

SEM/EDS analysis of soil and roasting vessels fragments from ancient mercury ore roasting sites at Idrija area

SEM/EDS analiza tal in prežganih koščkov keramike iz nekdanjih žgalnic živosrebrove rude na Idrijskem

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Ključne besede: živo srebro, žgalnice, SEM/EDS, Pšenk, Frbežene trate, Slovenija

Abstract

Numerous roasting vessels fragments can be found at ancient roasting site areas in the surroundings of Idrija town, which were used for ore roasting in the first 150 years of Hg production in Idrija. The earthen vessels fragments lay just below the surface humus layer and in some parts they stretch more than 1 meter deep; they are covered with red (cinnabar) or black (metacinnabar) coatings.

SEM/EDS analysis of roasting vessels fragments and soil samples from roasting site areas Pšenk and Frbežene trate was performed in order to characterize the solid forms of Hg in applied sampling material. Mercuric sulphide HgS was found to be the main mercury compound present in the samples. Analysis of earthen vessels fragments showed abundant HgS coatings on the surface of ceramics, forming either crust-like aggregates on matrix or isolated grains. Some well-shaped grains with indicated structure and the size of up to 200 µm could also be observed. In soil HgS was present as powder-like concentrations scattered in soil samples, frequently coating silicate and quartz crystals and clay-minerals. Polycrystalline, mercury- and sulphur- rich particles comprising silica, clay minerals and Al-, Fe- and Mg-oxides that were also observed in the samples were interpreted as soil aggregates infiltrated by mercuric and sulphur vapours and by liquid mercury spilled during roasting. These particles suggest a possible presence of mercury-sulphur associations other than HgS.

Izvleček

Na območjih nekdanjih žgalnic v okolici Idrije, ki so jih uporabljali za žganje živosrebrove rude v prvih 150 letih delovanja rudnika, najdemo številne ostanke glinenih žgalniških posod. Odlomki žgalniških posod ležijo tik pod površinskim organskim horizontom in segajo na nekaterih delih več kot 1 meter globoko; pogosto so na notranji strani prekriti z rdečimi (cinabarit) in črnimi (metacinabarit) oprhi.

SEM/EDS analiza tal in prežganih koščkov keramike iz žgalniških območji Pšenk in Frbežene trate, je bila uporabljena za opredelitev nosilcev živega srebra v izbranih vzorčnih sredstvih. Ugotovljeno je bilo, da Hg v obravnavanih vzorcih nastopa predvsem v obliki živosrebrovega sulfida HgS. Analiza prežganih koščkov keramike je pokazala številne obloge HgS na površini, ki se pojavljajo kot skorjasti skupki na osnovi ali kot individualna zrna. Nekatera lepo oblikovana zrna z nakazano strukturo dosežejo velikost do 200 µm. V vzorcih tal in SOM je se HgS pojavlja predvsem v obliki zelo drobnih razpršenih delcev na površini glinenih in drugih mineralov. Številni zelo drobni delci HgS brez dobro izražene strukture, vključeni v talne skupke in prekriti s tankimi glinenimi prevlekami, nakazujejo možen obstoj drugih vezav med živim srebrom in žveplom razen kristalnega HgS (živo srebro vezano na faze vsebujoče žveplo).

Introduction

In the initial period of mining activities in the Idrija basin, Hg was extracted primarily by washing native Hg from Carboniferous rocks. In the period up to the 17th century, Hg was extracted by igniting ore in the open air, initially in piles similar to those used in the extraction of charcoal,

and later in earthen vessels (VERBIČ, 1965; KAVČIČ, 2008; VERBIČ, 1970b). The procedure of ore roasting in earthen vessels, termed also German or Bavarian method, was described by VERBIČ (1965; KAVČIČ, 2008; VERBIČ, 1970a, 1970b, 1990, 1993), VALENTINITSCH (1981), ČAR & TERPIN (2005) and KAVČIČ (2008) and is summarized in GOSAR & ČAR (2006), TERŠIČ & GOSAR (2009) and TERŠIČ (2010a).

