1. Introduction

The Czech Republic (CR) is more or less self-sufficient in supplies of bituminous coal and lignite from its own deposits. More than 12 mill. tons of hard coal and about 49 mill. tons of lignite are extracted annually. The first written records of mining for coal in the territory of the present CR date from the year 1463. The exploitation of this raw material had become intensive by the second half of the 19th century so that the coal reserves in many deposits and/or the majority of coal basins were soon exhausted. Carboniferous bituminous coal is still mined only underground in the Czech part of the Upper Silesian Basin. Tertiary lignite is extracted mostly from large open-cast mines (99 %) in the North Bohemian (NBB) and Sokolov basins (SB) and from one underground mine in the South Moravian coal district of the Vienna Basin (Fig. 1). In the 1950s much the possible extraction of germanium and gallium was studied as strategic raw materials. Bouška and Pešek (1999a, b) summarized results of the analyses of elements in ash from all lignite basins published or stored in archives.

2. Short history of investigation of trace elements in coal

During combustion of coal, numerous trace elements are emitted into the atmosphere and may endanger the environment and human health. The first discussion of the distribution of trace elements in European coals was firstly given by Goldschmidt (1935), using for that time modern analytical methods – emission spectrographic and X-ray fluorescence analyses. His estimations of trace elements average contents were for many years unique data. At a later time some averages (Clarke values) were published, i.e. by Krauskopf (1955), Bethell (1962), Krejci-Graf (1972), Valkovič (1983), Yudovich et al. (1985), and Swaine (1990). In 1990s, due to serious environmental problems caused by wider consumption of coal in electric power plants, amount of trace element analyses extremely increased (Bragg et al. 1998). Quite a new data of coal Clarke values collected from more than hundred thousands analyses were published by Ketris and Yudovich (2008, 2009).

3. Methods of investigation

This paper provides a critical assessment of a database of chemical and technical analyses and contents of elements in ashes from all the bituminous coal basins of the CR (Fig. 2). The database was created through the acquisition of more than fifty thousand analyses published or stored in archives, including calculations of coal reserves held by the Czech Geological Survey – Geofond (the state organization responsible for storing unpublished reports and manuscripts). These data were supplemented by the study

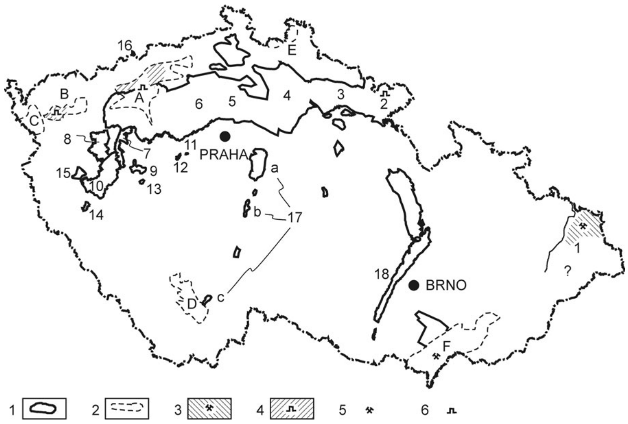

Fig. 1. Distribution of Upper Paleozoic and Tertiary coal-bearing basins in the Czech Republic. 1 – outline of Upper Paleozoic basins, 2 – outline of Tertiary basins, 3 – region with present underground mining activity, 4 – region with present open cast mining activity, 5 – recent local underground mining activity, 6 – local open cast mining activity; 1–10 Upper Paleozoic hard coal basins: 1 – Czech part of the Upper Silesian, 2 – Czech part of the Intra-Sudetic, 3 – Krkonoše Piedmont, 4 – Mnichovo Hradiště, 5–10 Central and West Bohemian: 5 – Mšeno-Roudnice, 6 – Kladno-Rakovník, 7 – Žihle, 8 – Manětín, 9 – Radnice, 10 – Plzeň, 11–15 Carboniferous relics (occurrences): 11 – Malé Přílepy, 12 – Lísek, 13 – Mirošov, 14 – Merklín, 15 – Vranov, 16 – Brandov, 17–18 grabens: 17 – Blanice, relics: a – Český Brod, b – Vlašim, c – České Budějovice, 18 – Boskovice; A–E most important Tertiary lignite basins: A – North Bohemian, B – Sokolov, C – Cheb, D – České Budějovice, E – Czech part of the Žitava, F – South Moravian coal district (part of the Vienna Basin).

