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Geochemical study of different-aged mining dump materials in the Freiberg mining district, Germany

M. Stockmann · D. Hirsch · J. Lippmann-Pipke · H. Kupsch

Abstract Historical mining dumps are useful archives for the investigation of weathering processes. The objective of this study was to investigate the weathering behavior of waste-rock material derived from the 800-year-old silver ore mining in Freiberg, Germany. For identifying time-dependent weathering indices, dumped material of four dumps of different ages and corresponding rock was examined regarding the geochemical composition. The dumped material is characterized by high contents of heavy metal containing sulfidic ores, such as pyrite, arsenopyrite, sphalerite and galena. Acid mine drainage is produced by the oxidative weathering of the sulfide minerals and causes the increased dissolving of soluble metals with increasing age of dumps. As a result of these weathering processes, a clear depletion of chalcophile elements in the older dump material (800 years) compared to the youngest dump (100 years) was observed. In the soil horizons downstream the dumps, high quantities of heavy metals (e.g., up to 12,000 ppm As, 3,300 ppm Pb, 640 ppm Zn), mainly adsorbed on organic matter, were determined and indicate a time-dependent element transfer from the dumps into their surrounding soils.

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Introduction

Mining of polymetallic ore deposits, where sulfide minerals contain heavy metals is a well-known environmental problem worldwide (e.g., Benvenuti et al. 1995; Cappuyns et al. 2006, Smuda et al. 2007, Keskin and Toptas 2012). Heavy metals are chemical elements that are metals or metalloids with a density greater than 5 g/cm^3 (Järup 2003). They are persistent in all parts of the environment because they cannot be degraded or destroyed. The most important heavy metal toxicants are As, Cd, Hg and Pb (As is a metalloid, but usually classified as heavy metal (Lide 1992; Järup 2003).

Important centers of the German ore mining activities were located in the low mountain ranges such as the Harz (since 968), the Schwarzwald (since 1028) and the Erzgebirge (since 1168) (Steuer 1993). One of the oldest and most important centers of medieval silver ore mining in Europe is the mining district Freiberg (Saxony, Germany). Up to the nineteenth century, the mining activities in Freiberg were concentrated mainly on Ag (in the sixteenth–eighteenth century: about 30 tons per year; Tichomirowa et al. 2010). Besides pure silver ores (e.g., argentite), numerous silver containing minerals were mined (e.g., galena can contain up to 2 wt % Ag). In the latest mining period, exclusive non-ferrous ores with Pb, Zn and Cu were extracted until 1968, when the mining decommissioned as a result of uneconomic conditions (Wagenbreth and Wächtler 1986).

The mining district Freiberg is a typical hydrothermal Pb–Zn–Ag deposit, which developed particularly in the

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course of the Variscan (Devonian–Permian) and Alpine Orogeny (Triassic–Tertiary) in Central Europe. The geological structure and the composition of this ore deposit is well described in literature, e.g., by Bernstein (1985), Wagenbreth and Wächtler (1986), Baumann et al. (2000). With more than 1,000 polymetallic ore veins, the site Freiberg is one of the largest ore occurrences in Europe. The mineralization is characterized by a heterogeneous mineral assemblage of pyrite (FeS_2), galena (PbS), chalcopyrite ($CuFeS_2$), sphalerite (ZnS) and arsenopyrite (FeAsS).

Numerous sulfide-rich dumps with high quantities of heavy metals result from the 800 years lasting ore mining activities in the Freiberg mining district (Beak 1997; Kupsch et al. 2004; Scheinert et al. 2009). Baake (2000) specified As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, S and Zn as important mining-related elements in the mining district Freiberg. In particular, the formation of acid mine drainage (AMD) resulting from oxidative weathering of sulfide minerals leads to generation of free acidity and the dissolving of soluble metals into the environment via the aquatic pathway (e.g., Singer and Stumm 1970; Mason and Moore 1985). Remarkably, the Freiberg deposit contributes 37 % of the Zn and 5 % of the Cd contamination of the Elbe River (Martin et al. 1994). However, there are still few studies on the subject of AMD formation in sulphidic waste-rock dumps (e.g., Marescotti et al. 2010), while AMD in mine tailings has been studied extensively (e.g., Jambor 1994; Boulet and Larocque 1998; Dold and Font-boté 2001).

Most studies of the weathering effects of toxic waste material have been published for modern mining areas which are subject to short periods of weathering time (<100 a, e.g., Boulet and Larocque 1998; Merkel 2006; Graham and Kelley 2009). In particular, studies of historical dumps and time-dependent weathering effects are rare (Beuge et al. 1998; Müller et al. 2008, Strosnider et al. 2011). However, to understand the long-term behavior of chemotoxic and radiotoxic metals, e.g., for repository-relevant processes, it is necessary to perform natural analogue studies on a time scale across the centuries (Liu et al. 1996; Havlova et al. 2006).

The aim of this study was to investigate the weathering behavior of different-aged waste-rock material at a site of mining of polymetallic deposits. The configuration of the dumps allows to study in detail (1) the geochemical composition of waste-rock material; (2) the metal enrichments in surrounding soils indicate the influence of the dumps; and (3) the time-dependent element transfer from the dumps into their surrounding soils for detecting time-dependent weathering effects.

The results will be used for quantification of geochemical processes throughout eight centuries and will serve as a natural analogue study for time scales of relevance for the validation of conceptual and numerical models for risk assessment prognosis calculations.

Study site

For the purpose of this study, four historical dumps of different age and comparable composition were investigated (Scheinert 2007). The selected dumps are centrally located in the mining district Freiberg, which is situated in the northeastern part of the Erzgebirge (Fig. 1). The climate is humid with an average rainfall of 780–900 mm/year and average annual temperatures of 6.7–7.5 °C (Fiedler and Hofmann 1976; Göhler 1999). The following four dumps (Fig. 1, filled triangles, no. 1–4) were selected: (1) Neue Reiche Zeche from the nineteenth–twentieth century (NRZ_100yrs); (2) Alte Reiche Zeche from the sixteenth–eighteenth century, but first mentioned in 1384 (ARZ_500yrs); (3) Shaft Drei Weiber (SDW_800yrs) and (4) Shaft Erasmus (SE_800yrs), the latter two from the twelfth–fourteenth century. The exact time of dumping is uncertain. Each dump represents one of the main mining periods in the Freiberg mining history (Wagenbreth and Wächtler 1986). In general, the dumps consist of waste-rock material from the hard rock gneiss dome of Freiberg. Typical mineral constituents of this biotite gneiss (grey paragneiss) are 30.5 wt % of quartz, 45.3 wt % of feldspar and 17.5 wt % of biotite (Baumann et al. 2000). The waste-rock material of the investigated dumps is characterized by high contents (5–10 %) of heavy metal containing ores which originate from the sulfide-rich ore vein *Hauptstollngang-Stehenden* in the Freiberg deposit (Beuge et al. 1998; Baumann et al. 2000).

Due to the high concentration of phytotoxically affective heavy metals in the waste-rock material and because of low pH values, the vegetation on the dump surfaces is still sparse. Göhler (1999) describes species-poor and rudimentary vegetation with chlorotic spots on plants, e.g., trees (birch) as well as bushes and grasses of herb layer, on mining dumps in the region of Freiberg caused by increased heavy metal concentrations of Pb, Zn, Cu, Cd and As.

The increasing mining productivity with time is reflected by increasing dimensions of the dumps. The youngest dump NRZ_100yrs is considerably larger than the medieval dumps and has a pronounced dump plateau. Due to the limited accessibility, the presented study deals with the northeastern dump area. The dimensions of the length, width and height of each dump were obtained by visual inspections as following: NRZ_100yrs (investigated subarea): 200 ± 1, 40 ± 1, 6 ± 1 m; ARZ_500yrs: 50 ± 1, 50 ± 1, 4 ± 1 m; SDW_800yrs: 40 ± 1, 8 ± 1, 1.5 ± 0.5 m and SE_800yrs: 40 ± 1, 10 ± 1, 1.5 ± 0.5 m.