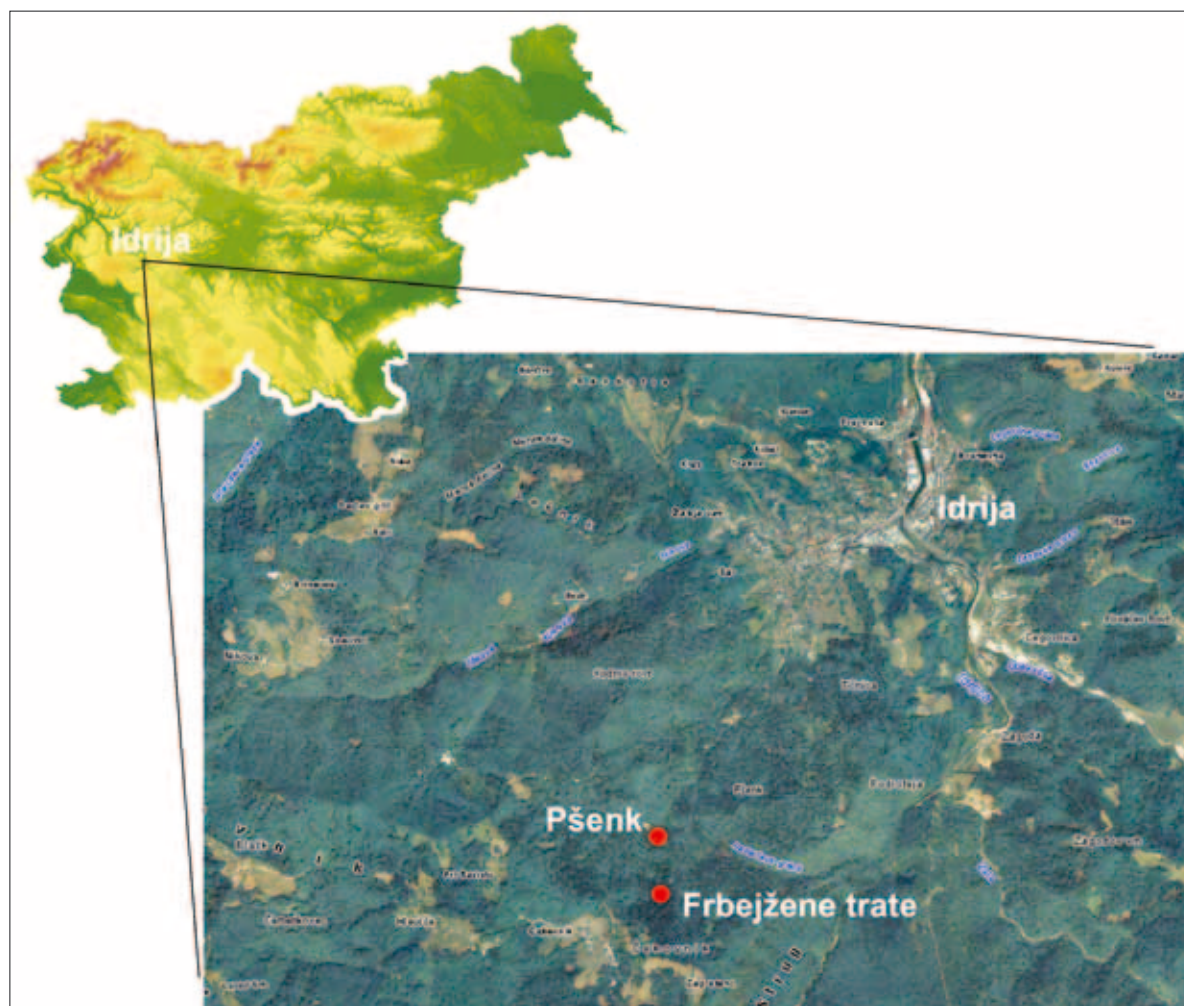


Fig.1. Locations of Pšenk and Frbežene trate roasting sites

The locations of ancient roasting sites Pšenk and Frbežene trate which are discussed in this paper are presented in Fig. 1.

At this method a suit of two earthen roasting vessels was used – the bigger upper, in the shape of longish gourd (*earthen vessel*), and smaller lower vessel (*receptacle*). Roasting vessels were formed specially for roasting of cinnabar ore. Pottery was mainly made from bad quality clay with a considerable amount of sand. After the roasting the vessels usually got the reddish brown colour. The lower vessels were made less precisely and usually from even worse quality clay than the upper vessels; they can be distinguished from the upper vessels in their colour, which is also the consequence of lower temperatures in the lower buried part. Roasting in earthen vessels gave a very poor yield and resulted in considerable losses. Because of the high temperatures usually a third of earthen vessels cracked during burning and mercury escaped from the vessels (VERBIČ, 1965; KAVČIČ, 2008).

Because at the time the chemical decomposition of HgS was not well known, it frequently happened that instead of mercury, red vermilion or black secondary mercury sulphide were formed during roasting. Nowadays we can still observe red and black coatings on pieces of pottery fragments. This deficiency was suppressed with the

addition of quicklime to the ore; so, the sulphur bounded with calcium to form calcium-sulphide (CaS) and gypsum (CaSO₄), and mercury accumulated in the lower vessel:



After the roasting, the ashes and other material were removed from the pile in order to accelerate cooling down of the vessels. Natural atmospheric cooling lasted for several days; afterwards the vessels were additionally cooled by watering. When the vessels were cold enough, the remained material was gradually removed, the vessels were separated and the mercury was collected from the bottom vessel (receptacle). The cracked or damaged vessels were discarded, crushed and used as a filling material at the next roasting (Fig. 2; ČAR & TRPIN, 2005). At present, large quantities of fragments of broken pottery are commonly found at ancient roasting sites.

The aim of this study was to characterize the solid forms of Hg in soil and SOM samples with the combination of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses. SEM/EDS was used to quantify the relative abundance of HgS particles in the fragments of cracked roasting vessels and in mercury-rich soil samples and to investigate the