of maceral composition of the coals and the chemical and technological parameters of 21 new samples that were collected from galleries and also from dumps at abandoned mines, taking into account that such samples could be as much as a few decades old. Contents of elements in such samples may be subject to leaching so that the analyses obtained may differ from those of "freshly" collected samples (cf. Swaine and Goodarzi, Eds 1995). New analyses come mostly from chip samples with ash content (A^d) < 55 % while contents of few samples undertaken from some unpublished reports reached up to 99.99 %. All newly collected samples were ashed by temperature 850 °C whereas temperature of ashing of older samples is not known. Nine of recently collected samples were analyzed at the US Geological Survey at Reston (USA) and another 16 samples were studied in the laboratories of the Czech Geological Survey. The concentrations of PGE in 13 samples were determined in the laboratories of the Faculty of Science at Charles University. The contents of trace elements in coal ashes were determined at Reston using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Coal ashes were also analyzed at the laboratories of the Czech Geological Survey by Flamed Atomic Absorption Spectrometry (FAAS) and/or Mercury Atomic Absorption Spectrometry (HGAAS; As and Bi) and by Atomic Absorption Method (AMA; Hg). The concentrations of Cl, Hg, S and Se were in coal established. Contents

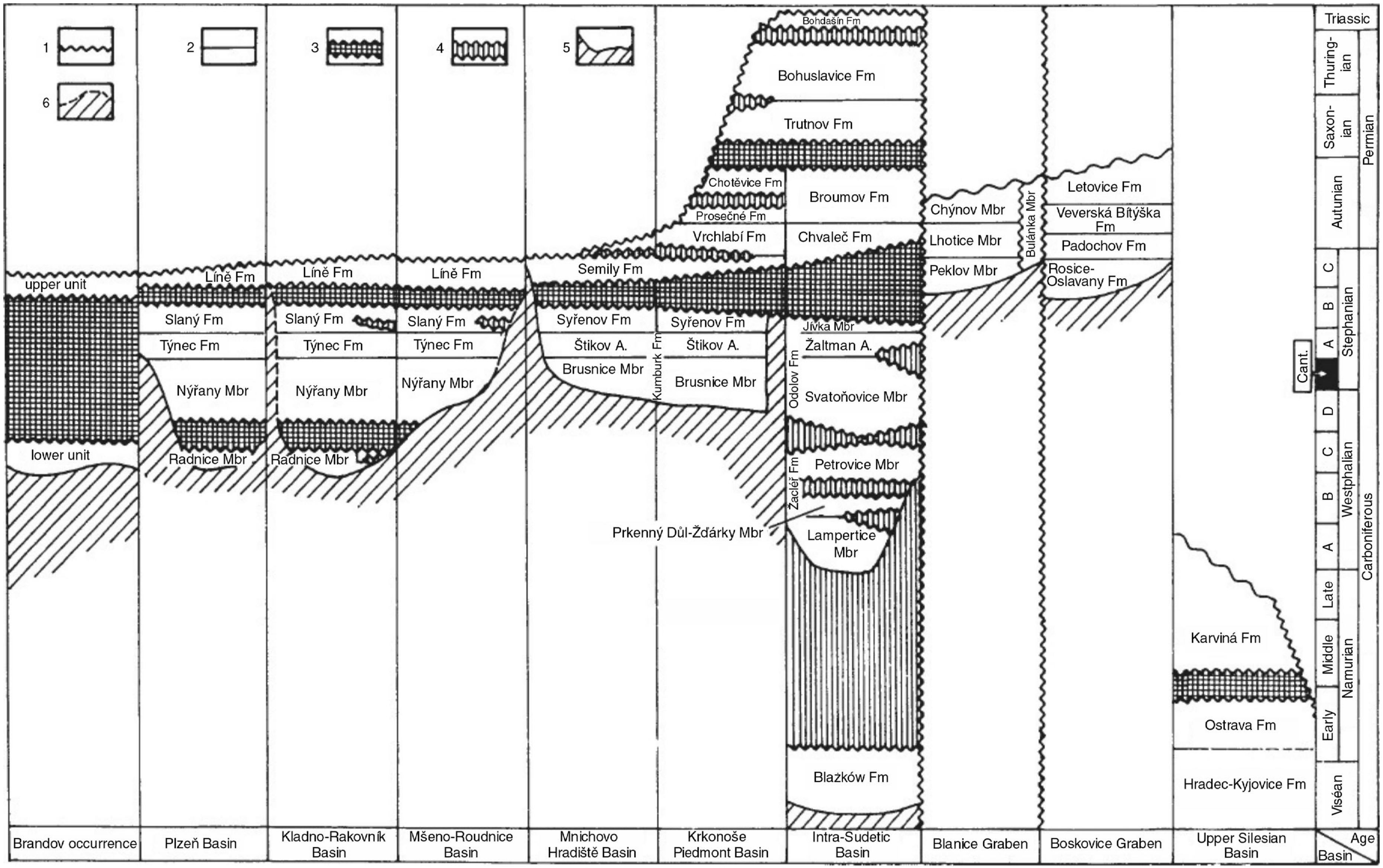

Fig. 2. Section showing the correlation of basic lithostratigraphic units in Upper Paleozoic basins in the Czech Republic (Pešek et al. 2005, adopted). 1 – present erosion level, 2 – continuous sedimentation, 3–4 hiatus: 3 – important, 4 – local, 5 and 6 boundary between the Upper Paleozoic and the basement: 5 – proved, 6 – inferred. Westphalian: A – Langsettian, B – Duckmantian, C – Bolsovian, D – Asturian; Stephanian: Cant. – Cantabrian, A – Barruelian.

