). In each step, the extraction was performed by shaking at room temperature for a period of 18 h in Oak Ridge teflon centrifuge test tubes (Nalgene, USA). The residue was separated from the extractant by centrifugation, following each centrifugation, the residue was washed with DIW and the solution was added to the individual extracts in 50-ml volumetric flasks. The NH₄OAc extract was acidified with HNO₃ (pH < 2). The 48% HF (solution 3) extract was separated from the solid phase and after addition of 0.5 ml HClO₄ was fumed to the damp residue, which was then dissolved in 2% (v/v) HNO₃. The individual steps should mobilize: (1) exchangeable ions and readily soluble carbonates; (2) more resistant carbonates, oxides, and some sulphides; (3) silicates; and (4) pyrite and marcasite and organometallic complexes (Finkelman et al., 1990; Huggins et al., 2002; Vassilev and Tascón, 2003). A time scale at intervals of 1, 12, 24, 48, and 168 h was also performed with these extracts. Individual extraction of

brown and bituminous coal with the given reagents (1)–(4) was performed for each time interval. All the experiments were performed in duplicate with procedural blanks.

The contents of Fe, Al, and S were measured in the mineralized residue and extracts using inductively coupled plasma optical emission spectroscopy (ICP OES, IRIS Thermo Analytical, USA).

The concentration of U and Pb and its isotopic concentration in the solutions were determined using an inductively coupled plasma quadrupole mass spectrometry (ICP QMS, PQ3 VG Elemental, UK). The measurement parameters are given in Table 2. The isotopic composition was measured by diluting the solutions to a concentration of < 20 µg L⁻¹, and a correction for mass bias was performed using SRM 981 (Common lead, NIST, USA) between measurement of the individual samples (Ettler et al., 2004).

The total amounts of S and C in selected samples were determined using the ELTRA CS 500 elemental analyzer (Eltra, Germany). The quality of the analytical data was tested using standard reference materials SRM 1632b (Trace elements in coal – bituminous), and SRM 1635 (Trace elements in coal – subbituminous) both certified by NIST (USA) standard reference materials.

The mineralogical composition was studied by X-ray diffraction analysis (XRD) performed using a PANanalytical X Pert Pro diffractometer equipped with a diffracted-beam monochromator and X'Celerator multichannel detector. The analyses were performed under the following conditions: CuKα radiation, 40 kV, 30 mA, step scanning at 0.02°/250 s in the range 3–80° 2 theta.

The NCSS software (Hintze, 2001) was used for the statistical calculations, in particular for correlation analysis and histogram creation.

4. Results and discussion

4.1. Speciation of Pb and mineral composition

The contents of Pb, Fe, Al, and S in the individual fractions determined by sequential extraction recalculated to the content in the solid sample are given in Table 3. The average values determined for bituminous and brown coal are depicted graphically in Fig. 2. Table 4 gives the mineralogical compositions of selected coal samples. Amongst the individual minerals determined in the analyzed samples, there is a predominance of kaolinite (Al₂Si₂O₅(OH)₄), illite (K_{0.8}Al_{1.9}(Al_{0.5}Si_{3.5}O₁₀(OH)₂), and quartz (SiO₂). Kaolinite was identified as common or present in bituminous coals from Kladno, Ostrava, Svatoňovice and Bílina. Quartz occurs in most of the brown coal samples. Some of the samples also contained pyrite (FeS₂) (Kladno, Rakovník, Frýdek Místek) and marcasite (FeS₂) or their alteration products (szomolnokite – FeSO₄ H₂O). Some

Table 2
Operating conditions used for ICP MS elemental and isotopic measurement

Parameter	Value	
Analyte	Pb, U	²⁰⁶ Pb/ ²⁰⁷ Pb, ²⁰⁸ Pb/ ²⁰⁶ Pb
Measured isotopes	²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²³⁸ U, ²⁰⁵ Tl*	²⁰² Hg, ²⁰⁴ Pb, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb,
RF power (W)	1450	1300
Reflected power (W)	< 1	< 1
Gas flows (l min ⁻¹)	Coolant 13.5, nebulizer 0.78, auxiliary 1.3	Coolant 13.2, nebulizer 0.70, auxiliary 1.4
Nebulizer	Meinhard type	Meinhard type
Acquisition mode	Peak jump	Peak jump
Acquisition time (s)	30	90
Points per peak	3	5
Dwell time (ms)	10	10 (²⁰² Hg, ²⁰⁸ Pb), 40 (²⁰⁴ Pb), 20 (²⁰⁶ Pb, ²⁰⁷ Pb)
Quadrupole settling time (ms)	10	10
Replicates	3	10
Number of sweeps	150	250
Detector mode	Dual	Pulse count

*Internal standard.

Table 3
Contents of Al, Fe, Pb and S determined in extractions with 1 M NH₄OAc (A), 3 M HCl (B), 48% HF (C) and 2 M HNO₃ (D) recalculated to mg/kg in solid sample