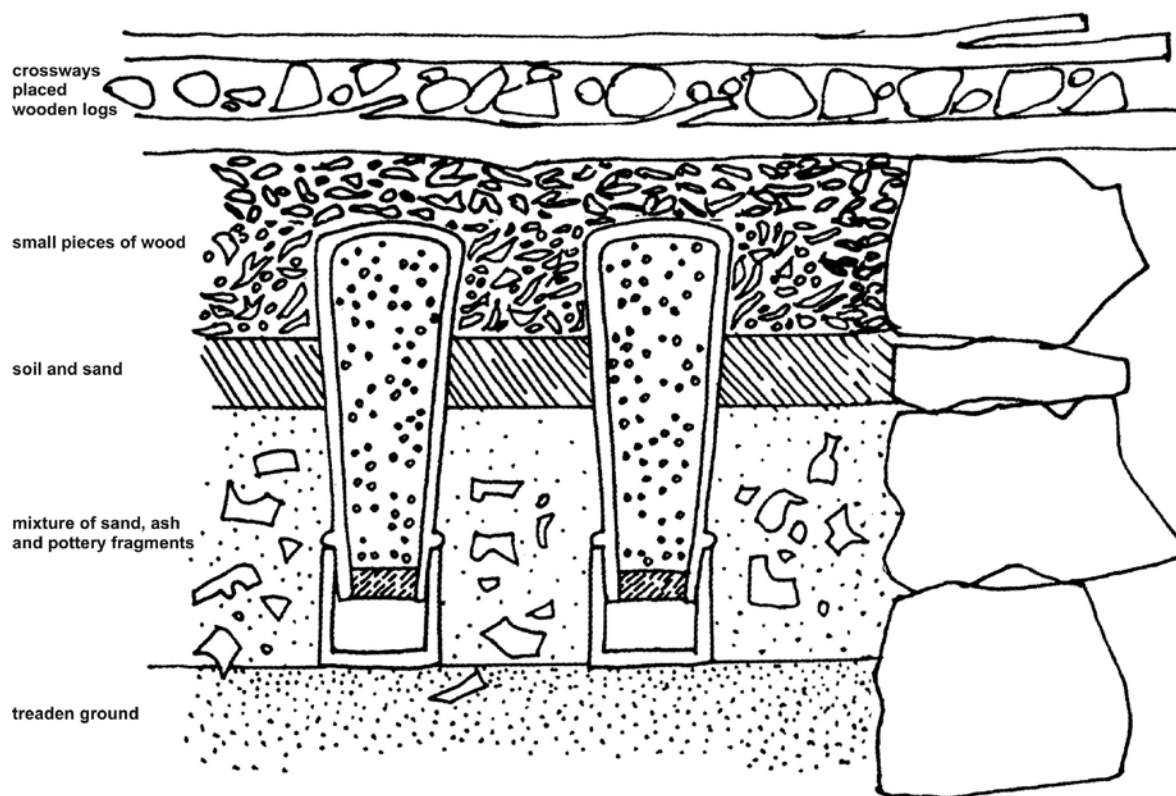
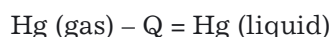
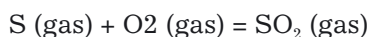
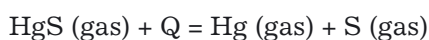
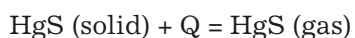


Fig. 2. Drawing of earthen vessels position at the roasting place (after ČAR & TERPIN, 2005)

possible association of Hg or HgS with specific matrix phases.

The process of extracting mercury from cinnabar ores

Mercury metal is produced from the cinnabar ore by roasting and condensing the vapour. By heating, HgS sublimates and decomposes to mercury and sulphur. In the presence of oxygen sulphur oxidize to SO₂, and mercury liquefies on the cold surfaces:

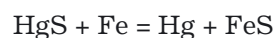
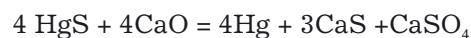


The vapour pressure of mercury sulphide is equal to atmospheric pressure at 583 °C; therefore this is the optimal temperature for ore roasting at the processes of extracting mercury. The decomposition is carried out also at lower temperature: at 350–500 °C, 80–92 % of HgS decomposes. It is important that there is enough oxygen present; otherwise the sulphur does not oxidize to SO₂ and between mercury and sulphur vapours the recurrent reaction runs. In this case black amorphous mercury sulphide is formed as a coating on the walls and bottom of condensers:



Similar can happen while cooling mercury vapours at the presence of water steam which again results in black coatings of HgS on cold parts of

condenser. To prevent repeatedly formation of HgS from mercury and sulphur vapours, lime or iron filings are added to the ore:



In both cases mercury segregates in a pure, elemental form and after cooling deposits in a condenser system as a liquid metal.

After the roasting, the gases that evaporate from the furnace need to be cooled down, since most of the mercury is present in the form of vapours. Condensation is more effective if the mercury vapours are more concentrated, which is dependent mostly on the percentage of mercury in the ore and upon the amount of the other components such as water steams or organic matter which come into the gases at combustion. More of these constituents in the gases deteriorate the condensation. For this reason, the roasting process with the addition of lime or iron filings, where the ore is heated in the closed space, is much better in comparison to the custom way of roasting, where the fuel gases mix with mercury vapours (KAVČIČ, 2008).

Materials and methods

Soil (5–20 cm) and SOM (surface organic matter rich soil layer; 0–5 cm) sampling was performed at the ancient roasting site areas Pšenk and Frbežene trate. Roasting vessels fragments were also collected. The detailed descriptions of sampling procedure, sampling locations and mercury distribution are given in the preliminary geochemical study at the Pšenk roasting site (TERŠIČ

& GOSAR, 2009) and in the study of environmental influences of historical small scale ore processing at Idrija area (TERŠIČ, 2010a, 2010b).

Three pieces of burned roasting vessels fragments with clearly visible black and/or red coatings as well as defined SOM and soil samples were chosen for SEM/EDS analysis; SOM and soil samples (5–20 and 20–30 cm) from one location (P-612) from Pšenk roasting site (Fig. 3) and soil samples (5–20 cm) from two locations (F-111 and F-217) from Frbežene trate (Fig. 4) were analyzed. Mercury contents in analyzed soil and SOM samples from before mentioned locations are listed in Table 1.

Sample preparation and SEM/EDS analyses

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to characterize the solid forms of Hg in soil samples and in roasting vessels fragments at the Geological Survey of Slovenia. Samples were analyzed using BSE mode on JEOL JSM 6490LV SEM coupled with Oxford INCA Energy EDS at accelerating voltage 20 Kv, working distance 10 mm and the acquisition time 95 s. This instrument was used for semiquantitative chemical point analysis, for microphotographs in back-scattered and secondary electron modes, and for X-ray elemental mapping (the relative element distribution).

The samples of roasting vessels fragments were observed in a low- and high-vacuum. The soil samples were observed in high-vacuum. Soil samples were sieved <2mm and sprinkled on double-sided carbon tape, the excess blown off with compressed air and sputter-coated with gold

Table 1. Mercury contents in analyzed soil samples from locations P-612 from Pšenk roasting site and F-111 and F-217 from Frbežene trate roasting site

Location	Depth (cm)	Hg (mg/kg)
P-612	0–5	2100
	5–20	8600
	20–30	7900
F-111	5–20	12020
F-217	5–20	19900

to achieve conductivity. Samples were scanned in back scattering mode. Mercury is an electron dense atom and an effective electron backscatterer. Consequently, it becomes visibly bright in a matrix consisting of low Z elements. The elemental composition of those Hg-rich particles identified was then studied by using energy dispersive x-ray spectrometer (EDS).