of PGE in coal ash were determined by the fire assay ICP-MS method. With the exception of samples from the Czech part of the Upper Silesian Basin (CPUSB), the analytical methods used to obtain the assays of most of the old samples were not specified. Kessler et al. (1965) only published the results of quantitative optical emission spectrochemical analyses (OES) of coal ash, whereas Dopita et al. (1997) used AAS, ICP, XRF or exceptionally even OES methods for analyses of coal ashes.

Results of previous analyses can be significantly influenced by the temperature of ashing. According to Ketris and Yudovich (2008) it is well known that some elements may be almost fully (Br, Hg, I) or partly (Ge, Mo etc.) volatilized by high-temperature ashing. Trace elements loss may be minimized only by low-temperature ashing (~ 130–150 °C).

Only quantitative analyses of old samples were incorporated in the database. However, problems arose when the numbers of samples analyzed were not specified. When such older samples were collected in adits or boreholes, the standard procedure was to subdivide a coal seam in 20 cm sections (i.e., a coal seam one meter thick was counted as 5 samples). The database incorporates the chemical and technological parameters of coal from the majority of the basins. As far as the distribution patterns of elements in continental basins is concerned, due to the known lateral variability of coal seams and also because the number of analyses was mostly small, the values obtained may not be statistically representative. Nevertheless, it is necessary to make the best use of the existing data so that we can learn as much as possible about coal deposits that are presently being mined and about resources now abandoned or exhausted.