Fig. 1 Sampling locations of dump samples (*triangles*) and soil samples (*circles*) in the mining district Freiberg (TK10 2010)
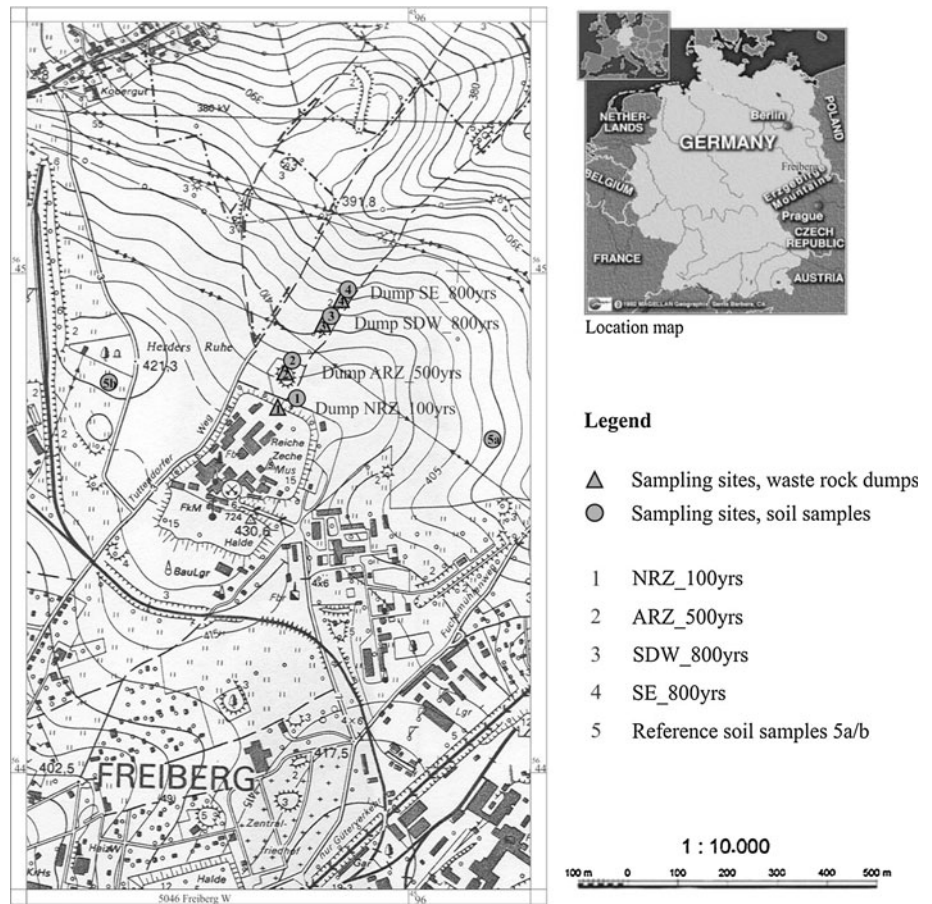
Sampling and analytical methods

Sampling

Knowledgeable and accurate sampling is the most important step towards representative results (Hämmann and Desaules 2003). Obviously, the dumped materials were highly heterogeneous in grain size and varied both in laterally and vertically. The sampling of dump material at the study site was performed by several composite samples, which comprised numerous individual samples (Oberfranken 2001). Therefore, the dumps were divided into square cells to form a sampling grid where several composite samples (about 5 kg), consisting of each about 20 individual samples, were collected by sampling the first 30 cm from the surface of each dump with a shovel (Table 1). Three composite samples were obtained from NRZ_100yrs, four from ARZ_500yrs and two from SDW_800yrs and from SE_800yrs. We decided on exclusively sampling the upper 30 cm of the dumps because the surficial material is suggested to be most affected by weathering agents. Unweathered gneiss and ore from the shaft *Neue Reiche Zeche* in Freiberg was used as reference material. The pH

was measured in situ with a portable pH instrument (MultiLine P4, WTW) in a suspension of small-sized dump material (<2 cm) and tap water, with a solid to liquid ratio of about 1:1. The characteristics of the dumps and reference samples as well as information on their sampling sites (latitude and longitude) are summarized in Tables 1 and 2.

To determine the metal distribution in the soils surrounding the dumps, soil profile samples were taken, where possible, from assumed dump leachate influenced sites (Fig. 1, filled circles, no. 14). The collecting of dump leachate from drainage systems was not possible due to missing base seal. We abstained from implementing test fields and collecting leachate samples as we expected to obtain the crucial information on the effect of ageing of historical mine dumps from analyzing the dump material and adjacent soils. Each sampling site is located downstream of the dump towards the northeast. The hypodermic outflow occurs in the direction of gaining stream Freiberger Mulde and Striegis (Baake 2000). For the acquisition of the variability of pedological parameters and the metal distribution in depth at each sampling site approximately 1 kg soil material was taken along 40–70 cm long vertical profiles in 10 cm depth intervals (Tables 3, 4). The A- and

Table 1 Description of dump samples and their sampling sites

Sample	Dump name	Material	Weathering degree	Exposing time to air (a)	Sampling site Latitude	Longitude
NRZ_100yrs	Neue Reiche Zeche	Gneiss	Low	~100	[45]95 520	[56]44 550
ARZ_500yrs	Alte Reiche Zeche	Gneiss	Moderate	~500	[45]95 554	[56]44 621
SDW_800yrs	Schacht Drei Weiber	Gneiss	High	~800	[45]95 624	[56]44 743
SE_800yrs	Schacht Erasmus	Gneiss	High	~800	[45]95 652	[56]44 797
Gneiss NRZ	Host rock	Gneiss	Unweathered	<1	Subsurface sampling	
Ore NRZ	Vein "Hauptstollngang"	Ore	Unweathered	<1	Subsurface sampling	

Table 2 Metal contents of mining-related elements (mg/kg) for dump samples and reference material

Dump sample	pH	As (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	S (mg/kg)	Zn (mg/kg)
NRZ_100yrs	5.1	38.8 ± 14.3	8.5 ± 8.4	52.0 ± 24.7	30,400 ± 5,200	320 ± 180	1,230 ± 1,260	960 ± 840
ARZ_500yrs	5.7	94.9 ± 60.3	0.7 ± 0.3	30.7 ± 7.6	33,700 ± 2,900	215 ± 16.2	520 ± 170	125 ± 33.9
SDW_800yrs	4.4	890 ± 1,100	0.5 ± 0.03	20.4 ± 2.4	27,100 ± 1,800	200 ± 41.0	350 ± 360	130 ± 49.6
SE_800yrs	4.8	28.7 ± 19.7	0.5 ± 0.01	22.6 ± 2.2	29,900 ± 790	43.4 ± 17.0	200 ± 100	120 ± 7.2
Gneiss NRZ	n.s.	45.6 ± 47.7	0.7 ± 0.1	38.8 ± 22.5	44,900 ± 220	47.1 ± 42.7	1,500 ± 50	200 ± 54.0
Ore NRZ	n.s.	25,400 ± 130	260 ± 0.8	1,900 ± 8	151,500 ± 6,800	67,200 ± 11,900	271,500 ± 5,700	42,800 ± 900
Clarke RG	n.s.	2.0 ± n.s.	1.0 ± n.s.	25.0 ± n.s.	35,800 ± n.s.	24.0 ± n.s.	n.s. ± n.s.	80.0 ± n.s.
Clarke UC	n.s.	2.0 ± n.s.	0.1 ± n.s.	14.3 ± n.s.	30,890 ± n.s.	17.0 ± n.s.	953.0 ± n.s.	52.0 ± n.s.

RG Regional Clarke content of Freiberger paragneiss (Pälchen et al. 1987), As and Cd value taken from Scherchan (1980); *UC* Clarke content of upper crust (Wedepohl 1995); Ore and Gneiss NRZ, subsurface sampling in former mining shaft *Neue Reiche Zeche* in Freiberg; *n.s.* not specified

B-horizons were carefully separated. Regional reference soil profile samples from two areas that were most likely not influenced by dumping activities were taken for comparison (Fig. 1, filled circles, nos. 5a and 5b).

Analytical methods

In the laboratory the soil samples were air-dried at room temperature for about 2 weeks and stored in a cold-storage room at 4 °C. Soil pH was measured in 0.01 M CaCl$_2$ solution (ratio of soil:CaCl$_2$ = 1:2.5) (Lewandowski et al. 1997).

The dump and soil samples were characterized using various analytical techniques. The measurement of major and minor elements (e.g., Al, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Pb, Zn) was carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES, SpectroFlame, Spectro, Germany) (Manning and Grow 1997). The trace elements (e.g., Ag, Bi, Cd, In, Rb, REE, Th, Tl, U, V) were determined by inductively coupled plasma mass spectrometry (ICP-MS PQEx-cell, ThermoElemental, UK) (Date and Gray 1985). The elements Si and Ti were analyzed by energy-dispersive X-ray fluorescence spectroscopy (XRF,

DX-95, EDAX Inc., USA) (Beckhoff et al. 2006). To determine the most important pedological parameters of soil samples, the content of carbon, hydrogen, nitrogen and sulfur was measured with a C, H, N, S elemental analyzer (Vario EL III elemental analyzer, Germany) (Ziechmann and Müller-Wegener 1990).