With a resolution of 133 eV for EDS, the S- K_{α} line (2.31 keV) and the Mo- L_{α} (2.28 keV) line overlap, so directly distinguishing between the two elements was not possible. To ascertain that the observed grains are HgS and not HgMo, the comparison of measured EDS spectrum for the grain which was supposed to be HgS with the synthesized EDS spectrum of HgS and HgMo was done. The measured spectrum was more similar to the spectrum of synthesized HgS, so we concluded that there is HgS in our samples. Another attempt was performed with analysis at accelerating rate of 30 keV, which should show another peak for Mo at approx. 17 keV (Mo- K_{α}). In our case no peak could be observed at 17 keV which proved that there is no Mo in our samples.

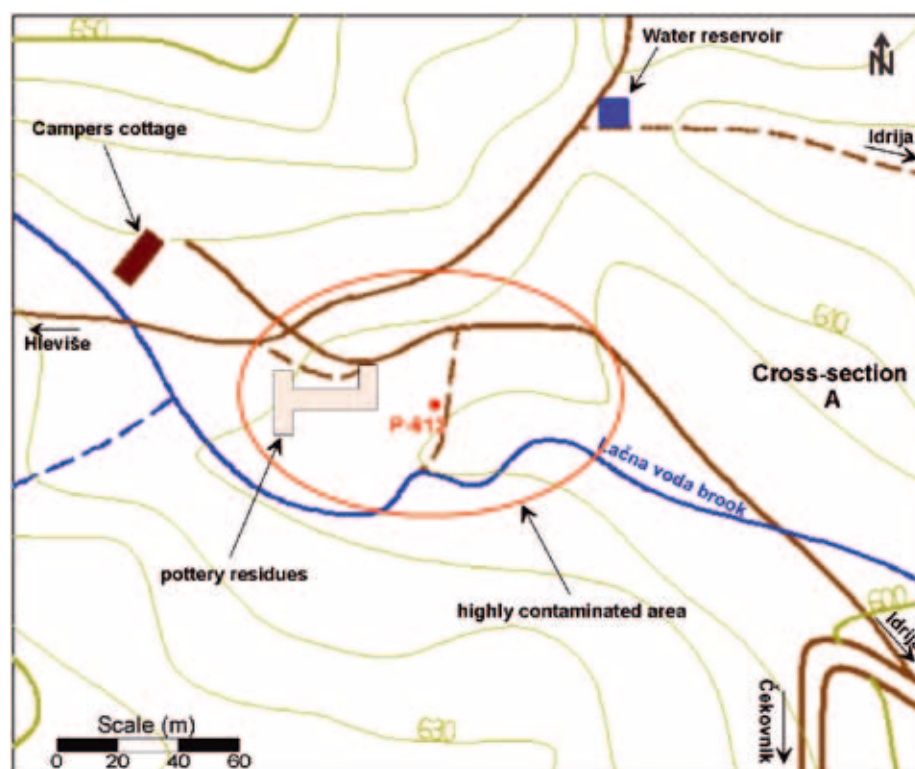


Fig. 3. Roasting site Pšenk with the location of sampling point P-612 and indicated area where pottery fragments were found in large quantities and area of highly increased mercury contents in soils and SOM.

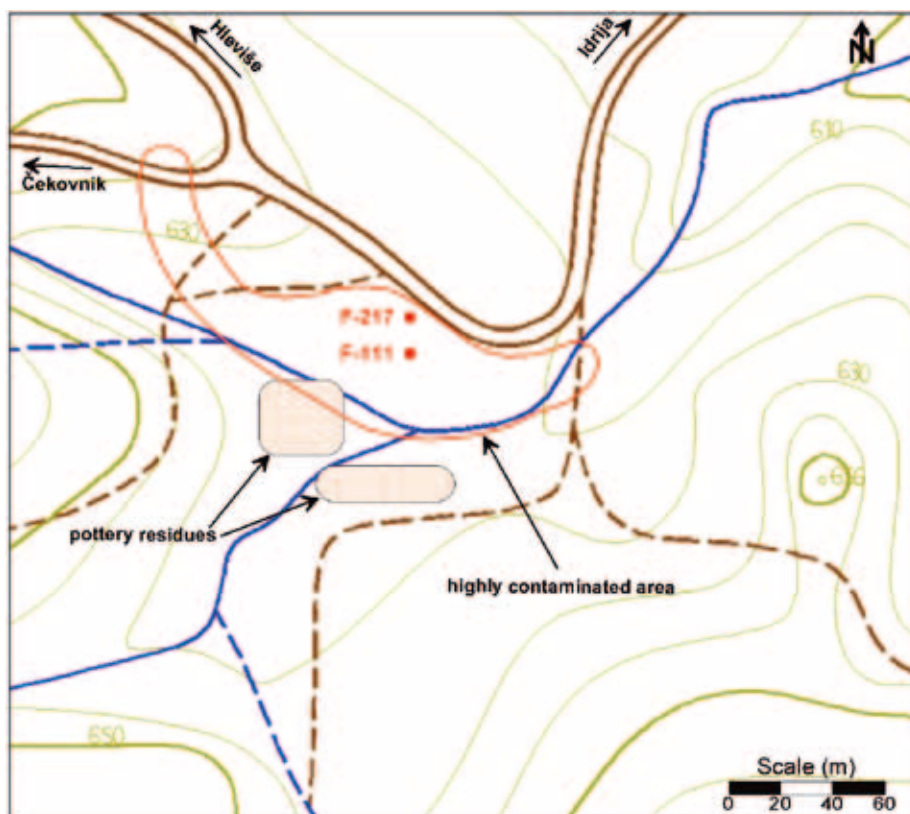


Fig. 4. Roasting site Frbežene trate with the location of sampling points F-111 and F-217, indicated area where pottery fragments were found in large quantities and area of highly increased mercury contents in soils and SOM.