Code	Extraction A (1 M NH ₄ OAc)				Extraction B (3 M HCl)				Extraction C (48% HF)				Extraction D (2 M HNO ₃)			
	Al mg/kg	Fe mg/kg	Pb mg/kg	S mg/kg	Al mg/kg	Fe mg/kg	Pb mg/kg	S mg/kg	Al mg/kg	Fe mg/kg	Pb mg/kg	S mg/kg	Al mg/kg	Fe mg/kg	Pb mg/kg	S mg/kg
<i>Bituminous coals</i>																
Kladno 1	<50	3	3.39	42.45	137	1067	44.0	48	24,170	376	8.16	19	1000	19	2.52	5.25
Kladno 2a	1771	17,940	38.5	42,890	2878	16,219	219	3122	27,050	3320	1.12	335	1976	225	14.16	122
Kladno 2b	265	15,900	15.8	35,890	1206	14,207	71.0	3079	9170	975	6.57	375	57	160	4.45	137
Kladno 3	<50	14.0	0.16	577	54	704	12.6	86	16,500	260	2.76	34	195	5.0	1.50	88.5
Kladno 4	<50	3	0.59	315	100	301	78.5	89	22,360	707	16.38	65	225	8.0	4.52	6.4
Kladno 5	<50	3	0.05	155	54	332	3.77	51	9320	167	0.47	33	118	2.0	0.67	7.65
Rakovník 6	<50	355	0.51	10,550	288	10,830	31.6	792	4193	926	2.56	80	69	75.5	0.46	67.9
Plzeň 7	<50	13.5	0.08	60.3	995	2989	2.10	108	8560	555	<0.05	18	76	5.5	2.26	8.85
Ostrava 8	<50	3	3.14	90.1	272	568	7.91	50	16,530	604	0.36	31	269	7.5	0.35	5.25
Ostrava 9	<50	15.5	0.05	227	200	1949	2.10	49	1320	321	<0.05	1	150	11.0	1.46	2.8
Ostrava 10	<50	11.0	0.45	48	139	543	1.87	51	5910	333	<0.05	1	106	3.0	1.50	2.85
Ostrava 11	<50	6.00	0.08	529	<50	876	2.80	82.1	4030	101	<0.05	29	101	3.0	0.08	5.3
Karviná 12	<50	3.0	0.05	24.7	190	2229	1.03	32	513	151	<0.05	1	<50	4.5	0.07	13.7
Karviná 13	<50	3.25	0.05	39.1	486	8224	1.85	36	1434	411	<0.05	1	85	6.0	0.04	1
Karviná 14	<50	9.50	0.03	261	1470	4611	1.53	101	2010	476	<0.05	1	127	28	0.08	10.1
Orlová 15	<50	6.00	0.03	212	88	560	0.74	47	1130	81	<0.05	1	79	7.5	0.52	1
Frýdek Místek 16	<50	39.5	0.03	1932	173	2756	1.64	350	3520	319	<0.05	62	749	72	7.13	60.7
Žacléř 17	<50	10.5	0.35	818	252	295	55.0	258	28,570	1910	<0.05	26	2051	101	0.08	26.9
Svatoňovice 1	<50	1.87	3.23	559	9310	4112	416	289	36,580	11,320	706	323	8025	419	414	128
Svatoňovice 2	<50	3.07	15.7	5275	192	17,110	9690	2233	9770	1207	194	952	387	149	2590	222
Svatoňovice 3	<50	5.27	<0.05	1140	658	5125	444	1115	8040	1220	14.1	127	865	52.6	69.4	32.9
Svatoňovice 4	<50	4.52	275	1041	912	8425	4270	766	33,500	4260	132	211	3375	220	339	55.0
<i>Brown coals</i>																
Bílina 18	<50	15.00	0.050	1039	1216	812	0.15	129	432	108	<0.05	1	<50	12	0.05	16.1
Bílina 19	<50	16.31	0.050	313	298	579	0.40	88	833	71	<0.05	1	<50	7.5	0.05	6.45
Bílina 20	<50	666	0.050	2380	<50	7026	0.24	882	259	144	<0.05	285	<50	74	0.44	43.9
Bílina 21	<50	7.00	0.181	308	2309	1075	2.19	48	1723	272	<0.05	1	1820	54	0.41	18.5
Most 22	<50	18.50	0.021	3060	2672	3209	4.06	311	1105	518	<0.05	88	68	94	0.51	90.8
Most 27	<50	29.49	0.039	3790	1733	5192	3.10	420	3028	707	<0.05	98	259	102	1.72	95.6
Sokolov 39	<50	3.0	0.033	821	138	434	2.08	88	12592	432	2.93	26	1890	48	0.48	7.65
Sokolov 42	<50	46.50	0.256	311	<50	1366	1.69	124	844	284	0.05	115	129	36	0.11	31.8
České Budějovice 43	333	6277	0.094	39260	718	19232	0.83	2211	1093	7111	0.05	125	51	76	7.09	54.7

bituminous coals contained calcite (CaCO₃) and other carbonates, dolomite (CaMg(CO₃)₂), ankerite (Ca(Fe²⁺,Mg,Mn)(CO₃)₂), and siderite (FeCO₃). Galena (PbS) and anglesite (PbSO₄) were identified in the sample with high Pb contents (Svatoňovice 2, 16 700 mg/kg Pb). Similar mineralogical composition (illite, kaolinite, carbonates, and quartz) is exhibited by high-ash coals from the Intra Sudetic Basin.

In most cases, Pb is extracted in 3M HCl (an average of 72% of the Pb in bituminous coal and 57% in brown coal), followed by extraction with 2M HNO₃ (an average of 17% of the Pb in bituminous coal and 28% in brown coal) (Fig. 2). An average of 5.3% of total Pb is extracted from both kinds of coal using 1M NH₄OAc. More than 10% of total Pb was extracted in the first step for two samples of bituminous coal containing an alteration