In preparation for elemental analyses, the dump and soil samples were crushed and sieved to <63 µm grain size. The dump material (approx. 0.1 g) was digested by adding HNO$_3$ (65 % v/v), HCl (37 % v/v) and HF (48 % v/v), the soil samples (approx. 0.1 g) by adding HNO$_3$ (65 % v/v), H$_2$O$_2$ (31 % v/v) and HF (48 % v/v) in closed Teflon vessels in a microwave system (MLS Ethos plus) at temperatures of 200 °C. Furthermore, glass pellets were prepared using an alkali fusion with di-lithium tetraborate (ratio 1:8) for XRF. Generally, the application of a total digestion provides a good overview of the total metal contents of the investigated samples.

The accuracy and precision of the analytical methods were verified by certified international standards (NIST) prepared like the samples, internal standards (Re and Rh for ICP-MS measurements), reagent blanks and replicates. The relative standard deviation (RSD) is given in Table 2

Table 3 Elemental compositions and descriptions for soil samples from the near-field of dumps and background

Soil sample	Depth (cm)	Horizon	Description	pH	C (%)	H (%)	N (%)	C/N ratio
NRZ_100yrs								
Soil 1-1	0–10	A	Humus-rich, dark brown, clayey-silty	6.2	3.3 ± 0.1	0.3 ± 11	0.3 ± 0.3	10.8
Soil 1-2	10–20			6.3	2.3 ± 0.2	0.3 ± 6.6	0.2 ± 3.3	10.3
Soil 1-3	20–30			6.4	2.2 ± 1.2	0.3 ± 19	0.2 ± 0.4	10.1
Soil 1-4	30–40	B	Light brown to ocher, clayey-sandy	6.4	0.9 ± 0.6	0.2 ± 7.1	0.1 ± 4.2	8.5
Soil 1-5	40–50			6.4	0.6 ± 1.6	0.2 ± 3.4	0.1 ± 2.6	7.5
Soil 1-6	50–60			6.4	0.5 ± 8.0	0.2 ± 6.2	0.1 ± 15.2	7.3
Soil 1-7	60–70			6.4	0.4 ± 4.5	0.1 ± 13	0.1 ± 6.0	6.5
Mean	0–70			6.4	1.4 ± 2.3	0.2 ± 9.4	0.2 ± 4.6	8.7
ARZ_500yrs								
Soil 2-1	0–10	A	Extreme humus-rich, brown	4.1	9.5 ± 0.6	1.3 ± 2.3	0.7 ± 2.7	13.0
Soil 2-2	10–20	B	Humus-rich, sandy-silty, yellow brown to ocher	4.1	2.2 ± 0.6	0.5 ± 1.0	0.2 ± 7.1	10.7
Soil 2-3	20–30			4.6	1.5 ± 1.1	0.4 ± 9.2	0.2 ± 2.5	8.7
Soil 2-4	30–40			4.7	1.0 ± 0.9	0.4 ± 10.2	0.1 ± 2.3	7.1
Mean	0–40			4.4	3.5 ± 0.8	0.7 ± 5.7	0.3 ± 3.6	9.9
SDW_800yrs								
Soil 3-1	0–10	B	Humus-rich, dark brown, silty-clayey	3.7	4.0 ± 0.2	0.3 ± 1.1	0.4 ± 0.2	10.0
Soil 3-2	10–20			4.2	2.7 ± 0.2	0.2 ± 2.3	0.3 ± 1.8	9.1
Soil 3-3	20–30			4.7	2.1 ± 3.6	0.2 ± 5.7	0.2 ± 2.5	9.0
Soil 3-4	30–36			4.7	1.5 ± 0.9	0.2 ± 0.7	0.2 ± 0.2	8.7
Soil 3-5	36–50	B	Light brown–ocher, silty-sandy, rocky with depth	4.7	1.2 ± 2.0	0.2 ± 2.9	0.1 ± 4.2	8.0
Soil 3-6	50–60			4.6	0.7 ± 0.2	0.2 ± 0.1	0.1 ± 2.0	8.2
Soil 3-7	60–70			4.4	0.9 ± 2.5	0.2 ± 4.1	0.1 ± 1.0	9.7
Mean	0–70			4.4	1.9 ± 1.4	0.2 ± 2.4	0.2 ± 1.7	9.0
SE_800yrs								
Soil 4-1	0–10	A	Humus-rich, dark brown, clayey-silty	4.4	3.8 ± 0.5	0.2 ± 12	0.4 ± 2.4	9.9
Soil 4-2	10–20			4.6	2.0 ± 2.2	0.2 ± 8.1	0.2 ± 2.0	9.2
Soil 4-3	20–30			4.8	1.9 ± 1.7	0.2 ± 7.3	0.2 ± 3.5	9.1
Soil 4-4	30–40	B	Light brown to ocher, sandy-rocky	5.0	1.1 ± 1.5	0.2 ± 1.0	0.1 ± 0.4	9.0
Soil 4-5	40–50			5.1	0.8 ± 1.1	0.2 ± 5.9	0.1 ± 6.3	8.5
Mean	0–50			4.8	1.9 ± 1.4	0.2 ± 6.8	0.2 ± 2.9	9.2
Reference soil								
Back-1	0–10	A	Humus-rich, dark brown, silty-clayey	5.8	3.1 ± 0.6	0.2 ± 35	0.3 ± 3.0	10.6
Back-2	10–20			6.2	2.4 ± 0.3	0.2 ± 3.7	0.2 ± 2.4	10.0
Back-3	20–27			6.4	2.4 ± 0.5	0.3 ± 0.8	0.2 ± 0.5	10.3
Back-4	27–40	B	Light brown to ocher, sandy-clayey, rocky with depth	6.5	1.2 ± 2.9	0.2 ± 0.9	0.1 ± 6.4	9.3
Back-5	40–50			6.5	0.7 ± 0.2	0.2 ± 2.1	0.1 ± 1.2	8.4
Back-6	50–60			6.4	0.4 ± 1.4	0.2 ± 8.6	0.1 ± 4.5	7.2
Back-7	60–70			5.9	0.2 ± 0.6	0.2 ± 2.8	0.0 ± 7.7	6.7
Mean	0–70			6.2	1.5 ± 0.9	0.2 ± 7.7	0.2 ± 3.7	8.9
RS	Topsoil	A		n.s.	n.s. ± n.s.	n.s. ± n.s.	n.s. ± n.s.	n.s.
EA	Topsoil	A		5.7	2.5 ± n.s.	n.s. ± n.s.	n.s. ± n.s.	n.s.

RS mean content of regional soils overlying Freiberger paragneiss (Klinger 1995), *EA* European topsoil average (Salminen et al. 2005), *n.s.* not specified

for dump and Tables 3, and 4 for soil samples. Obviously, RSD of dump material is increased resulting from the site-specific inhomogeneity of dumped material and indicates the difficulties of homogenizing ore sample material.

For the visualization of weathering effects in waste-rock material, investigations with scanning electron microscopes (SEM JSM 6600, JEOL, Japan or SEM Ultra55, Zeiss, Germany) were performed at the IOM (Leibnitz

Table 4 Metal contents of mining-related elements (mg/kg) for soil samples from the near-field of dumps and background

