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Characterisation of heavy metal-bearing phases in stream sediments of the Meža River Valley, Slovenia, by means of SEM/EDS analysis

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Abstract. Stream sediment reflects the rock structure of the catchment area, its geochemical characteristics and possible recent contamination upstream of the sampling point and thus, it is most frequently used in geochemical researches of heavy metal pollution. Stream sediment samples were collected along the Meža River and its tributaries and the Drava River, located in the NNE part of Slovenia. Previous geochemical studies have shown that these sediments are heavily polluted with heavy metals as a consequence of past mining of Pb-Zn ore and steelworks activities. Conventional geochemical analyses (ICP-MS, AAS, etc.) provided limited information on mineralogy, morphology and sources of heavy metal-bearing phases therefore SEM/EDS was utilized. Several problems were confronted with during EDS analysis, which are related to identification and quantification of light elements, identification of elements due to peak overlaps and quantification of spectra from unpolished samples. These problems were successfully dealt with. SEM/EDS enabled successful identification of heavy metal-bearing phases in stream sediments. Ore mineral phases, such as cerussite, sphalerite, smithsonite and galena, different heavy metal-bearing Fe-alloys, Fe-oxides and spherical particles and common rock-forming and accessory mineral phases, such as barite, rutile, ilmenite, zircon and monazite, were identified using solely SEM/EDS. These results were used for subsequent geochemical interpretation and source apportionment of heavy metals, according to associations of different heavy metal-bearing phases. Heavy metal-bearing phases were arranged by their source and genesis into three groups, denoted as geogenic/technogenic, technogenic and geogenic.

1. Introduction

An attempt to employ scanning electron microscopy energy-dispersive X-ray spectrometry (SEM/EDS) as an independent analytical method for identification and source apportionment of heavy metal-bearing phases in stream sediments is presented on the case of the Meža River, its tributaries and the Drava River (NNE part of Slovenia). Previous geochemical studies have shown that sediments in these streams are heavily polluted with heavy metals as a consequence of past mining of Pb-Zn ore and steelworks activities [1-4]. Problems related to EDS data acquisition and data interpretation are discussed in this study.

Conventional geochemical bulk sample analyses (ICP-MS, AAS, etc.) provide limited information on mineralogy of heavy metal-bearing phases [5], therefore SEM/EDS was utilized for the assessment of mineral phases and morphology of heavy metal-bearing phases, which enabled differentiation

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between geogenic/technogenic, technogenic and geogenic sources of heavy metals.

Stream sediment reflects the rock structure of the catchment area, its geochemical characteristics and possible recent contamination upstream of the sampling point and consists of rock fragments, organic matter and mineral grains, which are temporarily suspended on a stream bed [6]. Heavy metal-bearing particles in stream sediments can arise from many natural sources, but most abundantly from anthropogenic sources. Mineralogy and geochemistry of these particles depends on the original ore mineralogy and on processes that have occurred in the source areas during transport and deposition and during post-depositional early diagenesis [7].

2. Materials and methods

Most polluted stream sediments of the Meža River with its tributaries and the Drava River were studied. Morphological and qualitative X-ray microanalyses were carried out on particulate stream sediment samples. Air-dried and sieved (< 0.063 mm) sediments were mounted on carbon tape and coated with gold. Heavy metal-bearing phases were localised and identified in BSE mode using Jeol JSM 6490LV SEM coupled with Oxford Inca Energy EDS. Accelerating voltage 20 kV and working distance 10 mm, recommended by [8, 9], were chosen since some analysed grains were very small and contained, besides heavy metals, also light elements (C and O), which are important for mineral identification. Semi-quantitative point analysis and elemental mapping were performed on polished, carbon-coated samples embedded in araldite resin with acquisition times 60 s and 300 s, respectively. Elements in spectra were automatically identified using the Inca Energy software *Auto peak ID* function [8, 9]. However, most critical and overlapping peaks were also manually checked. In the case of possible overlap between Mo $L\alpha$ and S $K\alpha$, the presence of Mo $K\alpha$ was checked by increasing the AV to 30 kV [10]. Atomic proportions of constituent elements were calculated from atomic %, acquired by semi-quantitative X-ray microanalysis, and thus approximate empirical mineral formulas were constructed. Empirical formulas were compared to theoretical general chemical formulas of minerals, suggested by mineral database [11], and on basis of best fit of formulas, mineral phases were assessed. X-ray spectra were optimized for quantification using Co optimisation standard and the correction of EDS data was performed on the basis of the standard ZAF-correction procedure included in the Inca Energy software[®] [8].