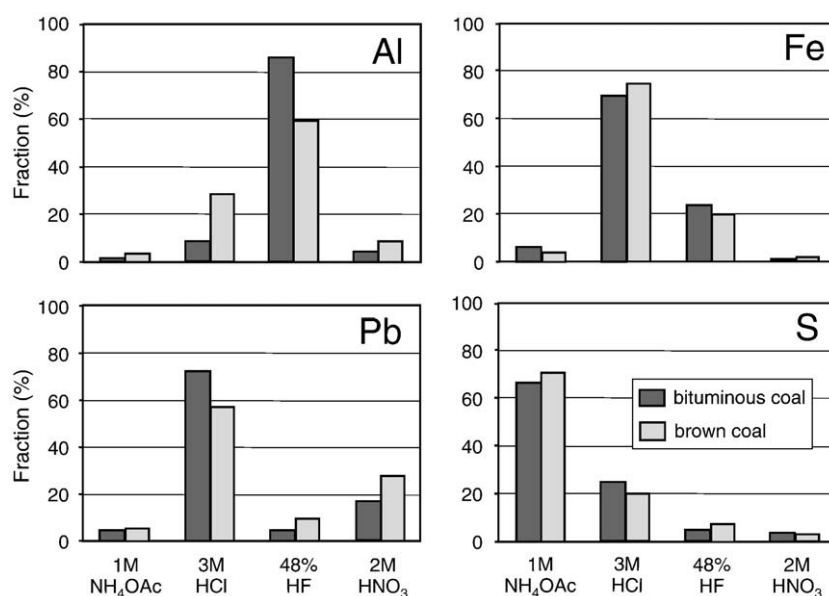


Fig. 2. Average percentage of Pb, Al, Fe and S mobilized by 1M NH₄OAc, 3M HCl, 48% HF a 2M HNO₃ in studied bituminous and brown coal.

Table 4
Mineralogical composition of coal samples as obtained by X-ray diffraction analysis

Code	Anatase	Illite	Jarosite	Calcite	Kaolinite	Ankerite/ dolomite	Quartz	Marcasite	Pyrite	Albite	Gypsum	Galena	Siderite	Szomolnokite	Others
<i>Bituminous coals</i>															
Kladno 1					XXX										
Kladno 2a		X			XX		XX		XX					XX	
Kladno 2b					XX		X		XXX					XX	
Kladno 3					XXX										
Kladno 4					XXX										
Kladno 5					XX		XX								
Rakovník 6					X		X		XX					X	
Plzeň 7					XX										
Ostrava 8					XXX		XX								
Ostrava 9				XXX											Halite
Ostrava 10					XX										
Ostrava 11					X										
Karviná 12					X	XX									
Karviná 13					X	XX							XX		
Karviná 14					X										
Orlová 15															
Frydek Místek 16						X	X		XX						
Svatoňovice 1		XXX				XX	XXXX			XX					
Svatoňovice 2					XX	XXXX (dol.)	X		XX			XX			Anglesite
Svatoňovice 3				XX	X	XXX (dol.)	X								
Svatoňovice 4		X			XX	XX (dol.)	XXX		X						
<i>Brown coals</i>															
Bílina 17		XXX			XXX		XX								
Bílina 18									X						
Bílina 19							X		X						
Bílina 20			X						XX					X	
Bílina 21							X								
Most 22									X						
Most 27					X		XX		XX						
Sokolov 39	XX				XX		XX								
Sokolov 42					X		XX	X							
České Budějovice 43							X				XX				

Relative abundance: XXXX – major, XXX – common, XX – present, X – trace.

product of the oxidation of Fe sulphides (szomolnokite – $\text{FeSO}_4 \cdot \text{H}_2\text{O}$) (Kladno 2a and Kladno 2b), and for other samples containing kaolinite and pyrite (Bílina 18, Sokolov 42) (Table 3). On the other hand, 3 M HCl is an extractant that should mobilize trace elements from carbonates and less stable sulphides. It is expected that the use of 2 M HNO_3 will lead to

extraction of Fe sulphides (pyrite, marcasite) and oxidation of organic materials (Vassilev and Tascón, 2003; Huggins et al., 2002). However, sequential extraction methods cannot be interpreted strictly as a means of determining the bonding of the studied element to the given material, but rather as a description of a state where the employed reagent

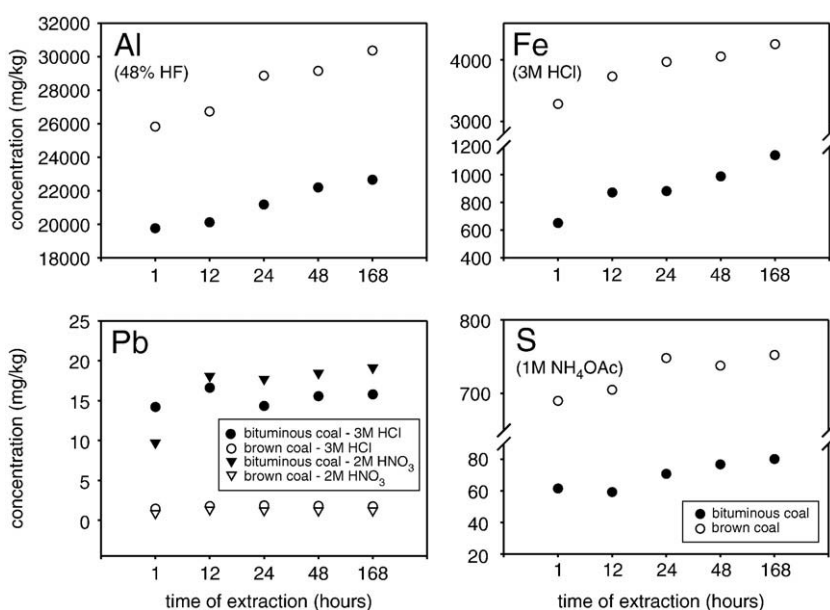


Fig. 3. Evolution of Al (extract in 48% HF), S (extract in 1 M NH_4OAc), Fe (extract in 3 M HCl), Pb (extract in 3 M HCl and 2 M HNO_3), contents in bituminous coal and brown coal (samples from Kladno and Bílina; in mg/kg recalculated to the solid sample).