Soil sample	Depth (cm)	Horizon	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	S (mg/kg)	Zn (mg/kg)
NRZ_100yrs										
Soil 1-1	0–10	A	520 ± 5.7	5.6 ± 0.1	54.0 ± 1.1	86.9 ± 3.4	29,100 ± 280	730 ± 12	830 ± 11	630 ± 6.2
Soil 1-2	10–20		530 ± 18	5.0 ± 0.1	55.6 ± 1.1	87.2 ± 0.3	31,600 ± 120	720 ± 12	710 ± 3.9	610 ± 3.3
Soil 1-3	20–30		560 ± 1.1	5.3 ± 0.05	57.6 ± 0.4	92.3 ± 1.3	32,500 ± 280	820 ± 75	710 ± 28	640 ± 23
Soil 1-4	30–40	B	200 ± 0.5	2.1 ± 0.1	57.9 ± 1.9	46.4 ± 1.5	31,100 ± 180	180 ± 5.2	280 ± 12	380 ± 5.8
Soil 1-5	40–50		110 ± 3.2	1.4 ± 0.03	57.0 ± 0.5	29.6 ± 0.04	23,700 ± 810	80.0 ± 1.3	130 ± 1.2	230 ± 6.8
Soil 1-6	50–60		94.5 ± 3.2	1.4 ± 0.1	57.3 ± 1.1	28.0 ± 0.2	24,600 ± 2,140	77.2 ± 0.1	120 ± 11	100 ± 6.5
Soil 1-7	60–70		69.2 ± 0.9	0.9 ± 0.02	53.7 ± 1.1	24.0 ± 0.7	24,100 ± 810	60.6 ± 0.1	91.6 ± 2.6	59.8 ± 0.5
Mean	0–70		300 ± 5	3.1 ± 0.1	56.2 ± 1.0	56.4 ± 1.1	28,100 ± 660	380 ± 15	410 ± 10	380 ± 7.5
ARZ_500yrs										
Soil 2-1	0–10	A	870 ± 23	3.3 ± 0.04	55.9 ± 0.4	79.5 ± 0.5	27,000 ± 280	1,200 ± 5.0	1,800 ± 11	570 ± 9.1
Soil 2-2	10–20	B	1,900 ± 17	2.6 ± 0.02	52.5 ± 0.3	110 ± 0.2	34,100 ± 618	1,800 ± 16	1,900 ± 13	390 ± 3.2
Soil 2-3	20–30		1,200 ± 75	3.7 ± 0.2	50.8 ± 3.3	66.8 ± 3.6	27,600 ± 610	950 ± 50	930 ± 45	500 ± 28
Soil 2-4	30–40		1,000 ± 6.6	2.3 ± 0.03	58.2 ± 0.2	58.4 ± 1.3	32,100 ± 590	440 ± 2.0	520 ± 3.0	480 ± 2.7
Mean	0–40		1,200 ± 30	3.0 ± 0.1	54.3 ± 1.0	78.7 ± 1.4	30,200 ± 525	1,100 ± 18	1,300 ± 18	480 ± 11
SDW_800yrs										
Soil 3-1	0–10	A	5,300 ± 46	7.3 ± 0.2	49.3 ± 3.6	65.0 ± 3.6	31,300 ± 1,260	1,600 ± 39	1,600 ± 59	460 ± 12
Soil 3-2	10–20		6,400 ± 120	7.6 ± 0.1	49.3 ± 3.4	63.9 ± 2.1	33,300 ± 750	1,700 ± 57	1,400 ± 42	460 ± 14
Soil 3-3	20–30		9,600 ± 180	7.4 ± 0.03	49.0 ± 2.5	62.4 ± 1.5	35,600 ± 450	2,000 ± 0.7	1,700 ± 23	440 ± 3.6
Soil 3-4	30–36		11,800 ± 210	5.2 ± 0.003	48.7 ± 1.1	63.8 ± 1.5	36,200 ± 210	2,500 ± 6.0	2,300 ± 24	480 ± 1.9
Soil 3-5	36–50	B	11,000 ± 55	5.6 ± 0.04	49.3 ± 1.3	57.6 ± 3.3	39,600 ± 2,620	2,600 ± 7.0	4,200 ± 27	410 ± 6.2
Soil 3-6	50–60		9,000 ± 72	5.9 ± 0.1	48.4 ± 1.9	58.3 ± 2.8	38,400 ± 620	2,800 ± 64	3,400 ± 38	420 ± 5.7
Soil 3-7	60–70		8,600 ± 16	0.8 ± 0.05	51.2 ± 1.5	45.5 ± 0.5	34,300 ± 690	3,300 ± 69	3,100 ± 41	190 ± 3.0
Mean	0–70		8,800 ± 100	5.7 ± 0.1	49.3 ± 2.1	59.5 ± 2.2	35,500 ± 943	2,400 ± 35	2,500 ± 36	410 ± 7
SE_800yrs										
Soil 4-1	0–10	A	1,200 ± 17	3.4 ± 0.005	52.4 ± 1.1	56.6 ± 1.8	25,200 ± 440	820 ± 0.6	1,000 ± 13	370 ± 1.0
Soil 4-2	10–20		1,500 ± 10	3.7 ± 0.03	51.5 ± 0.5	55.7 ± 0.7	28,200 ± 1,020	830 ± 2.8	840 ± 14	390 ± 3.9
Soil 4-3	20–30		1,500 ± 42	3.1 ± 0.01	51.4 ± 0.4	61.2 ± 1.0	26,900 ± 1,370	890 ± 4.2	800 ± 7.5	380 ± 4.9
Soil 4-4	30–40	B	670 ± 1.2	1.7 ± 0.01	51.1 ± 1.7	61.6 ± 2.7	26,800 ± 510	590 ± 18	450 ± 9.4	270 ± 8.5
Soil 4-5	40–50		550 ± 10	1.3 ± 0.05	53.0 ± 1.9	52.3 ± 1.3	24,600 ± 470	210 ± 7.4	250 ± 8.8	250 ± 3.5
Mean	0–50		1,100 ± 16	2.6 ± 0.02	51.9 1.1	57.5 ± 1.5	26,300 ± 762	670 ± 6.6	670 ± 11	330 ± 4.4
Reference soil										
Back-1	0–10	A	480 ± 2.2	4.7 ± 0.1	54.4 ± 1.0	65.5 ± 1.2	26,600 ± 1,530	650 ± 5.3	650 ± 9.5	570 ± 0.1
Back-2	10–20		460 ± 1.9	4.6 ± 0.1	55.1 ± 2.3	64.7 ± 1.6	28,000 ± 820	620 ± 3.0	590 ± 6.7	560 ± 2.1
Back-3	20–27		430 ± 4.7	4.4 ± 0.1	56.7 ± 1.0	64.1 ± 0.3	29,300 ± 1,120	570 ± 0.1	630 ± 18	540 ± 2.2

Table 4 continued

Soil sample	Depth (cm)	Horizon	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	S (mg/kg)	Zn (mg/kg)
Back-4	27–40	B	190 ± 0.1	2.4 ± 0.004	55.7 ± 1.3	47.2 ± 0.7	30,000 ± 70	250 ± 2.2	360 ± 0.2	360 ± 0.4
Back-5	40–50		140 ± 5.5	1.5 ± 0.1	55.7 ± 1.3	34.4 ± 0.8	25,900 ± 420	130 ± 1.7	300 ± 3.0	230 ± 0.3
Back-6	50–60		110 ± 1.6	1.0 ± 0.1	59.0 ± 1.9	27.2 ± 1.4	25,700 ± 1,020	92.0 ± 1.1	260 ± 12	170 ± 2.6
Back-7	60–70		90.0 ± 4.9	0.7 ± 0.05	52.6 ± 0.1	22.2 ± 0.3	26,200 ± 550	76.0 ± 0.8	200 ± 5.7	140 ± 2.2
Mean	0–70		270 ± 3	2.7 ± 0.1	55.6 ± 1.3	46.5 ± 0.9	27,400 ± 790	341 ± 2.0	430 ± 7.8	370 ± 1.4
RS[a]	Topsoil	A	60.0 ± n.s	0.3 ± n.s	63.5 ± n.s	13.5 ± n.s	32,950 ± n.s	234 ± n.s	450 ± n.s	133 ± n.s
RS[b]	Topsoil	A	n.s. ± n.s	0.5 ± n.s	32.0 ± n.s	21.0 ± n.s	n.s. ± n.s	85 ± n.s	n.s. ± n.s	100 ± n.s
EA	Topsoil	A	11.6 ± n.s	0.3 ± n.s	94.8 ± n.s	17.3 ± n.s	27,000 ± n.s	32.6 ± n.s	437 ± n.s	68.1 ± n.s

RS mean content of regional soils overlying Freiberger paragneiss, *EA* European topsoil average (Salminen et al. 2005), *n.s.* not specified

[a] Klinger 1995

[b] LABO (2003)

Institute for Surface Modification) (Reimer 1985). Therefore, the hard rock samples were cut in plane-thin pieces (2 mm thick) of approximately 1 × 1 cm size at the Institute of Mineralogy, University of Leipzig.

Calculating factors

A useful tool for the evaluation of metal enrichments in rock material and soil samples is the index of geoaccumulation I_{geo} proposed by Müller (1969) (Munendra et al. 2002; Akoto et al. 2008; Wakida et al. 2008; Nava-Martínez et al. 2012). The I_{geo} was utilized to evaluate the pollution of heavy metals in waste-rock material and soil samples at the study site, and is expressed as:

$$I_{geo} = \log_2 \frac{C_n}{1.5 B_n} \qquad (1)$$

with C_n the measured element content of a sample, B_n the regional background level of the same element and the factor of 1.5 accounting for weathering processes, the assumed driving long-term process. In this study, the published values of regional Clarke content of Freiberger paragneiss (Pälchen et al. 1987) were chosen as reference level for dump samples (RG, Table 2). Regional reference soils were sampled from proposed uninfluenced areas away from the dumps and considered as background values for soil samples. Additionally, published data for some site-specific metals were used for comparing topsoil overlying Freiberger paragneiss (Klinger 1995; LABO 2003). According to Müller (1981), I_{geo} classified geomaterial as following: no enrichment ($I_{geo} < 1$), moderate to higher enrichment ($1 \le I_{geo} \le 3$), very high enrichment ($3 < I_{geo} \le 5$) and extremely high enrichment ($I_{geo} > 5$).