3. Results and discussion

Heavy metal-bearing phases were identified by their chemical composition, based solely on the EDS analysis. Forms and quantities of identified heavy metal-bearing phases depend on the prevailing natural or anthropogenic processes in the sampling area. Individual heavy metal-bearing phases were classified into three groups according to their source and genesis that were defined on basis of their morphology, mineral and/or chemical composition. Each of these groups is characterized by a particular association of heavy metal-bearing phases. The first group is characterised by ore mineral phases, the second group by heavy metal-bearing phases, which could not be recognized as minerals and the third group, consisting of accessory and common rock-forming minerals. Most of minerals, belonging to the first and the third group, are sub-rounded and angular fragments of ore, accessory and rock-forming minerals with relatively simple chemical composition. Heavy metal-bearing phases from the second group are compositionally complex [12] non-stoichiometric compounds of heavy metals and thus they could not be recognized as minerals. These phases are morphologically represented mostly by rounded spherically shaped and sharp-edged angular particles.

Heavy metal-bearing phases are classified into groups as follows:

- **First group** of heavy metal-bearing phases is characterized by ore minerals: cerussite ($PbCO_3$) (figure 1), sphalerite (ZnS) (figure 2), smithsonite ($ZnCO_3$) (figure 3), galena (PbS), wulfenite ($PbMoO_4$) (figure 4), descloizite ($PbZn(VO_4)(OH)$), bindheimite ($Pb_2Sb_2O_6(O, OH)$), pyromorphite ($Pb_5(PO_4)_3Cl$) and strontianite ($SrCO_3$). Cerussite and sphalerite are the most abundant Pb- and Zn-bearing mineral forms that occur mostly associated with dolomite or as individual grains. The surfaces of cerussite and smithsonite and sometimes also sphalerite grains are often strongly

corroded. Galena and wulfenite usually appear very seldom and mostly as individual grains. Small amounts of Cd, which usually occurs as trace element in Pb and Zn ore minerals of the Mežica ore deposit [13], were detected in sphalerite and smithsonite grains. Descloizite and bindheimite usually occur in their original crystal forms. Descloizite crystals are commonly associated with smithsonite, calcite and Fe-oxy-hydroxides and bindheimite mostly occurs in the form of individual octahedral crystals. Pyromorphite and strontianite are minor mineral phases that occur in lower quantities. Abundance and grain size of ore minerals is shown in table 1.

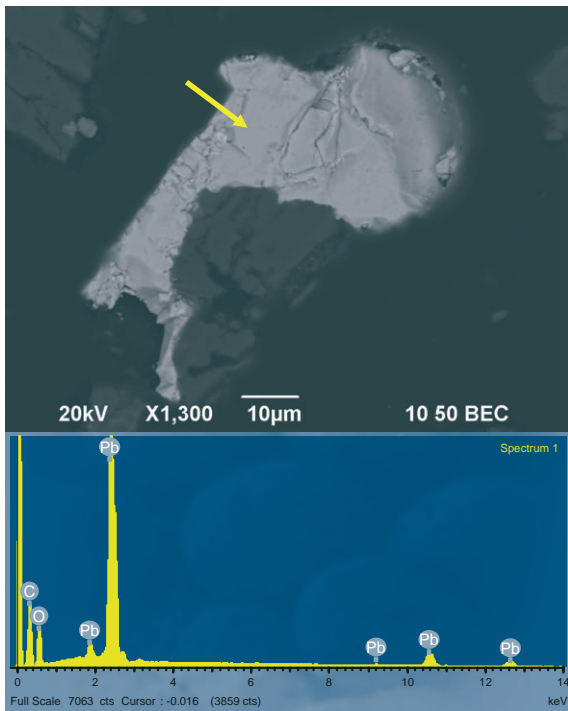


Figure 1. Polished section of cerussite.