Results

Roasting vessels fragments

Analysis of burned pottery fragments revealed the presence of abundant HgS coatings on the surface of ceramics, forming either crust-like aggregates on matrix (Figs. 5a, d) or isolated grains (Figs. 5e, f). In aggregates we could observe as well flat and smooth surfaces with good expressed and sharp edges as also more round-shaped and corroded surfaces (Figs. 5a, c). In parts HgS coatings are covering the large surfaces of the ceramics and in parts small dispersed HgS particles dominate (Fig. 5c). In places HgS grains are covered with clay coatings (Fig. 5b). Some well-shaped grains with indicated structure and the size of up to 200 μm could also be observed (Figs. 5e, f). The grains are captured or covered by the matrix ceramics material, with interesting surfaces showing traces of corrosion or perhaps dissolution. Solid HgS exists in two common forms, red cinnabar and black metacinnabar. Cinnabar is the thermodynamically stable form at low temperature; however, the presence of impurities (especially zinc, iron and selenium) impedes the conversion of metacinnabar to cinnabar by decreasing the inversion temperature and by retarding the kinetics of conversion (BARNETT et al., 1997). We believe that most of well-shaped grains with indicated structure are probably cinnabar particles (macroscopically red), while others HgS coatings could also present metacinnabar (macroscopically black). It is likely that both forms of HgS are present; at the roasting process commonly both compounds were formed (KAVČIČ, 2008). In the case there was not enough oxygen present, the recurrent reaction ran

between mercury and sulphur vapours and black amorphous mercury sulphide was formed as coatings on the walls and bottom of condensers.

Soil and SOM samples

The SEM/EDS study revealed that the sampled soil material consisted mainly of different clay minerals, K-feldspars, micas, Al-, Fe- and Mg- oxides and quartz grains. Individual small grains of zircon and rutile could also be found in soil samples. In SOM mainly clay minerals and abundant organic material were identified (Figs. 7a, b). Cinnabar was the only optically recognized Hg-bearing mineral. It was present as powder-like concentrations scattered in soil samples, frequently coating silicate and quartz crystals and clay-minerals (Fig. 6c). Also many individual grains could be observed in soil samples, either separately lying in soil substrate or incorporated in soil aggregates from less than 1 μm to 20 μm and more in size (Figs. 6a, b, 7e, f). Some well-shaped HgS grains with indicated structure could be recognized which are most probably cinnabar grains (Figs. 6d, 7c, d). In SOM individual HgS grains were up to 5 μm big, often encircled and coated with clay minerals or organic matter (Fig. 7b). Presence of clay minerals and Fe-oxyhydroxides suggested relatively favourable conditions for Hg adsorption to the mineral surfaces. The close association to the clay grains is the most common occurrence of HgS. Although the EDS analysis indicated a mercury-sulphur association in number of particles in the soil, these elemental relationships, although consistent with the presence of HgS, are not a definitive evidence of cys-