4. Results and discussions

4.1. CZECH PART OF THE UPPER SILESIAN BASIN

The Czech part of the Upper Silesian Basin is filled by the paralic Ostrava Formation (Lower Namurian, i.e. Upper Mississippian) and the continental Karviná Formation (Middle Namurian to Langsettian, i.e. Lower Pennsylvanian). The clastic and volcaniclastic deposits in the basin were folded during the Variscan orogeny and also partly affected by Alpine orogenic processes. Altogether there are 86 coal seams with an average thickness of 83 cm that have been locally mined in the Ostrava Formation, whereas the Karviná Formation contains 55 coal seams of an average thickness of 176 cm.

RESULTS OF EARLIER STUDIES

Coal seams and their quality

Coking and steam coal is extracted in the CPUSB. Medium to low volatile coals of the Ostrava Formation with reflectance values R_o of 0.75–2.00 % but even anthracites with reflectance exceeding 2.00 % R_o were mined in the past from the western part of the basin. The rank of coal decreases eastward and southward. The average technological parameters of the local coal are as follows: volatile matter (V^{daf}) 3–38 %, moisture (W_t^r) 0.6–4.0 %, ash (A^d) 1–40 %, calorific value (Q_s^{daf}) 20.0–36.9 MJ.kg^{-1} (Buchtele et al. 1995, Dopita et al. 1997, Sivek et al. 2005, Sivek et al. 2008). Bright banded coal and banded coal consisting of vitrite, clarite and trimacerite with a high proportion of vitrinite (50–95 vol. %), liptinite (0–35 vol. %) and inertinite (3–65 vol. %) prevail in coal seams of the Ostrava Formation, while the basal unit of the Karviná Formation – the Saddle Member – consists mostly of dull coal and dull banded coal characterized by an enhanced content of inertinite (10–83 vol. %), with variable amounts of vitrinite (3–90 vol. %) and liptinite (0–38 vol. %) (Fig. 3A). The proportion of banded and bright coal with a dominant proportion of vitrinite (45–90 vol. %), and a variable content of inertinite (7–65 vol. %) and liptinite (1–20 vol. %) increases upward to the hanging wall. This type of coal prevails in the upper part of the Karviná Formation (Buchtele et al. 1995, Dopita et al. 1997, Sivek et al. 2005). Clay minerals (Fig. 3B), quartz and carbonates (Figs 3C and D) are the most abundant inorganic components, whereas iron sulfides (Fig. 3E) are minor and iron oxides (Fig. 3F) are rare (Dopita et al. 1997). Generally, sulfur content in coal from the Czech part of the Upper Silesian Basin is lower than 1% S_t^d and recently extracted coals contain sulfur between 0.6 and 0.8 %. The higher sulfur contents up to 3.3 % in the Table 3 or up to 2.23 % S_t^d (Dopita et al. 1997) and some other elements (cf. Swaine 1990) are typical for thin coal seams below marine horizons (Bouška 1981). For the pyrite concretions are typical higher sulfur contents. The sulfur content in new samples studied from the Petřkovice, Hrušov and Suchá members varies from 0.49 % up to 1.96 % S_t^d in the Hrušov coal seams. Organic sulfur is prevailing form in most samples. Crystals and framboids and their clusters filling microfractures and microcavities are rare in majority of coal seams and dominate in sample from the Hrušov Member.

Numbers of studied samples

The comprehensive studies by Kessler et al. (1965) and Dopita et al. (1997), together with reports on calculated coal reserves and the results of nine new analyses of samples recently collected from several mines in this part of the basin, were used when compiling the database of coal ashes from the CPUSB. Because the database includes analyses by different methods of samples collected from various localities over a period of ca. 40 years, a wide range of concentrations of the elements under investigation is recorded. While Kessler et al. (1965) analyzed hundreds of samples from all units of the Ostrava and Karviná formations, Dopita et al. (1997) analyzed only from 1 to 37 samples from all the members of these formations, with the exception of uppermost unit – the Doubrava Member of the Karviná Formation. Authors of recent study analyzed one sample of coal ash from the Petřkovice and Hrušov basal members of the Ostrava Formation and seven samples from the Suchá Member of the Karviná Formation.