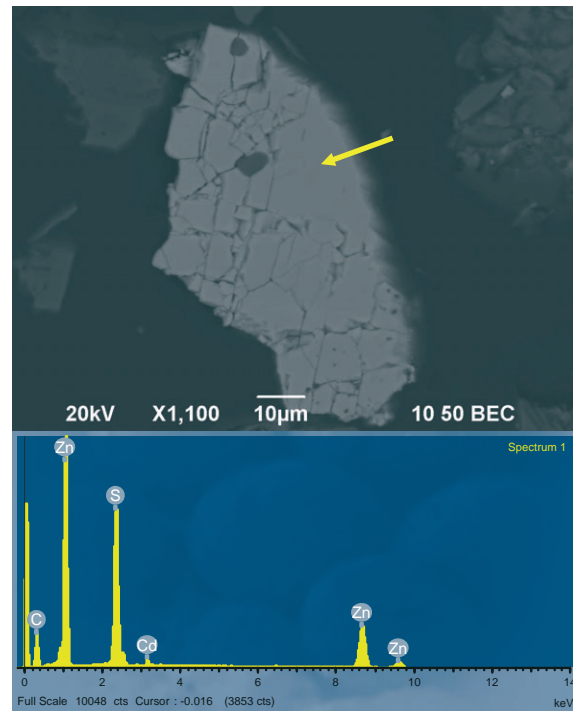


Figure 2. Polished section of sphalerite with Cd.

- **Second group** of heavy metal-bearing phases is represented mostly by: Fe-oxides ((Cr, V, Fe)-oxide, (Mo, W, V, Cr, Fe)-oxide (figure 5), (Mo, W)-oxide, (W, Cr, Fe)-oxide), Fe-alloys ((Cr, Ni, Fe)-alloy, (Cu, Ni, Fe)-alloy (figure 6), (Ni, Mo, Fe)-alloy and (Fe, Si)-alloy) and spherical particles ((Cr, Ni)-oxide or chromium-nickel-spinel, (Cr, Fe)-oxide or chromium-spinel (figure 7)). The most abundant are Fe-oxides that occur as individual grains, followed by spherical (Cr, Fe)-oxides, which are composed of dendritically shaped crystals of (Cr, V, Fe)-oxide, overgrown with Fe-oxide. Abundance and grain size of these phases is shown in table 1.
- **Third group** of heavy metal-bearing phases consists of accessory and common rock-forming minerals: barite (BaSO_4), rutile (TiO_2) (figure 8), zircon (ZrSiO_4) (figure 9), ilmenite (FeTiO_3), monazite ((Ce, La, Nd) PO_4) (figure 8), xenotime (YPO_4) (figure 10), chalcopyrite (CuFeS_2) and sphene (CaTiSiO_5). Zircon and monazite were found associated with K-feldspars, quartz and biotite, but individual grains were also found. Zircon and rutile appear euhedral and usually retain their original crystal form. Chalcopyrite was found associated with pyroxenes or amphiboles and sphene. Xenotime was found associated with K-feldspars or micas. Quantity of each mineral depends on the lithological composition of bedrock in the sampling point. Abundance and grain size of accessory and common rock-forming minerals is shown in table 1.