determines the “operational speciation” (Bacon and Davidson, 2008). Thus, the results of the extraction methods must be combined with other techniques, e.g. electron microanalysis, XRD, XAFS (X-ray absorption fine structure – e.g. Vassilev and Tascón, 2003; Font et al., 2005). The reasons why extraction methods cannot quantitatively determine speciation of the given substance from the solid phase include: (i) the possibility of redistribution of the analyte during extraction, (ii) lack of selectivity of the extractant used, (iii) imperfect extraction, and (iv) formation of other phases during extraction (Bacon and Davidson, 2008). Imperfect extraction, i.e. failure to dissolve or failure to establish an equilibrium between the solid phase and the solution probably occurs in dissolution of sulphides. The contents of the main elements are monitored to confirm the effectiveness of the given extraction step in relation to the dissolved phase during the extraction procedure (e.g. Pardo et al., 2003). However, the contents of S in the individual extractions do not confirm the expected extraction of sulphides in 3 M HCl (or 2 M HNO₃). More than 60% of the total S content is extracted in the studied samples in step 1 of the employed procedure (Fig. 2). This result is also valid for samples in which the presence of pyrite was confirmed by X-ray analysis. The S content decreases gradually in the following steps of the extraction. This means that the substances released from the dissolved sulphides can mobilize at the beginning of the extraction experiment and the amount of dissolved sulphide is given by the basic parameters of this kinetic process, such as time, specific surface, rate constant, temperature and composition of the specific extractant (e.g. Nicholson et al., 1988; Descostes et al., 2004). The Fe content in the NH₄OAc, HCl and HF extracts is substantially correlated with the S contents in the NH₄OAc and HCl extracts (correlation coefficients; c.c.=0.71–0.96, $p < 0.001$). In bituminous and brown coal samples, an average of 70% and 75% of the Fe is extracted into the 3 M HCl extractant (Fig. 2). The HF extractant is in second place, extracting an average of 24% of total Fe in bituminous coal and 20% in brown coal. A small amount of Fe is extracted using 2 M HNO₃ (an average of 1% for bituminous coal and an average of <2% for brown coal), including samples containing pyrite or marcasite. The predominance of Fe in the 3 M HCl extract can be caused by extraction of Fe from oxides and carbonates (Finkelman et al., 1990). However, if the Fe-sulphides were dissolved in the first step of the extraction procedure, documented by the S content in the extract from the first step, then Fe could be released from the structure of pyrite and marcasite. While sulphide S is oxidized to dissolved sulphates or thiosulphates, Fe in the NH₄OAc buffer solution precipitates as stable hydrated oxides, that are dissolved in the second step, i.e. during extraction with 3 M HCl. The behaviour of S and Pb can be interpreted similarly. Sulphides contained in coal are dissolved during the first step. On the other hand, Pb is mostly extracted in the second step by sequential extraction (Fig. 2). Although Pb is probably bonded in sulphides, following their oxidation and release of Pb into solution, during step 1, Pb is strongly adsorbed on the undissolved residue of coal material (Lao et al., 2005) and passes into the extract only in highly acidic medium in step 2 (3M HCl). The total S content in the samples is correlated with the ash content (c.c.=0.70, $p < 0.001$) and the ash content is correlated with the Pb content (c.c.=0.47, $p < 0.05$). The dissolution of aluminosilicates in coal is a good indication of the content of Al, which is higher in HF extracts (Fig. 2).

Kinetic curves of the contents of Pb, Fe, Al and S in extracts (1) to (4) are depicted in Fig. 3. For illustration, the figures depict those steps that were predictable in previous observations (i.e., e.g. Al would be extracted especially in HF) and those that exhibit maxima in the individual steps (i.e., e.g. S in the NH₄OAc extract, Fig. 2). While Pb exhibits stable values after 12 h of the experiment, aluminosilicates (Al curve) are decomposed by the 48% HF solution during the entire experiment. Similarly, a non-equilibrium interaction occurs on release of S from both kinds of coal. The curve of the S content increases throughout the entire kinetic experiment (Fig. 3). The recommended length of extraction (18 hours, Huggins et al., 2002) is thus insufficient for determining the speciation of some substances.

4.2. Content and isotopic composition of Pb

The content of ash, C, S, Pb, and U, and the isotopic composition of Pb in the studied coal are given in Table 5. The average Pb content in bituminous coal in the Czech Republic equals 33.8 mg/kg (min. 1.67; max. 177 mg/kg). It is apparent from the concentration histogram (Fig. 4a) that contents in the interval 2–5 mg/kg predominate in the studied samples. The ²⁰⁶Pb/²⁰⁷Pb ratio in bituminous coal varies in the interval 1.167–5.434, and the studied set has a predominance of coals with a ratio of ²⁰⁶Pb/²⁰⁷Pb=1.19–1.20 (Fig. 4b). Brown coal from the Czech Republic contains an average of 8.9 mg/kg Pb (min. 0.3, max. 27.3 mg/kg); almost 35% of all the values are less than 5 mg/kg (Fig. 4c). The ²⁰⁶Pb/²⁰⁷Pb ratio in brown coal varies in the interval 1.172–1.548. An isotope ratio of ²⁰⁶Pb/²⁰⁷Pb=1.18–1.19 predominates in the brown coal samples (Fig. 4d). Similar isotopic ratios for the composition of coal were found by Farmer et al. (1999) for Scottish coal (²⁰⁶Pb/²⁰⁷Pb=1.181±0.011) and for coal from

Table 5
Contents of ash, C, S, Pb, U and ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁶Pb in the studied samples

