

# Distribution of the Platinum Group Elements in Peat Deposit Near a Historic Lead and Silver Mining District

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Received: 19 September 2007 / Accepted: 17 March 2008 / Published online: 29 March 2008  
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**Abstract** Concentrations of platinum group elements (PGE) and Ag were studied in a minerotrophic peat deposit near a historic Pb–Ag mining district (Příbram, Czech Republic). The PGE determinations were performed by quadrupole ICP-MS after NiS fire assay procedure. In the individual peat layers (dated by measurement of  $^{210}\text{Pb}$  activity) the PGE concentrations were low and ranged from  $0.015 \text{ ng g}^{-1}$  (Ir) to  $11.8 \text{ ng g}^{-1}$  (Pt). The enrichment of PGE (especially Pt) compared to the Earth crust contents were observed during two periods. The peak in the second half of 19th century was explained by massive increase of ore mining and affinity of PGE to concentrate in molten lead during Pb processing. The recent PGE enrichment in peat layers might be explained by automobile (with catalytic converters) exhaust fumes or processing of computer electronic parts by the smelter.

**Keywords** PGE (platinum group elements) · Peat · Mining/smelting · Příbram

Peat bogs are widely used as geochemical archives of historical trends in the deposition of metallic elements

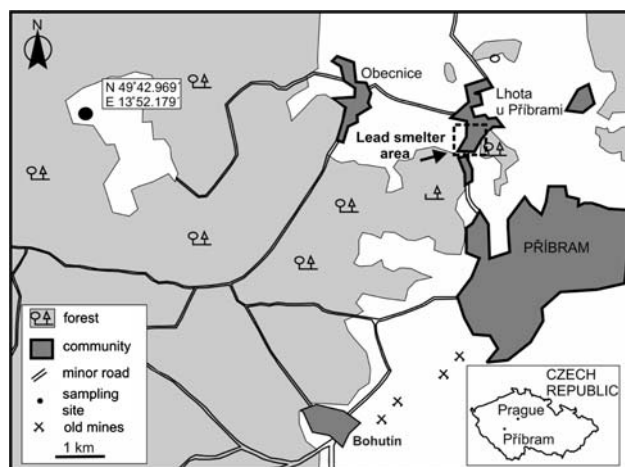
(Baes and McLaughlin 1984; Shotyk 1996). Their investigation is usually carried out at pristine sites and also in the vicinity of important emission sources, such as base metal mining districts and smelters (Savard et al. 2006; Mihaljevič et al. 2006). Research on the deposition of PGE is mostly concentrated in built-up areas close to major roadways, where increased environmental pollution by these elements can be expected (Palacios et al. 2000; Rauch et al. 2003). Elevated concentrations have been described in mountainous areas (Moldovan et al. 2007), and also in areas with permanent ice cover, e.g. in Greenland (Brabante et al. 2001). Nonetheless, potential sources of elevated PGE concentrations in distant areas and the relationship to automotive emissions or other human industrial activities have not yet been satisfactorily explained.

Elevated contents of Pb in peat cores (Mihaljevič et al. 2006) and in mosses (Sucharová and Suchara 2004) have previously been found on the ridge of the Brdy Hills in the vicinity of the Pb–Ag mining and smelting area near Příbram, Czech Republic (Fig. 1). Individual layers of the peat profiles were dated using  $^{210}\text{Pb}$   $\alpha$  spectrometry and the maximum for Pb metallurgical production corresponded to the highest deposition rates recorded in the 1960s (Mihaljevič et al. 2006). The aim of this work is to explain the distribution of the vertical concentration trends of PGE and Ag at this peat deposit. The possible influence of mining and smelting activities or automotive emissions were studied on the PGE concentration profiles, comparing with historical Pb–Ag ores mining and Pb production by smelting (Fig. 2). Deposition into the ecosystem following the industrial revolution in the peat bog on the ridge of the Brdy Hills in a relatively clean area that is far from major roadways, but is affected by emissions from Pb–Ag metallurgy.