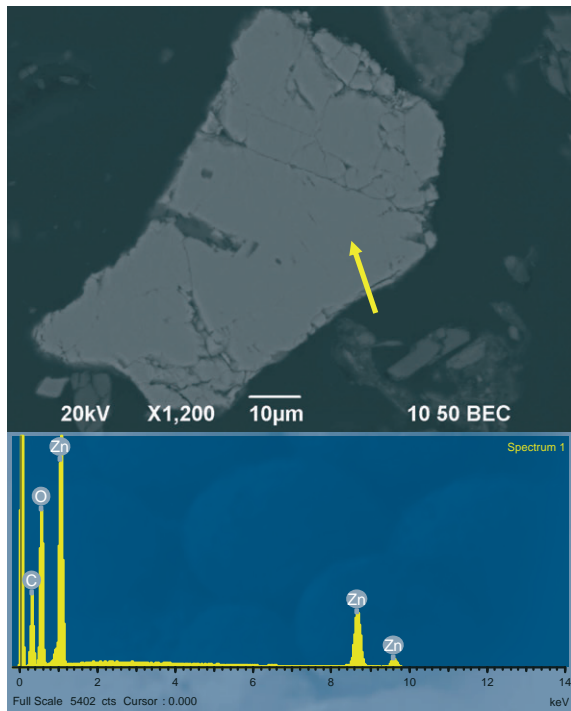


Figure 3. Polished section of smithsonite.

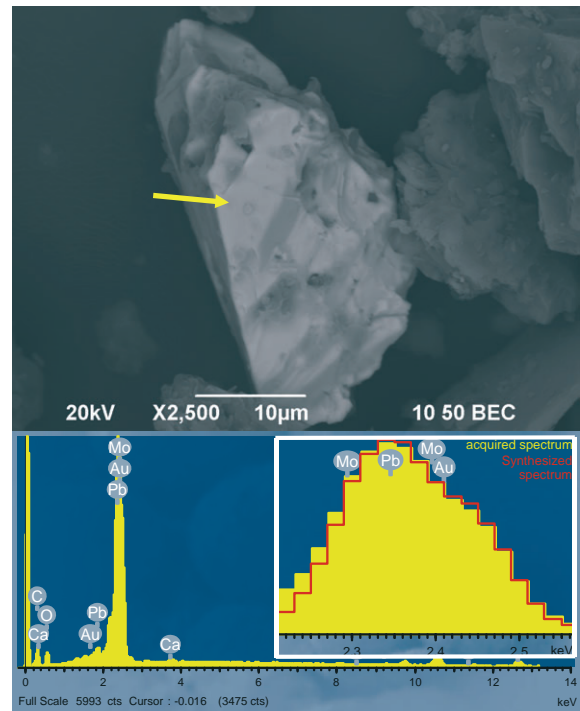


Figure 4. Wulfenite grain. Spectrum detail shows fit between acquired (yellow) and synthesized spectrum (red line).