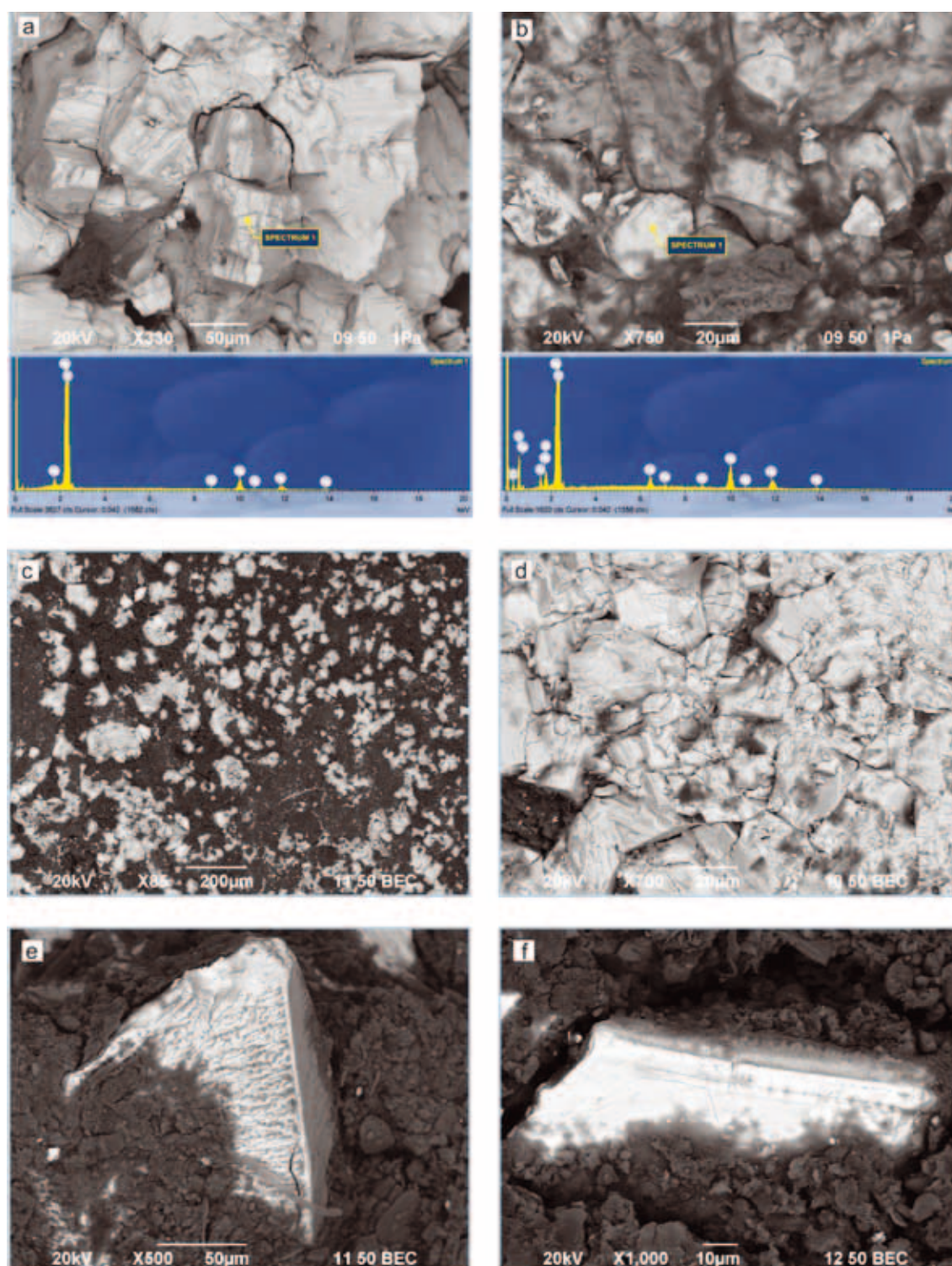


Fig. 5. SEM backscatter images of particles of roasting vessels fragments with EDS spectrums which indicate the chemical composition. (a, d) aggregates of HgS; (b) clay coatings covering HgS aggregates; (c) HgS grains scattered in ceramics matrix; (e, f) SEM backscatter images of some well-shaped HgS grains with indicated structure and the size of up to 200 µm.

talline HgS because a variety of mercury–sulphur associations are possible in soil (e.g., mercury sorbed to a sulphur-containing phases) (BARNETT et al., 1997).

Discussion

Backscatter SEM study of the studied samples revealed an obvious visual presence of mercury-bearing particles in all samples, especially in roas-

ting vessels fragments. Semi-quantitative SEM analyses of individual HgS grains from our samples indicate abundant cinnabar with possible presence of metacinnabar. Figures 5 to 7 illustrate the diversity of the mercury-bearing particles with a range of HgS morphologies, from anhedral to spherical. Several angular monomineralic grains could be observed, although they were normally found embedded within clay mineral agglomeration encased by thin clay coatings or rarely attached to other