Code	C	S	Pb	U	ash	²⁰⁶ Pb/ ²⁰⁷ Pb		²⁰⁸ Pb/ ²⁰⁶ Pb	
	%	%	mg/kg	mg/kg	%	Mean	SD	Mean	SD
<i>Bituminous coals</i>									
Kladno 1	69.6	0.29	84.8	3.94	16.1	1.182	0.005	2.08	0.01
Kladno 2a	35.9	LOD ^a	149	2.10	45.1	1.191	0.005	2.067	0.014
Kladno 2b	– ^b	–	–	–	–	1.202	0.007	2.042	0.013
Kladno 3	67.8	0.42	18.3	2.81	6.50	1.204	0.005	2.047	0.009
Kladno 4	63.6	0.54	75.2	7.87	11.8	1.199	0.005	2.06	0.011
Kladno 5	67.9	0.26	10.5	3.56	2.98	1.2	0.005	2.065	0.01
Rakovník 6	57.5	0.51	178	2.02	11.8	1.185	0.004	2.075	0.009
Pižeň 7	71.6	0.67	2.76	0.357	5.62	1.201	0.003	2.046	0.008
Ostrava 8	76.8	0.59	20.8	8.58	9.57	1.234	0.004	1.988	0.008
Ostrava 9	79.7	0.71	3.71	0.386	10.3	1.19	0.005	2.061	0.01
Ostrava 10	79.7	0.51	6.57	1.89	4.53	1.224	0.004	2.000	0.009
Ostrava 11	82.8	0.58	5.18	0.475	2.4	1.18	0.003	2.084	0.007
Karviná 12	81.4	0.20	2.72	0.032	2.26	1.173	0.002	2.089	0.008
Karviná 13	81.1	0.20	2.97	0.041	2.86	1.167	0.004	2.102	0.011
Karviná 14	82.0	0.34	1.77	0.098	2.48	1.172	0.003	2.094	0.007
Orlová 15	78.8	0.48	1.66	0.343	1.45	1.195	0.004	2.048	0.007
Frýdek Místek 16	84.2	1.44	4.44	0.746	5.48	1.195	0.004	2.06	0.012
Žacléř 17	68.4	0.94	6.23	2.49	2.76	1.183	0.002	2.081	0.009
Svatoňovice 1*	3.56	0.19	1890	5300	93.7	1.312	0.006	1.856	0.005
Svatoňovice 2	45.3	2.34	16700	9682	44.9	1.208	0.004	2.029	0.006
Svatoňovice 3	43.3	1.2	4230	10600	42.3	1.302	0.006	1.870	0.007
Svatoňovice 4	49.7	0.7	129	28700	36.2	5.434	0.01	0.322	0.005
<i>Brown coals</i>									
Bílina 18	65.5	0.53	LOD	0.158	3.28	1.204	0.004	2.07	0.005
Bílina 19	70.4	1.23	0.65	0.137	3.73	1.209	0.004	2.075	0.006
Bílina 20	65.6	6.13	LOD	0.016	10.9	1.204	0.006	2.072	0.007
Bílina 21	62.1	0.43	1.46	LOD	1.45	1.192	0.003	2.076	0.007
Most 22	58.8	2.00	5.99	1.27	6.53	1.191	0.003	2.079	0.008
Most 23	–	–	8.38	1.87	17.5	1.185	0.008	2.082	0.021
Most 24	–	–	10.8	1.31	20.1	1.194	0.004	2.075	0.015
Most 25	–	–	1.95	0.464	5.49	1.187	0.007	2.079	0.015
Most 26	–	–	8.84	1.53	13.1	1.185	0.008	2.094	0.015
Most 27	62.4	2.15	10.9	1.59	19.2	1.189	0.011	2.075	0.024
Most 28	62.8	0.77	2.79	0.341	6.27	1.175	0.011	2.099	0.031
Most 29	–	–	18.3	2.32	34.3	1.185	0.009	2.076	0.014
Most 30	–	–	6.81	1.22	34.7	1.184	0.009	2.095	0.009
Most 31	–	–	15.7	2.66	26.8	1.185	0.009	2.061	0.022
Most 32	–	–	15.2	2.67	26.6	1.192	0.009	2.076	0.034
Most 33	–	–	27.1	1.37	19.8	1.182	0.01	2.072	0.03
Most 34	–	–	10.0	4.42	27.2	1.175	0.012	2.095	0.02
Most 35	–	–	4.91	1.09	29.7	1.193	0.009	2.074	0.02
Most 36	–	–	7.61	1.71	19.2	1.181	0.009	2.083	0.021
Most 37	–	–	18.5	4.55	45.5	1.186	0.005	2.079	0.024
Most 38	–	–	27.3	5.17	34.5	1.172	0.009	2.095	0.023
Sokolov 39	62.8	0.77	8.83	4.31	11.9	1.24	0.004	2.001	0.009
Sokolov 40	–	–	5.68	3.88	12.1	1.22	0.011	2.039	0.014
Sokolov 41	–	–	3.82	3.39	5.85	1.208	0.006	2.052	0.011
Sokolov 42	74.9	LOD	8.56	138	6.68	1.548	0.003	1.565	0.004
České Budějovice 43	39.9	5.84	0.465	0.483	20.3	1.197	0.005	2.078	0.009

*Carbonaceous shale.

^aLOD – below the limit of detection; ^b – not determined.