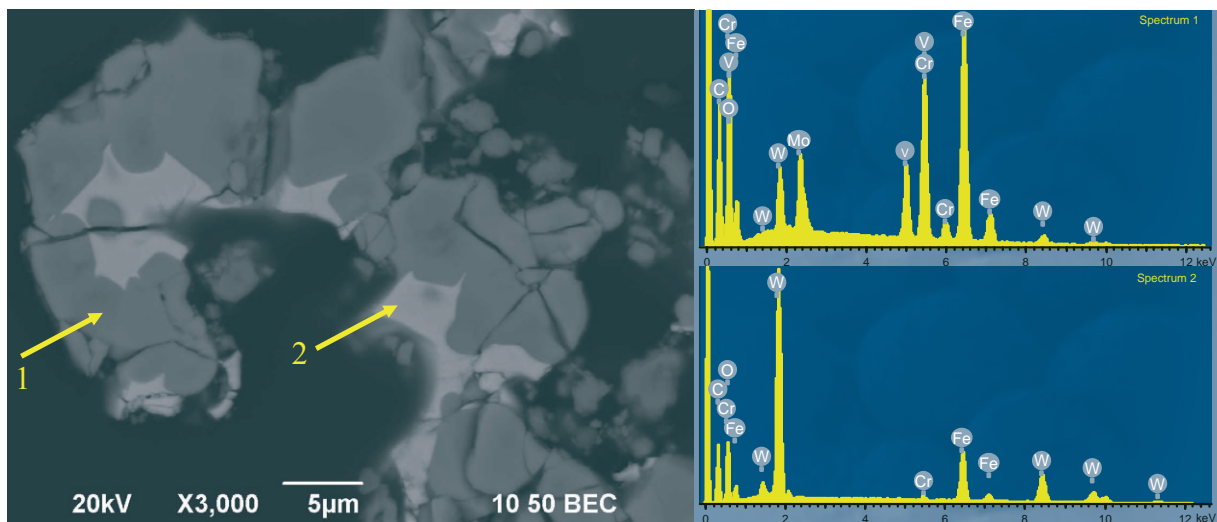


Figure 5. Polished section of (Mo, W, V, Cr, Fe)-oxide (1 – spectrum 1) and (W, Cr, Fe)-oxide (2 - spectrum 2).

Table 1. Abundance and grain size of studied heavy metal-bearing phases.

Heavy metal-bearing phase	Abundance (%)	Grain size (μm)		
		Min.	Max.	Mean
galena	4.5	13.7	93.0	55.4
cerussite	20.6	2.9	163.8	58.3
sphalerite	20.6	6.4	119.4	52.4
smithsonite	11.0	3.8	120.8	71.3
wulfenite	0.6	38.8	48.5	43.7
descloizite	0.9	3.0	24.0	9.9
bindheimite	1.2	4.5	77.4	29.7
pyromorphite	0.3	4.8	4.8	4.8
strontianite	0.3	31.5	31.5	31.5
(Cr, Ni, Fe)-alloy	1.5	1.8	50.9	26.1
(Cu, Ni, Fe)-alloy	0.3	56.3	56.3	56.3
(Ni, Mo, Fe)-alloy	0.3	16.8	16.8	16.8
(Fe, Si)-alloy	1.2	77.4	110.4	94.7
(Cr, V, Fe)-oxide	1.8	38.6	122.9	73.8
(Mo, W, V, Cr, Fe)-oxide	1.8	36.8	120.5	77.8
(Mo, W)-oxide	0.3	9.7	9.7	9.7
(W, Cr, Fe)-oxide	1.2	0.6	70.4	11.1
(Cr, Ni)-oxide (spinel)	2.4	1.6	65.6	10.9
(Cr, Fe)-oxide (spinel)	4.8	4.9	65.9	48.5
barite	2.7	92.0	20.2	55.2
rutile	3.3	1.7	133.4	30.1
ilmenite	6.6	2.0	121.0	53.3
sphene	2.1	2.5	104.5	54.6
zircon	4.5	2.0	152.4	64.1
chalcopyrite	0.3	11.1	11.1	11.1
monazite	4.8	1.5	47.8	15.5
xenotime	0.3	26.8	26.8	26.8

Although ore, accessory and common rock-forming minerals are relatively simple compounds of heavy metals and light elements (C, O, H), the basic problem occurs in identification and quantification of light elements due to absorption of their X-rays by heavy metals. Only problems with identification of ore, accessory and common rock-forming minerals are discussed here.

Since most of these mineral phases were identified on basis of semi-quantitative X-ray analyses of carbon-coated polished sections, carbon could not be quantified. Some of minerals were recognized only in gold-coated particulate samples on basis of qualitative X-ray data. In minerals that were only qualitatively analysed, oxygen was not quantified so their identification was based on atomic ratios between cations.