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**Fig. 1** Location of the sampling site and mines/smelter of the Příbram district

## Materials and Methods

The studied peat core was sampled in the same area as those studied by Mihaljevič et al. (2006). The studied peat core was taken in unforested parts of the top ridge of the Brdy Hills (865 m above sea level, average precipitation 710 mm year<sup>-1</sup>), 9 km WSW of the town of Příbram, 8 km W of the Pb smelter and 10 km NW of the main base-metal mining district (Fig. 1). Cambrian psephitic and psamitic sediments are located in the basement of the peat deposit. The core was taken using a PVC sampling tube in an unforested area and was transferred to the laboratory in the sampling tube, immediately frozen (at temperature of -20°C) and divided into 2-cm sections, dried at room temperature (25°C) and homogenized in an agate mortar. The peat was mineralized in a Linn (Germany) programmable furnace by the dry ashing of 5 g of sample (each

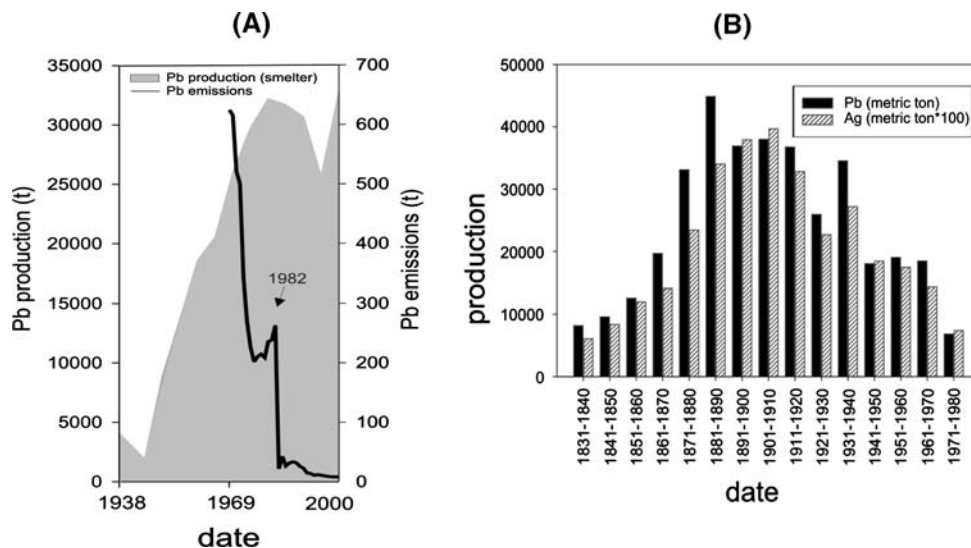
2-cm section) with a temperature increase of 5°C min<sup>-1</sup> to a maximum temperature of 550°C.

An improved nickel-sulphide fire-assay extraction procedure with ICP-MS (inductively coupled plasma-mass spectrometry) has been revisited for quantification of trace concentrations of PGE (here Rh, Pd, Ir and Pt). This extraction procedure leads to the removal of matrix elements that could affect the determination using ICP-MS. The nickel-sulphide buttons were prepared by a modified approach according to Paukert and Rubeška (1993). The amount of fluxes and collector used were minimized (22 g of Na<sub>2</sub>B<sub>4</sub>O<sub>6</sub> and 11 g of Na<sub>2</sub>CO<sub>3</sub> and 1.9 g of nickel and 1.5 g of sulphur) and the total fusion time was set to 45 min at a temperature of 1,050°C. The final digest (obtained by selective dissolution of Ni-S button) was evaporated and transferred into a 25 mL volumetric flask with 1 M HCl. The samples were diluted twice (in 1% v/v HCl) and then measured using ICP-MS. Decompositions of the peat samples for determination of Ag were done using acid digestion (HF + HNO<sub>3</sub>) and followed procedure as described by Mihaljevič et al. (2006).

All the chemicals used in this procedure were reagent grade (Merck®, Germany and Penta Chrudim, Czech Republic). The nickel powder was of ultrapure quality (INCO type, Canada). Analytical-grade hydrochloric acid (Penta Chrudim, Czech Republic) was double-distilled. Purified water (Millipore® system Academic, USA) was used for all the dilutions.

The PGE concentrations were analyzed using a standard configuration of quadrupole-based ICP-MS (VG Elemental PQ3, UK) equipped with a water-cooled (~4°C) spray chamber with Meinhard-type nebuliser. The data were acquired in the peak jumping mode with 3 points measured per mass peak and instrument sensitivity at 4 × 10<sup>4</sup> cps per 1 ng mL<sup>-1</sup> <sup>103</sup>Rh. The total acquisition time was 5 × 30 s.