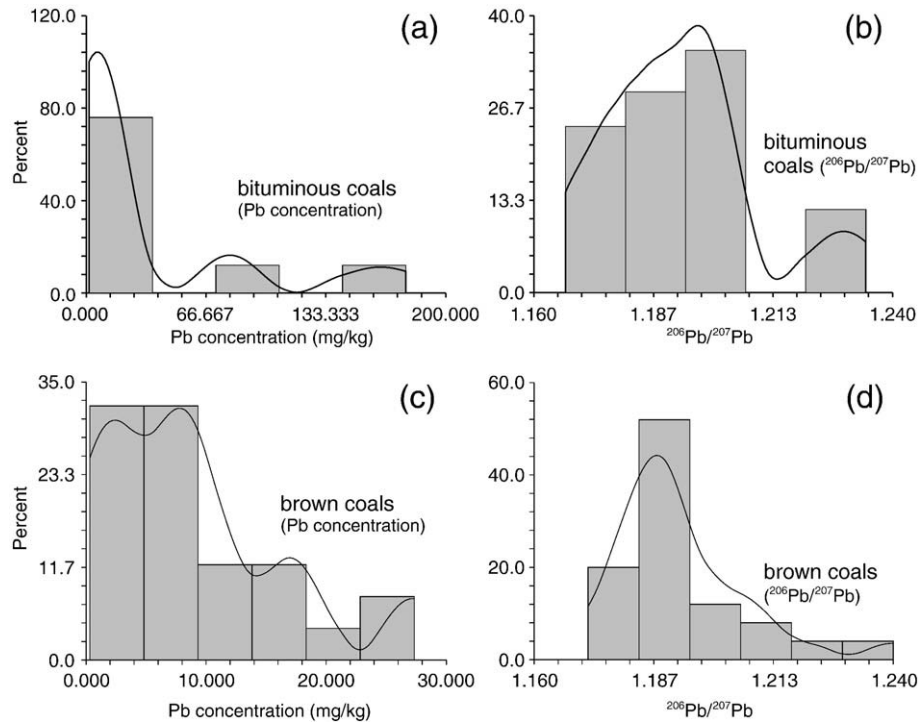


Fig. 4. Frequency of concentrations of Pb (a) and frequency of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (b) in bituminous coals ($n=18$), frequency of concentrations of Pb (c) and frequency of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio (d) in brown coals ($n=25$). Outlying values from Svatoňovice 1–4 and Sokolov 42 were not considered.

England and Wales ($^{206}\text{Pb}/^{207}\text{Pb}=1.184\pm 0.006$). A slightly greater scattering of the data ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.13\text{--}1.268$) is given for samples of Spanish coal by Díaz-Somoano et al. (2007). A more uniform ratio of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ in coal in the Czech Republic of 1.19 ± 0.006 and 2.465 ± 0.006 ($n=7$), respectively, is given by Novák et al. (2003). However, in the same work, on the basis of the Pb isotopic composition of the peat material in the nearby bituminous coal district, the authors assume a ratio of $^{206}\text{Pb}/^{207}\text{Pb}=1.17$ and a ratio of $^{206}\text{Pb}/^{207}\text{Pb}=1.19$ in the vicinity of brown-coal-burning power plants. The $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios are depicted in Fig. 5. Lead or its parent isotopes (^{235}U , ^{238}U and ^{232}Th) could enter the coal-forming environment in clastic or dissolved form during peat formation and also during the early and later stages of the diagenesis of the accumulated organic material by

precipitation from the circulating solutions (Swaine, 1990; Kolker and Chou, 1994). Lead is efficiently adsorbed on coal material; Lao et al. (2005) give a maximum adsorption capacity of 250 mg/kg Pb for leonardite. The studied samples did not exhibit any inverse proportionality between the Pb content and the radiogenicity observed for some samples of American coal (Chow and Earl, 1972). This means that, in most cases, the signature of the primary Pb precipitated in the coal-forming environment was not substantially affected at a later date by U and Th compounds as parent isotopes particularly of ^{206}Pb and ^{208}Pb . The isotopic fingerprints of the studied samples (Fig. 5) were probably affected by the hydrothermal activities bound to the Variscan plutons (e.g. polymetallic Ag–Pb deposits Příbram, Jáchymov, Stříbro, Kutná Hora) and other occurrences of polymetallic ore formation in the Bohemian Massif. The isotopic composition

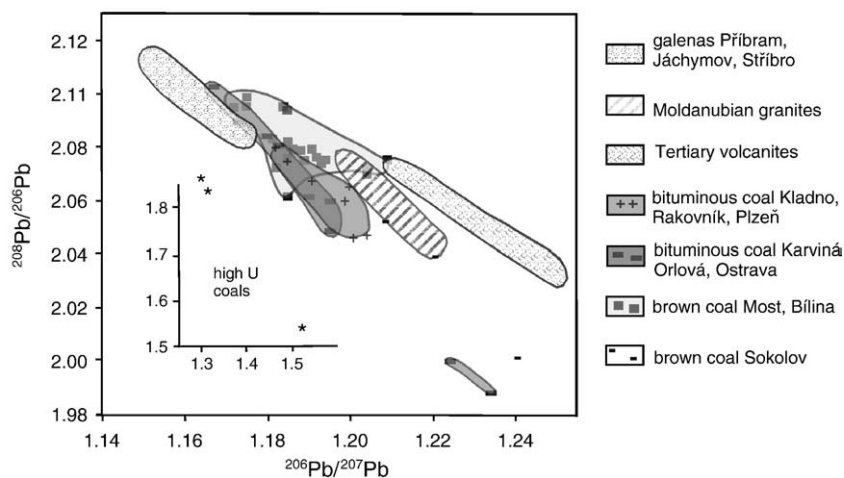


Fig. 5. Three-isotope plot ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$) depicting the composition of brown coal, black coal, coal samples with anomalous U contents, galenas and Pb deposits (Příbram, Stříbro and Jáchymov), data from Legierski and Vaněček (1967), Tertiary galenas (Roztoky and Teplice), data from Legierski and Vaněček (1967), and Tertiary volcanites from East and West Eifel volcanic field (Wörner et al., 1986).

of galena in these deposits varies in the range $^{206}\text{Pb}/^{207}\text{Pb}=1.15\text{--}1.202$ (Legierski and Vaněček, 1967). Other potential sources include the Variscan plutonites (especially Moldanubian (330–300 Ma), with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the range 1.19–1.23, or Tertiary volcanites and their hydrothermal galenas with a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the range 1.206–1.25 (Legierski and Vaněček, 1967; Wörner et al., 1986). The probable different U/Pb and Th/Pb compositions and ages of the source Moldanubian plutonites and Tertiary volcanites differentiate these rocks in the $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ diagram (Fig. 5). For a given $^{206}\text{Pb}/^{207}\text{Pb}$ ratio, the tertiary rocks exhibit a higher $^{208}\text{Pb}/^{206}\text{Pb}$ ratio. It is apparent from Fig. 5 that the North Bohemian tertiary coals have an isotopic composition affected by the hydrothermal galenas of the most important polymetallic deposits of the Bohemian Massif and Tertiary volcanites. Central Bohemian bituminous coals have an isotopic composition of Pb in the range between galenas of the important hydrothermal components relating to the Variscan plutons and the granitoids of these plutons.