In cases of carbon and oxygen containing Pb- and Zn-bearing ore minerals, only atomic ratios of heavy metals versus oxygen were calculated. The ratio between Zn and O corresponds best only to smithsonite and the ratio between Pb and O agrees well with cerussite [11]. It also needs to be considered that quantification of light elements (C, O) using EDS is very difficult

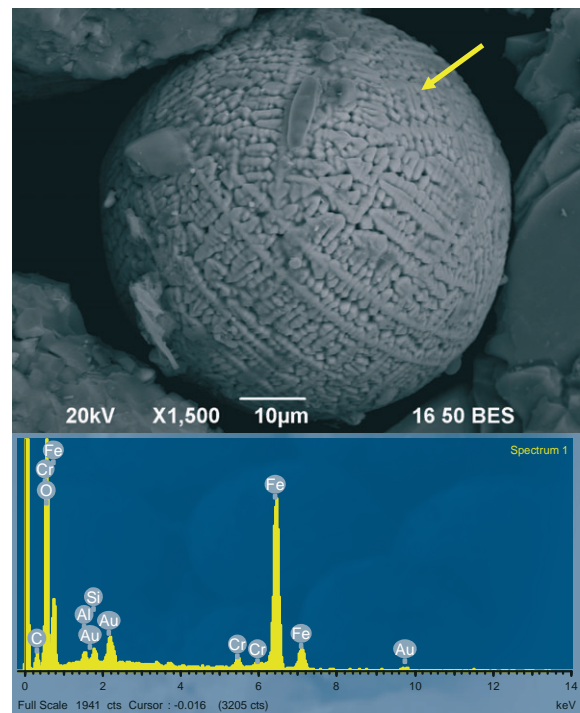
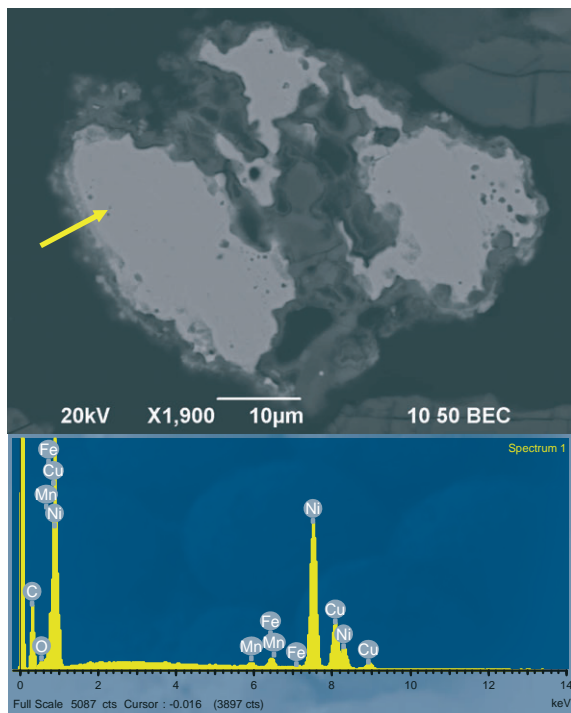


Figure 6. Polished section of (Cu, Ni, Fe)-alloy. **Figure 7.** Spherical particle of (Cr, Fe)-oxide.