For the interpretation of I_{geo} it is important to consider whether significant mass loss of the material occurs. We choose the immobile elements Ti and Zr as suitable indicators for weathering-induced mass loss (Anderson et al. 2002). As in this study constancy of I_{geo} for Ti and Zr were observed (Fig. 2), a decreasing I_{geo} of any other metal clearly indicates its discharge, while an increasing I_{geo} indicates its accumulation.

The last part of this work was aimed at calculating the time-dependent element transfer between the dump (as source) and their surrounding soil (as sink). Therefore, a further parameter is needed for its quantification. The following equation defines the Geochemical Transfer Factor (GTF) as a means to quantify the (time-dependent) transfer of mining-related elements (As, Cd, Cu, Fe, Zn and S) from the dumps into the 0.7-m-thick soil section surrounding each dump

$$\text{GTF} = \frac{\text{length} \times \text{width} \times 0.7 \times C_{n\_soil} \times \rho \text{ soil}}{0.5 \left(\text{length} \times \text{width} \times \text{height}\right) \times C_{n\_dump} \times \rho \text{ dump}} \qquad (2)$$
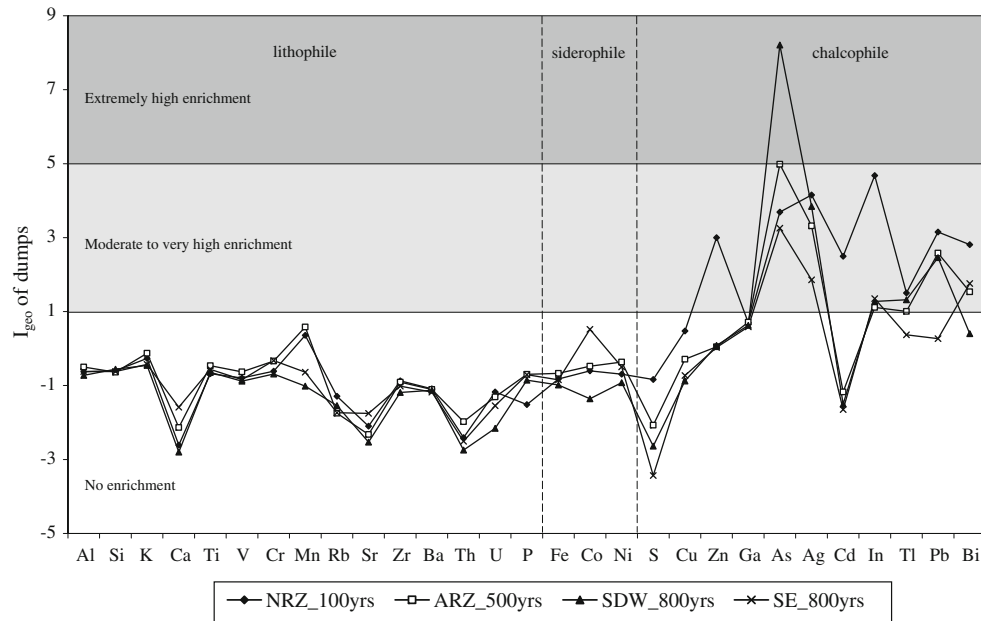
Fig. 2 I_{geo} of dump samples from the mining district Freiberg

with length, width and height (in m) being the dimensions of the dumps (see Sect. "Study site"), C_{n_soil} the background-corrected soil element content (Table 4), C_{n_dump} the respective dump element content (Table 2), ρ_{soil} the soil density of 1.5 t m^{-3} (Müller 1999), ρ_{dump} the saturated packing density of 2 t m^{-3} and a factor 0.5 accounting for the flattened shape of the dumps (Oberfranken 2001). Generally, the soil samples downstream each dump were considered as well representing the soil underneath the dumps. For comparability of the transfer factor obtained at the individual sites, the trend of the metal content in soil profiles shorter than 0.7 m were extrapolated to this depth. The overall uncertainty is calculated by error propagation on the basis of the uncertainty of the dump dimension, the standard deviation of the mean metal contents of composite samples and the uncertainty of the background content of soil samples. The resulting total volumes V and total masses M (t = 10^3 kg) are listed in Table 5.

Results and discussion

Characteristics of the dump materials

The geochemical characteristics of the dump samples and information on sampling sites (latitude and longitude) are presented in Tables 1 and 2.

The investigated dumped material consists mainly of the metamorphic gneiss. The measured pH values decreases with increasing age of dump (NRZ, pH 5.1; ARZ, 5.7; SDW, 4.4; SE, 4.8). Such higher acidity in historical

mining residues was expected due to the oxidative weathering of the sulfide minerals. No measured carbonate content in the samples indicates a calcareous-free nature of these waste-rock materials.

Geochemical analysis indicates expected quantities of heavy metals, especially As, Cd, Cu, Pb, S, and Zn, in all dump samples, which are comparable with published data for waste material in the mining district of Freiberg (Böhmer 1999; Göhler 1999). The element contents of the unweathered rock material compare well with the regional Clarke values for paragneiss from Pälchen et al. (1987) and Kardel et al. (1996). The content of mining-related elements in dump material as well as in unweathered gneiss is shown in Table 2. To compare element contents in waste-rock material with regional Clarke contents of paragneiss as background values (Pälchen et al. 1987), the I_{geo} were calculated (see Eq. 1). In Fig. 2 I_{geo} is plotted versus the analyzed elements arranged according to the Goldschmidt classification in lithophile, siderophile and chalcophile elements (Goldschmidt 1937).

Two general features are obtained. First, the general high values ($I_{geo} > 1$) of chalcophile elements in the dump material are related to the kind of deposit. Significantly, maximum values of up to 960 mg/kg Zn ($I_{geo} = 3$), 890 mg/kg As ($I_{geo} = 8$), 320 mg/kg Pb ($I_{geo} = 3$) and 8.5 mg/kg Cd ($I_{geo} = 3$) were determined. This reflects the site-specific mineralization of sphalerite (ZnS), arsenopyrite (FeAsS) and galena (PbS) in the Freiberg deposit. The high content of Cd is well known within sphalerites (Vaughan and Craig 1978). Lithophile elements, such as those of alkali and alkaline earth metals, as well as the

Table 5 Geochemical transfer factors (and their ranges) of mining-related elements for mining dumps in Freiberg

Sample location	As	Cd	Cu	Fe	Pb	S	Zn
NRZ_100yrs (V = 24,000 ± 4,000 m³) (M = 48,000 ± 8,100 t)							
Dump inventory (kg)	1,860 ± 750	406 ± 409	2,500 ± 1,260	1,458,300 ± 351,500	15,340 ± 9,130	58,860 ± 61,240	46,060 ± 41,220
Soil inventory (kg)[a]	220 ± 270	2.9 ± 2.8	83 ± 50	6,000 ± 25,120	350 ± 340	0 – 223	64 ± 340
GTF	0.12 ± 0.14	0.007 ± 0.01	0.033 ± 0.025	0.004 ± 0.016	0.023 ± 0.025	0 – 0.004	0.0014 ± 0.007
ARZ_500yrs (V = 5,000 ± 1,260 m³) (M = 10,000 ± 2,520 t)							
Dump inventory (kg)	950 ± 650	6.7 ± 3.1	310 ± 110	337,200 ± 89,600	2,160 ± 570	5,230 ± 2,170	1,240 ± 460
Soil inventory (kg)[a]	2,530 ± 350	0.9 ± 0.9	85 ± 22	7,390 ± 8,550	2,020 ± 310	2,300 ± 370	310 ± 140
GTF	2.66 ± 1.85	0.14 ± 0.14	0.28 ± 0.12	0.022 ± 0.024	0.93 ± 0.28	0.44 ± 0.19	0.25 ± 0.14
SDW_800yrs (V = 240 ± 90 m³) (M = 480 ± 170 t)							
Dump inventory (kg)	430 ± 570	0.25 ± 0.09	9.8 ± 3.7	13,030 ± 4,730	95.2 ± 39.3	170 ± 180	61.2 ± 32.3
Soil inventory (kg)[a]	2,870 ± 610	0.99 ± 0.40	4.4 ± 4.2	2,740 ± 2,480	680 ± 170	700 ± 180	13.6 ± 28.5
GTF	6.71 ± 8.93	3.90 ± 1.52	0.45 ± 0.26	0.21 ± 0.12	7.17 ± 2.94	4.12 ± 4.49	0.22 ± 0.25
SE_800yrs (V = 300 ± 100 m³) (M = 600 ± 210 t)							
Dump inventory (kg)	17.2 ± 13.3	0.29 ± 0.10	13.6 ± 4.9	17,940 ± 6,280	26 ± 14	120 ± 73.0	73.6 ± 26.0
Soil inventory (kg)[a]	340 ± 81	0 – 0.13	4.6 ± 4.3	0 – 1,530	140 ± 50	100 ± 49.9	0.0 – 9.2
GTF	19.6 ± 15.2	0 – 0.17	0.34 ± 0.21	0 – 0.038	5.31 ± 2.94	0.83 ± 0.54	#