The U concentrations in most of the studied samples are comparable with those in coals from other regions (Bouška, 1981; Van Der Flier and Fyfe, 1985; Swaine, 1990; Yang, 2007). Uranium can be bonded to the organic material of the coal and also to the inorganic components (Swaine, 1990). In this case, the isotopic composition of the coal is a result of mixing of the isotope ratios of common Pb in organic material at the time of its sedimentation and the radioactive products of the subsequently transported U and Th. Because of the predominance of ^{238}U in natural isotopic mixtures, the fingerprints of ^{206}Pb are substantially affected by systems highly enriched in U. This anomalous isotopic composition of Pb and the influence of U on the Pb isotopic ratio are exhibited by brown coal from Sokolov ($^{206}\text{Pb}/^{207}\text{Pb}=1.58$, U=138 mg/kg) and bituminous coal from the Intra-Sudetic Basin ($^{206}\text{Pb}/^{207}\text{Pb}=1.302\text{--}5.43$, U=10,600–28,700 mg/kg). These occurrences of coal material with higher U contents are unique in the Bohemian Massif, were not intended for energy-production purposes and their impact on the isotope fingerprint of Pb in the exogenous environment will be only local.

5. Conclusions

Sequential extraction experiments performed on the studied coal samples confirming the oxidation of sulphides in the first step of the extraction and mobilization of Pb in the subsequent step probably indicate the sulphidic bonding of Pb in coal. The average contents of Pb in bituminous and brown coals in the Czech Republic attain values of 22.7 mg/kg and 9.61 mg/kg, respectively. The isotopic compositions of bituminous and brown coals ($^{206}\text{Pb}/^{207}\text{Pb}$) vary in the ranges 1.167–1.234 and 1.172–1.24, respectively. The isotopic compositions of the studied coal samples were formed by a combination of lithogenic Pb and Pb from hydrothermal deposits accompanied by Variscan and Tertiary volcanites. Coal samples with elevated U contents exhibit anomalous isotopic composition ($^{206}\text{Pb}/^{207}\text{Pb}>1.3$). It was not possible to demonstrate any statistical dependence between the isotopic composition of Pb in the coal, the mineralogical composition, and the defined extraction step for the studied set of coal samples.