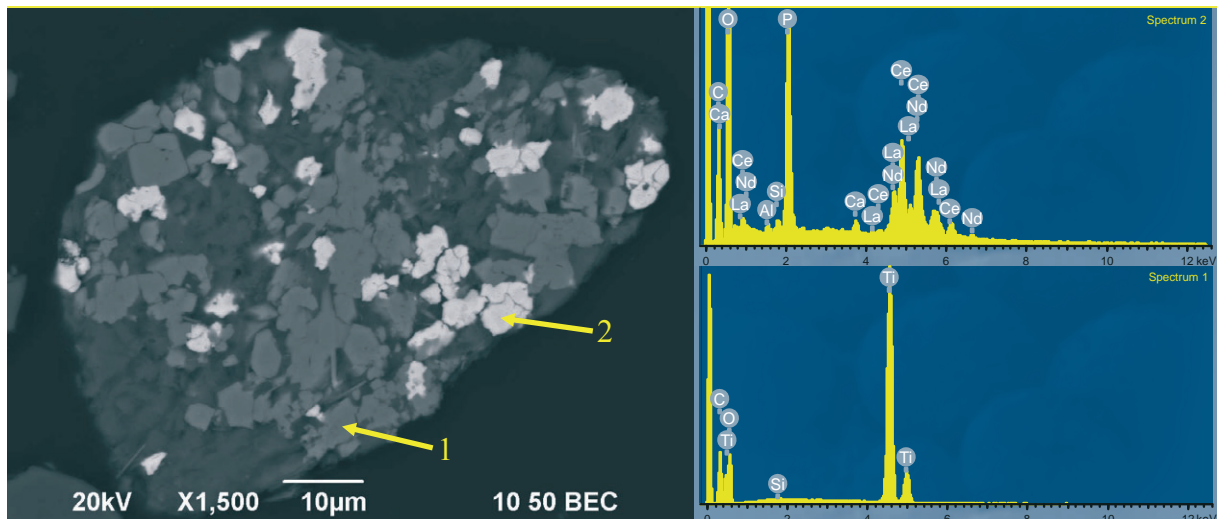


Figure 8. Polished section of polymineral grain: rutile (1 – spectrum 1) and monazite (2 – spectrum 2).

and could be misleading, especially when applied to compounds of heavy metals and light elements. In spectrum of Pb-bearing sulphide, Pb $L\alpha$ line was quantified to avoid Pb $M\alpha$ and S $K\alpha$ overlap problems and the analysis showed composition consistent with mineral galena. Spectra of Pb- and Zn-bearing sulphide minerals sometimes show oxygen peaks, which was interpreted as a consequence of incomplete oxidation of sulphides, based on the fact that their formulas do not agree stoichiometrically with any of the Pb- and Zn-bearing sulphates. A problem with overlapping peaks

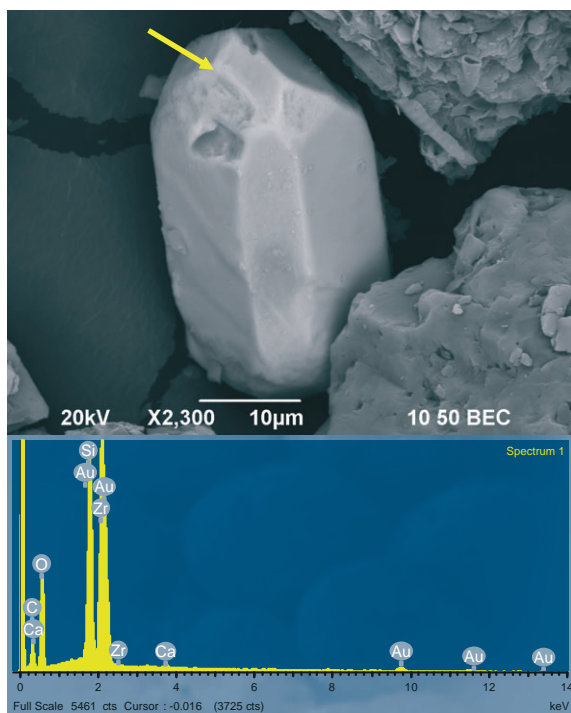


Figure 9. Zircon crystal.