V total volume of dump, M total mass of dump (t = 10³ kg)

Within limits of uncertainty below zero

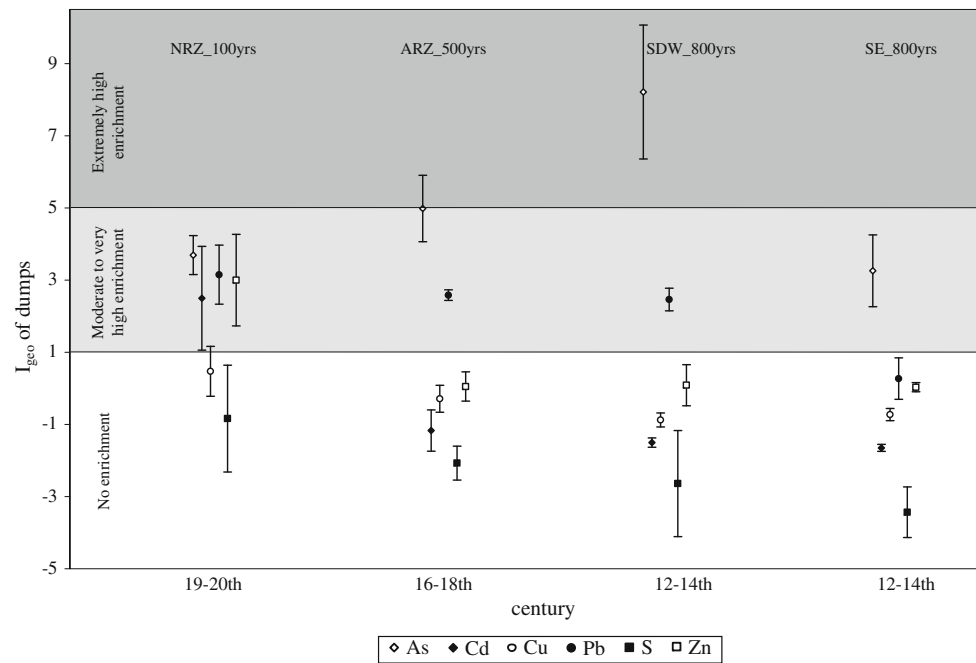[a] Background-correlated with regional reference soil Back-1 (see Table 4)

Fig. 3 I_{geo} of mining-related elements for dump samples plotted versus the century of mine deposition

siderophile elements correspond to regional background values of paragneiss.

Second, the I_{geo} of the chalcophile elements differ significantly amongst themselves. A possible explanation for this could be the certain variety of metal contents in the original dump materials (despite their same ore vein), e.g., due to geogenic conditions or inefficient mining techniques in earlier times. The heterogeneity of dump materials is a well-known problem (Brüschke 2001). Especially, as a consequence of the bulk dumping, the dumps are strongly heterogeneous. It is obvious that the representative sampling is the most important step towards a good analytical result.

However, some distinct chalcophile elements like S and Cu are generally not enriched, independent of the age of the investigated dump materials, while some, like As and Ag, are generally enriched. Furthermore, some distinct chalcophile elements show a larger variability of the I_{geo}, like S, As, and Cd, while others show quite homogeneous I_{geo}, like Cu, Ga and Tl. Finally, some I_{geo} of distinct chalcophile elements clearly demonstrate decreasing values with the increasing age of the dumps, like S and Pb, while others show no clear trend, like As and Ag. From Fig. 3 it is recognizable that the I_{geo} for the mining-related elements As, Cd, Cu, Pb, S, and Zn are decreased with the increasing age of the dumps except those of arsenic. Specifically, the S content of the youngest dump is about the same as the one of the background paragneiss ($I_{geo} = -0.8 \pm 1.5$) and significantly decreases with time to $I_{geo} = -3.4 \pm 0.7$; the Pb and Zn contents of the youngest

dump exceed the background value significantly ($I_{geo} \geq 3 \pm 1.3$) and drop with time towards the background value ($I_{geo} \leq 0.3 \pm 0.6$). A possible explanation for the exception of As could be the high original As content in the inventory of the dump SDW_800yrs as well as their high acidity (pH 4.4) (Table 2). For all other elements (not shown) the same temporal trend is identified; however, it is not significantly due to the large variability of the metal contents in the sampled material. The observed temporal trend for all analyzed metals is plausible.

Characteristics of the soil samples

Site-specific pedological and geochemical characteristics of the soil samples are given in Tables 3 and 4. In the study area Freiberg, the soil type Parabraunerde-Pseudogley can be found overlying the bedrock biotite gneiss as described in Schmidt-Hammel (undated). The pH values are in the range of 3.7–6.4 depending on the age of a dump, with a generally decreasing trend with deposition age. The pH of the topsoil nearest to the oldest dump (SDW_800yrs) is strongly acidic (pH 3.7) with lightly increasing values throughout the A-horizon towards the base of the profile (≤pH 4.7). This indicates high AMD released from the waste-rock material of the older dumps and corresponds with the results of the characterization of the dump material. In contrast, the soil profile nearby the youngest dump (NRZ_100yrs) shows quite homogeneous pH values (pH 6.2–6.4) similar to the regional reference soil values (pH 5.8–6.5) and typical rainfall with an average of pH 5.4
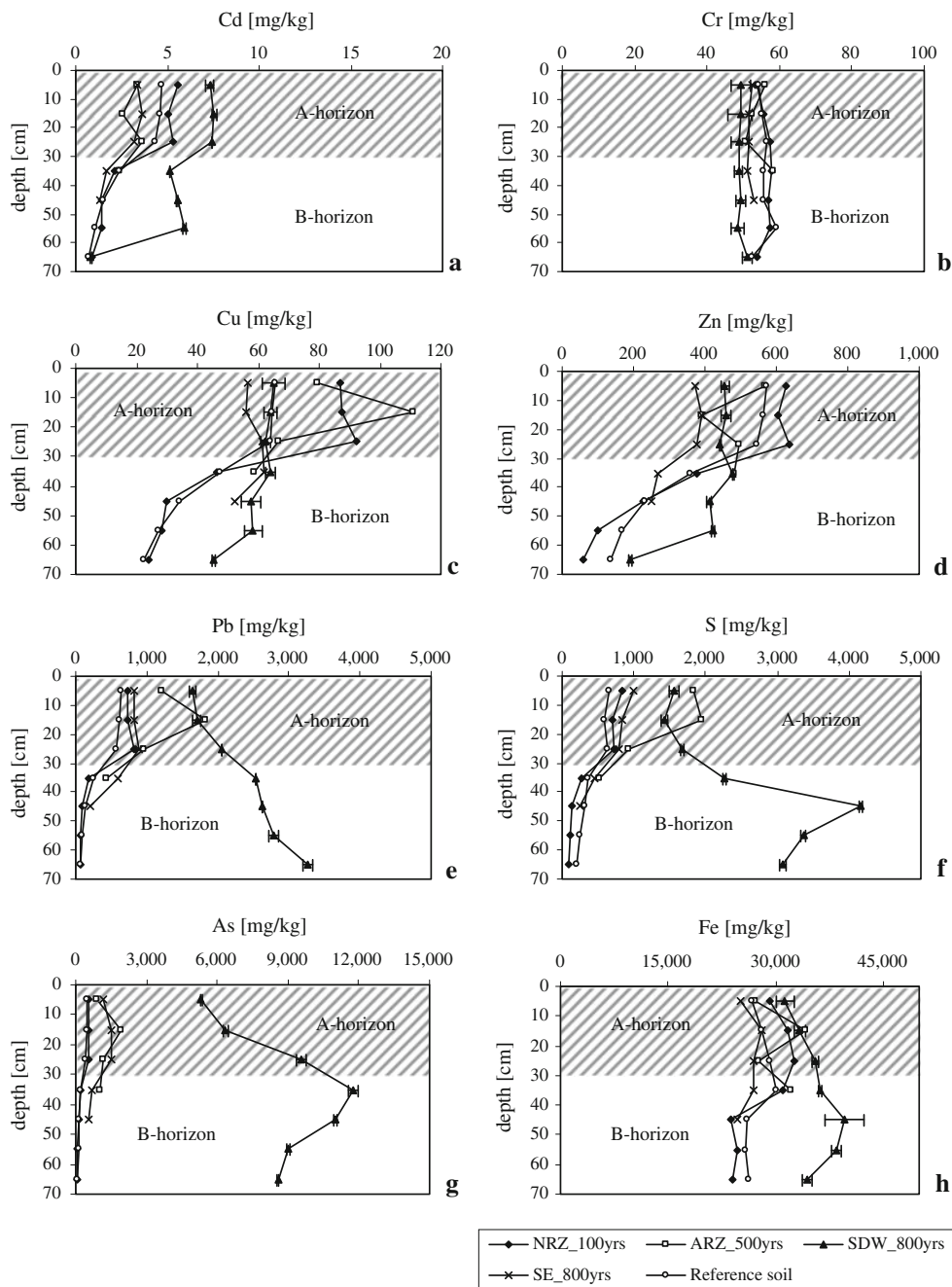
Fig. 4 a–h Vertical distribution of mining-related element contents in soil (mg/kg soil), a typical depth of 30 cm for the A-horizon is *hatched*

(Möller and Horváth 1988). This indicates lower AMD due to the shorter time of deposition.