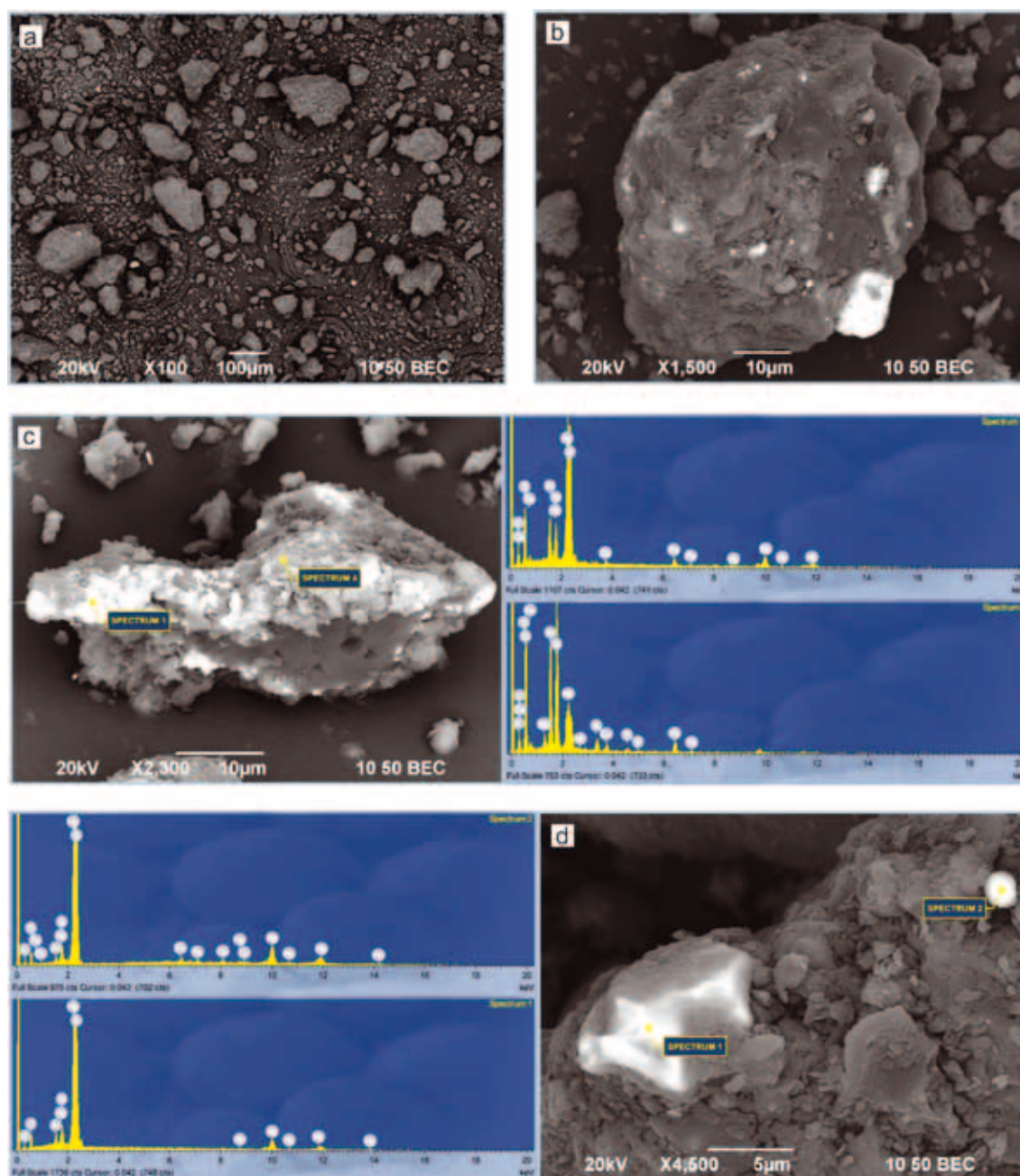


Fig. 6. SEM backscatter images of mercury-bearing particles (bright) in soil samples. (a) low magnification of a soil sample F-111 (5–20 cm) showing bright particles incorporated in soil grains and several isolated HgS particles; (b) soil grain of a soil sample P-612 (20–30 cm) coated with small HgS particles (c) image of a soil grain (sample F-111) with bright coatings; EDS spectrums of bright coatings (HgS) and soil grain composition (Si, Al, Fe). (d) well-shaped HgS grain (left) and spherical Hg-bearing particle; EDS spectrums indicate that both are HgS.

(quartz) grains. Monomineralic cinnabar grains, armoured multigrain agglomerations, and clay-coated particles were present in all soil and SOM samples. Polycrystalline, mercury- and sulphur-rich particles comprising silica, clay minerals and Al-, Fe- and Mg-oxides that were also observed in the samples could be interpreted as soil aggregates infiltrated by mercuric and sulphur vapours and by liquid mercury spilled during roasting, whereas cinnabar was most probably introduced via careless transport, stockpiling, and loading of roasting vessels during the old days of the roasting sites; in addition, cinnabar particles in soil are probably also due to the inefficient and incomplete roasting process and to the discarding of burned roasting vessels with HgS coatings at the sites.

Mercuric sulphide was found to be the main mercury compound present in the samples; cinnabar is the thermodynamically stable form at low temperatures and reducing conditions. Moreover, HgS is kinetically resistant to oxidation, and once formed, HgS may remain in soils even under oxidizing conditions (BERNAUS et al., 2005). Metacinnabar, a less stable polymorph form of cinnabar was reported to be the main component in slag samples of the Almadén mercury mine in Spain (BERNAUS et al., 2005), which was explained by the high working temperatures of the mineral processing for Hg extraction. These high temperatures enhance the structural conversion of HgS, which, in addition, is stabilised by the presence of impurities, especially zinc, iron and selenium that