**Fig. 2** (A) Total Pb production from the Příbram smeltery and (B) Pb and Ag production from the Příbram mined Pb–Ag ores (data from Bambas 1990; modified according to Mihaljevič et al. 2006)



**Table 1** Preferred isotopes and detection limits for ICP-MS and measured data for WGB-1 reference material and basement rocks

		Isotope (m/z)	Abundance (%)	Detection limit (ng g <sup>-1</sup> ) Dilution factor = 10	Reference material			Cambrian sediments (basement)
					WGB-1 (CCRMP)			
					Certified (ng g <sup>-1</sup> )	Meisel and Moser (2004) (ng g <sup>-1</sup> )	This study, n = 5 (ng g <sup>-1</sup> )	
Rh	103	100	0.0085	0.32	0.23 ± 0.05	0.30 ± 0.03	0.051	
Pd	105	22.5	0.040	13.9 ± 2.1	13.9 ± 2.6	12.8 ± 1.2	0.49	
Ir	193	62.7	0.010	0.33	0.21 ± 0.03	0.25 ± 0.08	0.11	
Pt	195	33.8	0.100	6.1 ± 1.6	6.39 ± 3.6	5.4 ± 0.3	1.56	
Nb <sup>a</sup>	93	100						
In <sup>a</sup>	115	95.7						
Tl <sup>a</sup>	205	70.5						

<sup>a</sup> Internal standard

The three point calibration curves (blank, 0.5 ng mL<sup>-1</sup> and 5 ng mL<sup>-1</sup>) were prepared with calibration standards ARI-STAR (BDH Laboratory Supplies, UK). The isotopes used (<sup>103</sup>Rh, <sup>105</sup>Pd, <sup>193</sup>Ir and <sup>195</sup>Pt) were selected with respect to their most abundant species and free from isobaric overlap. The data were processed on-line using VG PlasmaLab software and applying corrections for the instrumental drift. The count rates for the measured elements were corrected on the basis of interpolation of the <sup>93</sup>Nb, <sup>115</sup>In and <sup>205</sup>Tl correction factors. The analytical precision of the ICP-MS data (calculated as one relative standard deviation, RSD) for all the analyzed elements ranged from 1% to 20% relative. The detection limits (DL) for analyzed elements were calculated as the 3σ level of the procedural blank (Table 1). The accuracy of this analytical method was controlled using the WGB-1 reference standard (CCRMP Canada; Meisel and Moser 2004; Table 1) as no plant reference material with certified PGE concentrations is actually available.

The PGE (Rh, Pd, Ir and Pt) enrichment factors standardized to Zr (EF Rh (Zr), EF Pd (Zr), EF Ir (Zr) and EF Pt (Zr)) were calculated according to Eq. 1.

$$\text{EF PGE (Zr)} = (\text{PGE/Zr})_{\text{sample}} / (\text{PGE/Zr})_{\text{crust}} \quad (1)$$

where (PGE/Zr)<sub>sample</sub> is the average composition of the Earth's crust (Taylor 1992; Peucker-Ehrenbrink and Jahn 2001) and (PGE/Zr)<sub>sample</sub> is the composition in the analysed sample. The dating of individual layer was done using α spectrometry of <sup>210</sup>Pb. The exact procedure is described elsewhere (Mihaljevič et al. 2006).

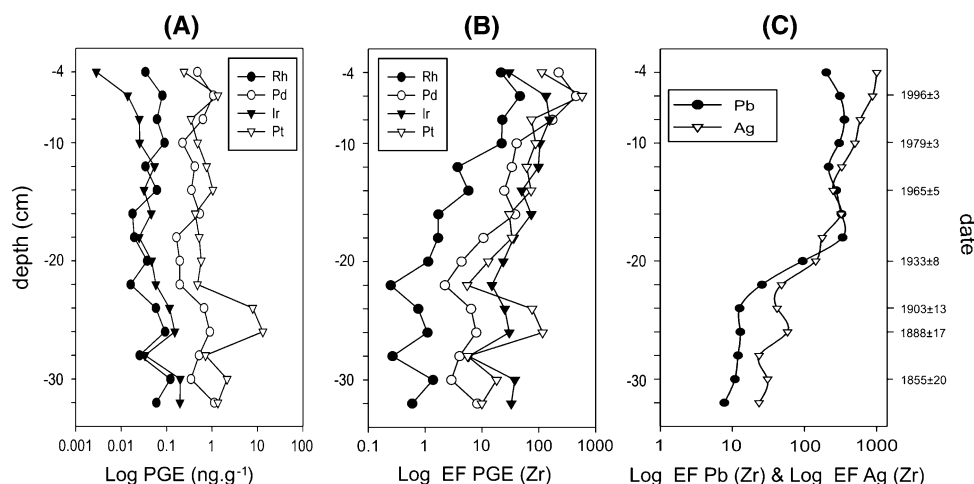
## Results and Discussion

The measured data for PGE exhibit a wide range of concentrations from 0.015 ng g<sup>-1</sup> Ir to 11.8 ng g<sup>-1</sup> Pt. Platinum exhibits the highest average concentration in the