The elemental compositions (C, H, N) of soil samples are listed in Table 3. Generally, the A-horizons of the soil samples are characterized by C and N contents of 2–4 % and 0.2–0.4 %, respectively. The resulting C/N ratios of 9.9–10.8 are typical values of A-horizons (Scheffer and Schachtschabel 2010).

Major and trace element analysis of the soil samples shows that besides alkali (e.g., K and Rb) and alkaline

earth metals (e.g., Ca, Sr and Ba), the chalcophile elements (e.g., Cu, Zn, As, Pb) are the main metal constituents. The contents of the site-specific elements As, Cd, Cr, Cu, Fe, Pb, S and Zn and their vertical distribution in soil profile are presented in Table 4 and Fig. 4a–h. In the A-horizons the chalcophile elements As, Cu, Cd, Pb, S and Zn are enriched in all profiles except those of dump SDW_800yrs. These findings are not surprising, as in other Pb–Zn–Ag mining areas increased concentrations of Cu, Pb and Zn were identified in the upper soil layers of the near-field of
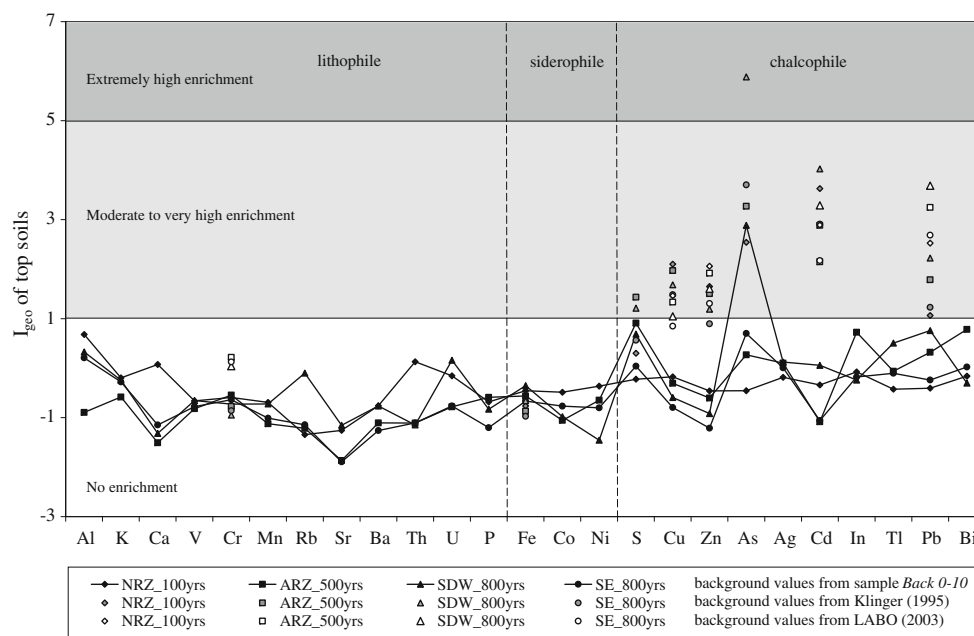
Fig. 5 I_{geo} of topsoils (0–10 cm) in the near-field of dumps

dumps (e.g., Ullrich et al. 2000; Taylor et al. 2010; Aleksander-Kwaterczak and Ciszewski 2012). It is well known that heavy metals tend to form stable complexes with natural organic material (NOM) of upper soil layers. Such metal–NOM complexes are able to bind chalcophile metals permanently due to their functionality and high reactivity and cause an immobilization of heavy metals (Brümmer et al. 1986; Kördel et al. 1997; Matschullat et al. 1997; Franke et al. 2000). For the study area, such complexation of heavy metals with NOM in soil adjacent the dumps was already proven by Scheinert (2007). Moreover, metal–NOM complexes were detected surrounding further historical dumps in the mining district Freiberg (Wolf 1999; Franke 2003).

In particular, the acidic conditions cause the uniformly continuous element discharge throughout the eight centuries in the mining area of Freiberg. Obviously, in other mining areas such as copper ore mining area in the Mansfelder Land, Germany, the acidification of the dumps is effectively inhibited by the buffering capacity of the deposited carbonatic material (mainly black shale) and thus no clearly time-dependent weathering-induced transfer of heavy metals could be observed (Müller 2008).

The lithophile and siderophile elements are rather uniformly distributed all along the vertical profiles as shown exemplarily for Cr and Fe in Fig. 4b, h. The spatial distribution of the alkali and alkaline earth metals (not shown) does not show significant differences in the soil.

Apparently, the vertical element distribution in the soil samples downstream to the dump SDW_800yrs is remarkably different in comparison to all other sites.

However, the element contents of As, Pb and S increase with depth. This is explained by the high As, Pb and S content as well as the high acidity (pH 4.4) of the corresponding dump material (Table 2), which causes the reducing of the complex binding capacity in the A-horizon and disabled its natural retention function due to the formation of soluble sulfato-complexes. This effect has already been identified by Wolf (1999).

For comparison of these results with regional background values, the I_{geo} of topsoil samples were calculated (see Eq. 1). In Saxony, there exist even local and regional scale geochemical data that would give a good overview of soil background values (Klinger 1995; LABO 2003). Furthermore, a background soil profile sample, taken from two areas in the study area that were most likely not influenced by dumping activities, were used for comparison (sample Back-1). In Fig. 5, the obtained I_{geo} for soil samples are plotted versus the lithophile, siderophile and chalcophile elements according to Goldschmidt (1937). Two general features are discussed: first, lithophile element contents, such as those of the alkali and alkaline earth metals, as well as the siderophile element contents are consistent with regional soil background values and show no enrichments ($I_{geo} < 0$); second, I_{geo} for chalcophile elements differ strongly. I_{geo} calculated with background sample Back-1 show no enrichments of chalcophile elements, except for As, which is classified with higher enrichment (I_{geo} of 3) in the topsoil downstream to the dump SDW_800yrs. This high I_{geo} obtained for arsenic indicates its high mobilization in acidic waters and its sorption in soil (c.f., Asta et al. 2010).
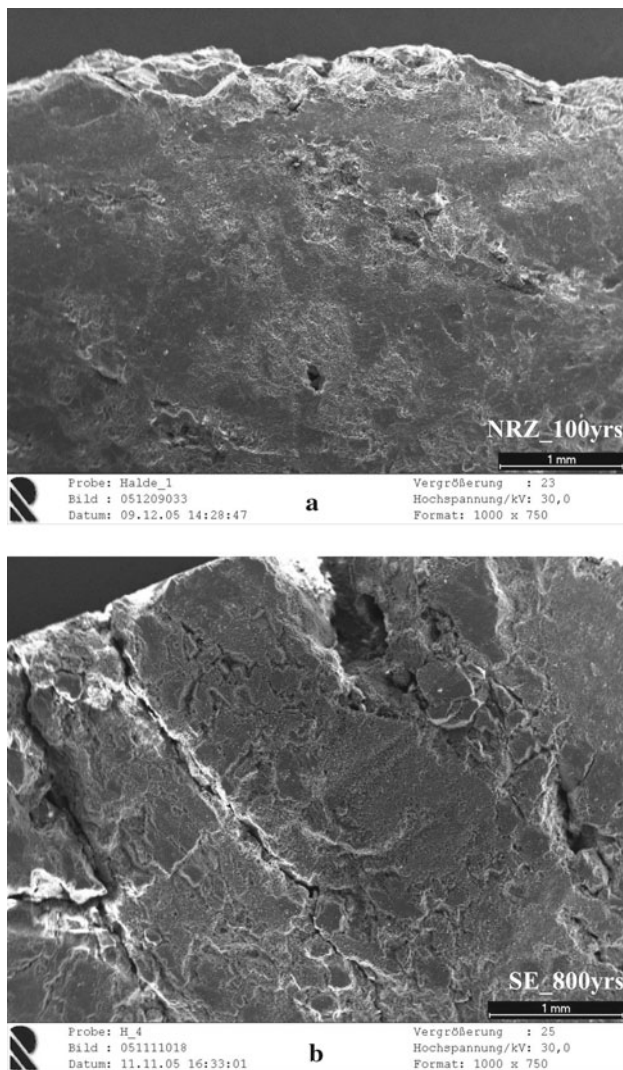
Fig. 6 SEM images of two different-aged dumped materials: **a** dump NRZ_100yrs from nineteenth–twentieth century and **b** dump SE_800yrs from twelfth–fourteenth century