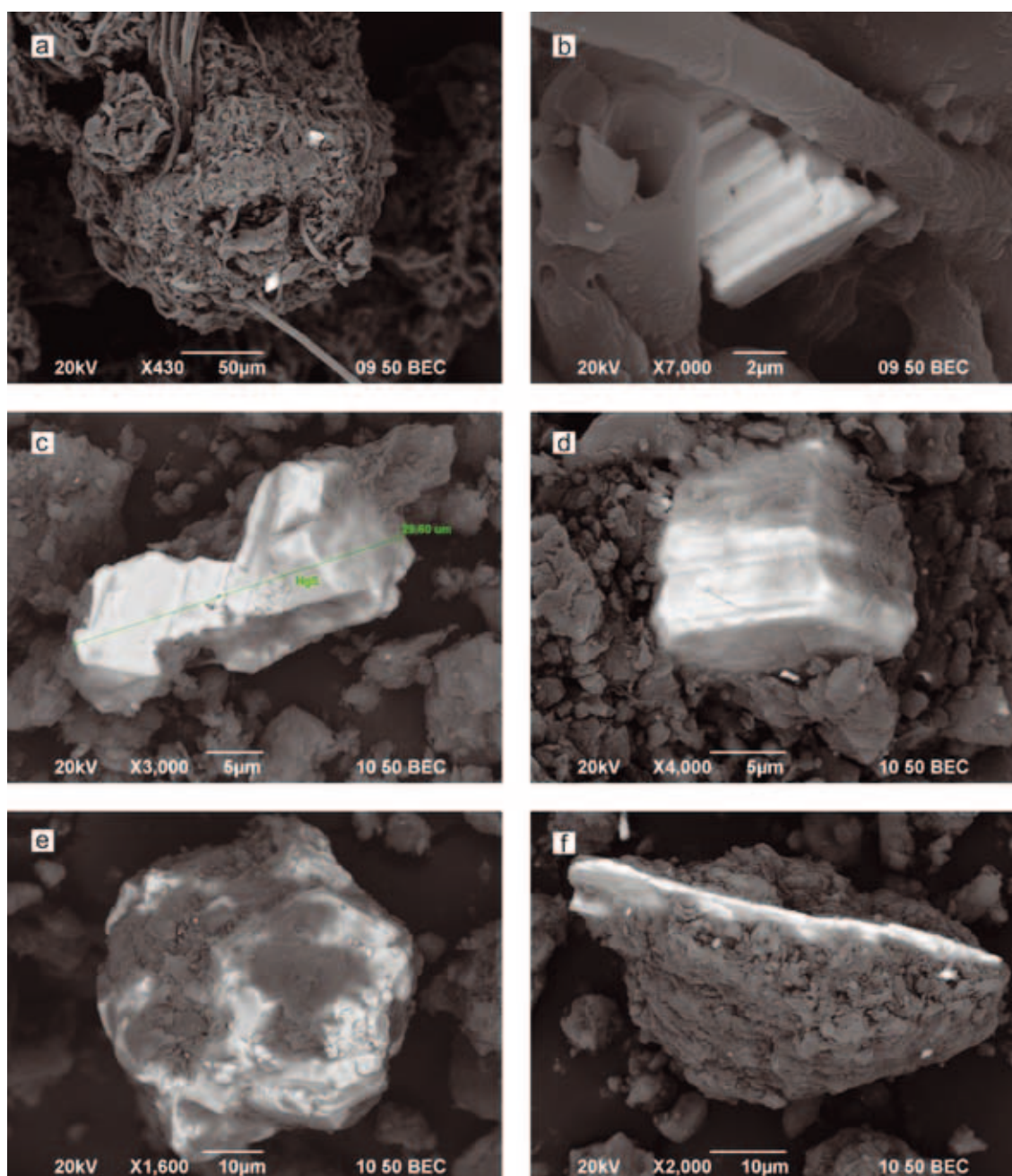


Fig. 7. SEM backscatter images of SOM sample from P-612 (a, b) and soil samples from F-217 (c, d, e, f). (a) HgS grains incorporated in SOM aggregate. (b) HgS grain in SOM sample surrounded with organic material. (c) individual well-shaped HgS grain, separately lying in soil substrate. (d, e) HgS grains with thin clay coatings. (f) Hg-bearing particle incorporated or encircled with clay minerals.

hinders the conversion of metacinnabar to cinnabar by decreasing the inversion temperature and by retarding the kinetics of conversion (BARNETT et al., 1997). Because byproduct Hg compounds are a minor component of the roasting residues, these compounds are often difficult to identify. However, previous studies using edge-extended X-ray absorption fine structure analysis have identified several oxides, chlorides, oxichlorides, and sulphates (KIM et al., 2000) in various calcine samples, and many of these Hg compounds are water-soluble.

Analyses of mercury contaminated environmental media using SEM/EDS or similar methods were applied also at mercury mining area in Almadén. Ore, slag and soil samples collected at

the entrance and exit of the oven and within the mine surroundings (BERNAUS et al., 2005) as well as resuspended airborne particles (PM) extracted from mine waste, retort site soil, and urban car park dust (MORENO et al., 2005) were investigated. The study of BERNAUS et al. (2005) which was supplemented by a synchrotron-based spectroscopic technique, revealed cinnabar as the main mercury compound in ore and soil samples, while metacinnabar was the main component in slag samples. Backscatter SEM analysis of Hg-rich dust samples (MORENO et al., 2005) showed abundant mercury-bearing particles, similar in shape and size to those from our soil samples. Mostly, cinnabar (and possibly metacinnabar) was recognized, but also native Hg and the chlorine phase egglestonite

($\text{Hg}_6\text{Cl}_3\text{O}(\text{OH})$) could be observed. HgS particles were found as monomineralic grains, frequently coated with clay minerals or embedded within clay mineral agglomerations or attached to calcite particles. Soil samples with high Hg content ($> 5000 \text{ mg/kg}$) from Almadenejos metallurgical precinct were investigated also with TEM-EDX (HIGUERAS et al., 2003). The study showed that mercury was present in the form of detrital cinnabar particles, adsorbed to the surface of chlorite grains. Scanning electron microscopy-energy-dispersive X-ray spectroscopy and electron probe microanalysis of Hg contaminated soils and mine waste in the Valle del Azogue mining area (an abandoned Sb-Hg mineral deposit) revealed that in contaminated soils and mine wastes, the predominant Hg species was cinnabar, whereas in calcines and tailings the dominant species was metallic Hg (NAVARRO et al., 2006). Cinnabar was found to be associated with Sb and As secondary minerals, while metallic Hg particles were found filling voids or coating silicate crystals. The presence of powder-like cinnabar associated with Fe oxides and hydroxides, resulting from the oxidation of pyrite was explained to be the result of supergene alteration of pyrite. By the use of SEM/EDS it was confirmed that cinnabar was a secondary phase, precipitated after the alteration of a Hg-bearing pyrite (NAVARRO et al., 2006). In the continuation detailed SEM/EDS study of the mine waste samples showed the presence of primary and secondary cinnabar associated with barite and pyrite and several small particles that might be associated to calomel (Hg_2Cl_2) and kuzminite ($\text{Hg}_2(\text{Br},\text{Cl})_2$) (NAVARRO et al., 2009).

The use of TEM (transmission electron microscope) and SEM with energy- and wavelength X-ray dispersive spectroscopy (EDS/WDS) in analysis of mercury-contaminated soil from the flood plain of East Fork Poplar Creek in Oak Ridge, Tennessee (BARNETT et al., 1997), revealed the presence of submicron, crystalline mercuric sulphide in the form of metacinnabar. Tremendous quantities of elemental mercury were released to the creek during 1950s and 1960s. In addition to many different sequential extractions procedures, which already suggested that mercury in the flood plain soils had been converted to mercuric sulphide, with this technique the presence of crystalline HgS was unequivocally identified. HgS grains occurred mostly associated to clay grains, but also some isolated HgS grains were identified, which produced much better EDS spectra (BARNETT et al., 1997). Our observations of soil samples from Pšenk and Frbežene trate showed quite similar appearance of HgS particles, although much more isolated and bigger grains were identified in our study and also the signal of grains incorporated in soil aggregates was much better, suggesting the existence of HgS. These differences are due to different origin of mercury in soils; in our case cinnabar particles were introduced to soils, so we can observe many primary particles, weathered and changed through time. Because elemental mercury was most probably also introduced to soils

at the time of roasting, it is possible that similar processes studied in the research of BARNETT et al. (1997) would lead to conversion of metallic Hg in our soils to HgS.

Conclusions

Regarding our observations of soil samples and comparison to other investigations of mercury-contaminated environmental media using SEM/EDS, the combination of SEM images and EDS spectrums indicates a mercury-sulfur association in majority of particles in the investigated media, which are most probably cinnabar (macroscopic red) or metacinnabar (macroscopic black). A number of very small HgS particles without well-expressed structure incorporated in soil aggregates and covered by thin clay coatings, suggest a possible presence of mercury-sulphur associations other than HgS. However, a detailed SEM/EDS study and others more sophisticated Hg speciation studies are needed to determine the phase chemistry.

Acknowledgments

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