profile, with a value of 2.15 ng g<sup>-1</sup>. Other elements exhibit significantly lower average values: Pd (0.43 ng g<sup>-1</sup>), Rh (0.064 ng g<sup>-1</sup>), Ir (0.070 ng g<sup>-1</sup>). In most cases, these were relatively low values compared to the data for other peat bog studies (Rauch et al. 2004, 2005), which were done in regions significantly influenced by PGE deposition. In addition, research on the deposition of platinum group elements in the peat profile in the Tunguska region, in an area of assumed impact of an extraterrestrial body is still unique (Hou et al. 2000).

The values for Rh, Pd and Ir are similar or slightly elevated in absolute comparison with the values for the UCC (Upper Continental Crust) but do not exhibit any substantial enrichment. When the EF PGE (Zr) factor is used, an increasing trend is observed towards the upper part of the peat profile (Fig. 3a, b). A substantial increase, especially in EF Pt (Zr), exhibit two marked local enrichments in the lower part of the peat core in the 24–26 cm and the 26–28 cm layers (corresponding to ages of 1888 ± 17 and 1903 ± 13, respectively) and in the upper part in the 4–6 cm layer (corresponding to age of 1996 ± 3; Fig. 3b). The first peak might correspond to the period of a massive increase in mining and processing of Pb–Ag ores in the Příbram area (Fig. 2b). It is important to note that the concentrations of PGE in surrounding rocks and Příbram ores are very low (Table 1). However, these elements are siderophile and during the Pb metallurgical process are strongly partitioned into the molten Pb. This process enables us to separate PGE from silicate matrix and is widely used as pre-concentration step in gold and PGE analysis by fire assay (e.g. Diamantatos 1984). A large proportion of produced Pb, pre-concentration of PGE from silicates to manufactured Pb might explain the peak in PGE contents and PGE enrichment in peat layers dated to second half of 19th century. The substantial increase in mining was also documented by an increase in the EF Pb (Zr) and the EF Ag (Zr) (Fig. 3c) values and a change in the

**Fig. 3** (A) Profiles of the Rh, Pd, Ir and Pt concentrations and (B) enrichment factors and comparison with Pb and Ag in the peat core (C). Data for Pb were taken from Mihaljevič et al. (2006)



Pb isotope composition in the peat profile (Mihaljevič et al. 2006).

There has been a substantial reduction in emissions of the Příbram metallurgical works since the 1980's and thus also a reduction in Pb deposition, as is also very well documented by the peat record (Figs. 2a and 3c). Although the enrichment factors EF Pb (Zr) began to decrease from about the middle of the 1980s, according to our data the calculated EF Ag (Zr) values have increased smoothly since the end of the 19th century. The reason for this fact is not clear. It is possible that deposition of Ag in the peat bogs in the past few decades may be influenced by intensive recycling of precious metal containing computer electronic parts.

The steeper increase in EF Pt (Zr) and EF Pd (Zr) values in the upper 6–8 cm and 4–6 cm peat layers (Fig. 3b) is probably related more to the increasing use of automobile catalytic converters at the end of the 1980s and beginning of the 1990s and thus to increased deposition of these metals as a consequence of their presence in automobile exhaust fumes (Palacios et al., 2000; Rauch et al., 2001; Rauch et al., 2005), although this trend is not completely apparent in the absolute concentrations of these metals. Further determination of PGE at other locations within the Czech Republic would be useful to obtain a larger set of data and also for determining the general variability in PGE deposition.

**Acknowledgements** We wish to thank M. Fayadová for her help with the pre-concentration procedures. Financial support from Charles University (GAUK 274/2006) and from ASCR (KJB 300130612) and from the Ministry of Education (MSM 0021620855) is gratefully acknowledged. The ICP-MS facility at Charles University was funded by a PHARE Project.

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