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References

- Bacon, J.R., Davidson, C.M., 2008. Is there a future for sequential chemical extraction? *Analyst* 133, 25–46.
- Bouška, V., 1981. *Geochemistry of coal*. Academia, Prague. (284 pp).
- Bouška, V., Pešek, J., 1999. Distribution of elements in the world lignite, average and its comparison with lignite seams of the North Bohemian and Sokolov basins. *Folia Mus. Rerum Natur. Bohem. Occident. Geol.* 42, 3–50.
- Chow, T.J., Earl, J.L., 1972. Lead isotopes in North American coals. *Science* 176, 510–511.
- Descostes, M., Vitorge, P., Beaucaire, C., 2004. Pyrite dissolution in acidic media. *Geochim. Cosmochim. Acta* 68, 4559–4569.
- Díaz-Somoano, M., Suárez-Ruiz, I., Alonso, J.I.G., Ruiz Encinar, J., López-Anton, M.A., Martínez-Tarazona, M.R., 2007. Lead isotope ratios in Spanish coals of different characteristics and origin. *Int. J. Coal Geol.* 71, 28–36.
- Ettler, V., Mihaljevič, M., Komárek, M., 2004. ICP-MS measurement of lead isotopic ratios in soils heavily contaminated by lead smelting: tracing the sources of pollution. *Anal. Bioanal. Chem.* 378, 311–317.
- Farmer, J.G., Eades, L.J., MacKenzie, A.B., Kirika, A., Bailey-Watts, T.E., 1996. Stable lead isotope record of lead pollution in Loch Lomond since 1630 A.D. *Environ. Sci. Technol.* 30, 3080–3083.
- Farmer, J.G., Eades, L.J., Graham, M.C., 1999. The lead content and isotopic composition of British coals and their implications for past and present releases of lead to the UK environment. *Environ. Geochem. Health* 21, 257–272.
- Finkelman, R.B., 1994. Modes of occurrence of potentially hazardous elements in coal: levels of confidence. *Fuel Process. Technol.* 39, 21–34.
- Finkelman, R.B., Palmer, C.A., Krasnow, M.R., Aruscavage, P.J., Sellers, G.A., Dulong, F.T., 1990. Combustion and leaching behavior of elements in the Argonne Premium coal samples. *Energy Fuels* 4, 755–766.
- Font, O., Querol, X., Huggins, F.E., Chimenos, J.M., Fernández, A.I., Burgos, S., Peña, F.G., 2005. Speciation of major and selected trace elements in IGCC fly ash. *Fuel* 84, 1364–1371.
- Hintze, J., 2001. NCSS and PASS. Number Cruncher Statistical System. Kaysville, Utah (Available from www.ncss.com).
- Huggins, F.E., Huffman, G.P., Kolker, A., Mroczkowski, S.J., Palmer, C.A., Finkelman, R.B., 2002. Combined application of XAFS spectroscopy and sequential leaching for determination of arsenic speciation in coal. *Energy Fuels* 16, 1167–1172.
- Kolker, A., Chou, C.L., 1994. Cleat-filling calcite in Illinois basin coals: trace-elements evidence for meteoric fluid migration in coal basin. *J. Geol.* 102, 111–116.
- Komárek, M., Ettler, V., Chrástný, V., Mihaljevič, M., 2008. Lead isotopes in environmental sciences: A review. *Environ. Int.* 34, 562–577.
- Kopáček, J., Veselý, J., 2005. Sulfur and nitrogen emissions in the Czech Republic and Slovakia from 1850 till 2000. *Atmos. Environ.* 39, 2179–2188.
- Laban, K.L., Atkin, B.P., 1999. The determination of minor and trace element association in coal using a sequential microwave digestion procedure. *Int. J. Coal Geol.* 41, 351–369.
- Lao, C., Zeledón, Z., Gamisans, X., Solé, M., 2005. Sorption of Cd(II) and Pb(II) from aqueous solutions by a low-rank coal (leonardite). *Sep. Purif. Technol.* 45, 79–85.
- Legierski, J., Vaněček, M., 1967. Lead isotopic composition of some galenas from the Bohemian Massif. *Acta Univ. Carol., Geol.* 2, 153–172.
- Long, L., 1999. Lead isotopes. In: Marshall, C.P., Fairbridge, R.W. (Eds.), *Encyclopedia of Geochemistry*. Kluwer Academic Publishers, Dordrecht, pp. 363–368.
- Mastalerz, M., Drobnik, A., 2007. Arsenic, cadmium, lead and zinc in the Danville and Springfield coal members (Pennsylvanian) from Indiana. *Int. J. Coal Geol.* 71, 37–53.
- Mihaljevič, M., Zuna, M., Ettler, V., Šebek, O., Strnad, L., Goliáš, V., 2006. Lead fluxes, isotopic and concentration profiles in a peat deposit near a lead smelter (Příbram, Czech Republic). *Sci. Total Environ.* 372, 334–344.
- Mihaljevič, M., Zuna, M., Ettler, V., Chrástný, V., Šebek, O., Strnad, L., Kyncl, T., 2008. A comparison of tree rings and peat deposit geochemical archives in the vicinity of a lead smelter. *Water Air Soil Pollut.* 188, 311–321.
- Monna, F., Lancelot, J., Croudace, I.W., Cundy, A.B., Lewis, J.T., 1997. Pb isotopic composition of airborne particulate material from France and the southern Europe: implications for Pb pollution sources in urban areas. *Environ. Sci. Technol.* 31, 2277–2286.
- Monna, F., Poujol, M., Losno, R., Dominik, J., Annegarn, H., Coetzee, H., 2006. Origin of atmospheric lead in Johannesburg, South Africa. *Atmos. Environ.* 40, 6554–6566.
- Nicholson, R.V., Gillham, R.W., Reardon, E.J., 1988. Pyrite oxidation in carbonate buffered solution. *Geochim. Cosmochim. Acta* 52, 1077–1085.
- Novák, M., Emmanuel, S., Vile, M.A., Erel, Y., Veron, A., Pačes, T., Wiedner, K.R., Vaněček, M., Štěpánová, M., Břízová, E., Hovorka, J., 2003. Origin of lead in eight Central European peat bogs determined from isotope ratios, strengths, and operation times of regional pollution sources. *Environ. Sci. Technol.* 37, 437–445.
- Opluštil, S., 2005. The effect of paleotopography, tectonics and sediment supply on quality of coal seams in continental basins of central and western Bohemia (Westphalian), Czech Republic. *Int. J. Coal Geol.* 64, 173–203.
- Opluštil, S., Cleal, C.J., 2007. A comparative analysis of some Late Carboniferous basins of Variscan Europe. *Geol. Mag.* 144, 1–32.
- Pardo, P., López-Sánchez, J.F., Rauret, G., 2003. Relationships between phosphorus fractionation and major components in sediments using SMT harmonised procedure. *Anal. Bioanal. Chem.* 376, 248–254.
- Rajchl, M., Uličný, D., 2005. Depositional record of an avulsive fluvial system controlled by peat compaction (Neogene, Most Basin, Czech Republic). *Sedimentology* 52, 601–625.
- Roy, S., Négrel, P., 2001. A Pb isotope and trace element study of rainwater from the Massif Central (France). *Sci. Total Environ.* 277, 225–239.
- Swaine, D.J., 1990. *Trace elements in coal*. Butterworth and Co Publishers, London. (296 pp).

- Van Der Flier, E., Fyfe, W.S., 1985. Uranium-thorium systematics of two Canadian coals. *Int. J. Coal Geol.* 4, 335–353.
- Vassilev, S.V., Tascón, J.M.D., 2003. Methods for characterization of inorganic and mineral matter in coal: a critical overview. *Energy Fuels* 17, 271–281.
- Watmough, S.A., Hughes, R.J., Hutchinson, T.C., 1999. $^{206}\text{Pb}/^{207}\text{Pb}$ ratios in tree rings as monitors of environmental change. *Environ. Sci. Technol.* 33, 670–673.
- Weiss, D., Shotyk, W., Appleby, P.G., Kramers, J.D., Cheburkin, A.K., 1999. Atmospheric Pb deposition since the industrial revolution recorded by five swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environ. Sci. Technol.* 33, 1340–1352.
- Wörner, G., Zindler, A., Staudigel, H., Schmincke, H.U., 1986. Sr, Nd and Pb isotope geochemistry of Tertiary and Quaternary alkaline volcanics from West Germany. *Earth Planet. Sci. Lett.* 79, 107–119.
- Yang, J., 2007. Concentration and distribution of uranium in Chinese coals. *Energy* 32, 203–212.