I_{geo} calculated with regional background values from literature (Klinger 1995; LABO 2003) show generally higher enrichments ($I_{geo} > 1$). These differences can be interpreted as due to the geogenic conditions with site-specific higher background values in many soils of Saxony (Scherchan 1980; Fiedler et al. 1990; Ossenkopf et al. 1993). Measured values of regional background soil sample Back-1 confirm such high quantities of heavy metals (e.g., 480 mg/kg As, 4.7 mg/kg Cd, 650 mg/kg Pb, 570 mg/kg Zn) and sulfur (650 mg/kg S) due to the geogenic conditions (and most often caused by emission), which cause the low I_{geo} of dump-influenced soils. Generally, the regional soils of the study area Freiberg are enriched in heavy metals and sulfur compared to the European topsoil average values from Salminen et al. (2005) (see Table 4).

Time-dependent weathering effects

Time-dependent weathering phenomena in dump samples are documented by scanning electron microscopy (SEM). Figure 6 enables a direct visual comparison of the surface areas of two samples from different-aged dump material. The surface area of the younger dump material (NRZ_100yrs, Fig. 6a) does not show any micro-cracks, whereas the older one (SE_800yrs, Fig. 6b) shows numerous micro-cracks. Along the surfaces and inside the cracks oxidic compounds are visible (light areas). This oxidation is more pronounced in the older dump material indicating an increasing accretion of weathering products with the increase in age. We suggest that primarily sulfidic minerals (e.g., pyrite, galena) have progressively experienced a loss of sulfur leaving the oxidized remains behind. The younger dump material of NRZ_100yrs shows only smaller and less oxidic areas. This indicates weaker effects of exogenic weathering due to the shorter time of deposition.

For quantifying the time-dependent transfer of the mining-related elements As, Cu, Fe, Pb, S and Zn from the investigated dumps to the surrounding soils, the geochemical transfer factor (GTF, see Eq. 2) was calculated. The resulting GTF (Table 5), shows an increasing trend in time, and for most elements this trend is actually significant. This is in particular remarkable, as large overall uncertainties exist that account for the conditions of a historic mining area with considerable anthropogenic impact on a heterogeneous regional scale.

In Fig. 7 the GTF is plotted versus the century of waste deposition. It can be shown that for dumps NRZ_100yrs, ARZ_500yrs and SDW_800yrs the GTF increase over four orders of magnitude with increasing age, for As, Cd, Fe, Pd and S this trend is significant. The time series of the GTF including the other 800-year-old dump SE_800yrs shows timely trends for As, Cu, Pb and S (with those for As and Pb being significant), whereas the soil inventories of Cd, Fe and Zn are indistinguishable from regional reference soil entailing GTF below, equal or at the upper range of the stated uncertainty to positive values. These low GTF of dump SE_800yrs are eventually caused by a disadvantageous distance between dump and soil profile. As a rule of thumb for dumps older or equal to 500 years, the effective GTF are greater than 0.1, or after about 500 years an amount ≥10 % of the metal dump inventory is located in the soil surrounding it. Soils surrounding younger dumps (~100 years) hold less than 10 % of the metal dump inventory, characterized by GTF smaller than 0.1, respectively. This observation is plausible, as the progressive weathering of sulfide minerals in dump material results—under the given environmental conditions of the mining area in Freiberg—in a progressive acidification and, consequently, in an increasing solubility of heavy metals.
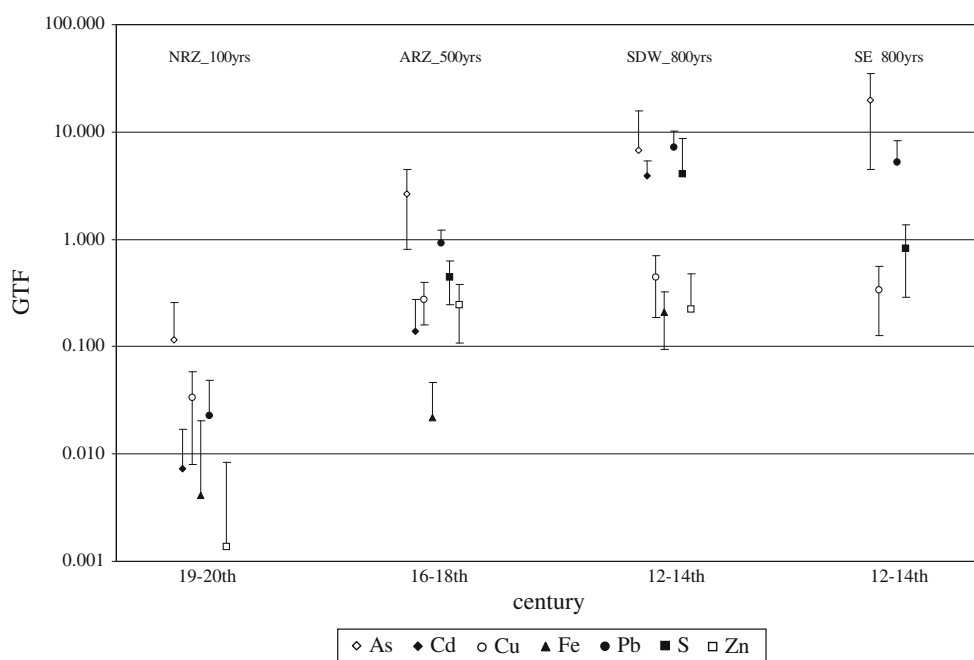
Fig. 7 Geochemical transfer factors (*GTF*) of mining-related elements for mining dumps in Freiberg plotted versus the century of mine deposition

Conclusion

In this study, the distribution of heavy metals and other mining-related elements in waste-rock material of four different-aged mining dumps of the Freiberg mining district and their contents in surrounding soils were examined. The measurements of the metal contents in the dumped material indicate high quantities of chalcophile elements due to the sulfidic mineralization of this deposit. Generally, the chalcophile elements in the older waste-rock material (800 years) are depleted compared to the youngest dump material (100 years). The results confirm the basic assumption that progressive weathering of sulfide minerals causes increasing AMD (see data on pH, Table 2) and consequently induces the effective long-term discharge of heavy metals from the dumps throughout the course of the past eight centuries. Obviously, the I_{geo} is a useful parameter for the quantification of the weathering potential of the dump material, as the unweathered gneiss serves well as a reference for waste-rock material. In contrast, the stated I_{geo} for the soils represent most conservative assessment values of the metal pollution because the former mining activities have certainly influenced the regional reference soil (e.g., via emission) and imply the underestimation of metal enrichments in the soil downstream the dumps. Compared to the natural background soil, the dump-influenced soil samples show high contents of sulfur (4,200 mg/kg) and heavy metals (e.g., up to 12,000 ppm As, 3,300 ppm Pb, 640 ppm Zn), mainly adsorbed on organic matter.

Thus, a discharge of mining-related elements with increasing age of the dumps could be observed due to weathering. Having quantified both, the dump and the soil profile inventories, a clear timely trend for the discharge of the most relevant heavy metals and sulfur is obtained. The resulting trend of increasing element-specific transfer factors with dump age is the most comprehensive (e.g., As, Cd, Cu, Pb, Zn; Table 5) and longest trend (800 years) of this kind.

It is important to note that due to the variation in historical ore winning methods throughout the course of the last eight centuries, the initial inventories of the dumps must have been considerably different, and any direct comparison between the dumped materials would not have shown any timely trend. Only referring the soil inventory surrounding each dump to the inventory of the directly related dump enabled us to disclose the timely trend so clearly.

The obtained results show that this study of the quantification of time-dependent geochemical transfer factors (GTF) induced by weathering processes throughout the eight centuries serves as a unique natural analogue study for time scales of relevance for the validation of conceptual and numerical models of risk assessment prognosis calculations.

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