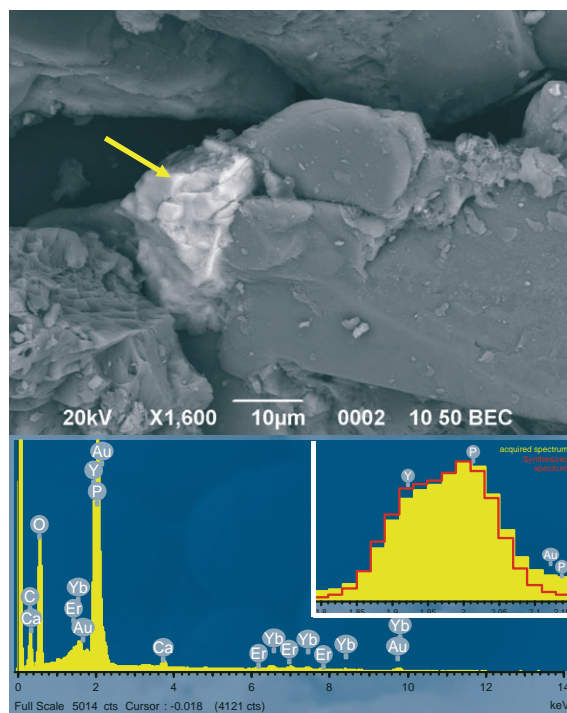


Figure 10. Xenotime in K-feldspar or muscovite. Spectrum detail shows fit between acquired (yellow) and synthesized spectrum (red line).

between Pb, Mo and S is obvious in the case of Pb-molybdate (wulfenite) (figure 4) and Pb-sulphate (anglesite), which are both present in the Mežica ore deposit. There is no difference in atomic ratios between Mo and O in wulfenite and S and O in anglesite. However, the wulfenite spectrum showed good correlation with the synthesized spectrum of Pb-molybdate (figure 4) [8]. The test of presence of Mo K α peaks showed no Mo K α peaks in other sulphur containing Pb-bearing minerals. (Pb, Zn, V)- and (Pb, Sb)-containing phases, interpreted as (Pb, Zn)-vanadate hydroxide (descloizite) and (Pb, Sb)-oxy-hydroxide (bindheimite), respectively, were recognized on basis of atomic ratios between constituent cations, their crystal structure and the fact that no other minerals containing such element combinations were found in mineral database [11]. Small grains of Pb-phosphate were identified in particulate samples. Small grain size caused electron beam to overlap onto adjacent phases. Nevertheless, by considering beam overlaps, the atomic ratios of Pb, P and Cl, calculated from qualitative X-ray analysis, corresponded to pyromorphite stoichiometry.

Identification of accessory and common rock-forming minerals was based on the results of qualitative and semi-quantitative analyses. Semi-quantitative analysis of Ba-sulphate showed good correlation with barite stoichiometry. In the spectrum of Ba-sulphate, a distinctive Sr peak was identified, which was interpreted as a result of substitution of Ba ions with Sr in the Ba-sulphate crystal lattice. Zircon and ilmenite were identified on basis of atomic ratios between Zr and Si and Fe and Ti, obtained by qualitative X-ray analysis, which are 1:1. Identification of Ti-oxide, based upon qualitative EDS analysis, is more complicated, since it consists of only one cation and no reliable atomic ratios between Ti and O can be calculated. Fortunately, most of Ti-oxide grains retained their crystal structure, which indicated that Ti-oxide could be recognised as rutile or possibly anatase.

Semi-quantitative composition of Ce-phosphate corresponded to two possible mineral series; monazite and rhabdophane. However, Ce was clearly predominant over La and Nd, respectively, therefore, Ce-monazite was chosen. In the case of Y-phosphate there is a possible overlap between

Y $L\alpha$ and P $K\alpha$. For this reason, the acquired spectrum was compared to synthesized spectrum of Y-phosphate [8]. The comparison showed relatively good correlation between both spectra (figure 10). Analysed Y-phosphate also contains rare earth elements (Yb and Dy), which are characteristic elements of Yb-xenotime. Semi-quantitative analysis of (Cu, Fe)-sulphide and atomic ratios between Cu, Fe and S showed perfect match with chalcopyrite stoichiometry [11]. Chalcopyrite was found associated with sphene. Due to beam overlap with adjacent mineral sphene, small peaks of Ca and Ti are present in the chalcopyrite spectrum. Sphene was identified by the typical association of constituent elements (Ca, Ti and Si) and their atomic ratios, which generally agree with sphene stoichiometry.

Based on information about morphology, mineral and/or chemical composition obtained by the SEM/EDS analysis, the three groups of heavy metal-bearing phase associations were denoted, according to their source and genesis, as geogenic/technogenic, technogenic and geogenic, respectively. Geogenic/technogenic heavy metal-bearing mineral phases are interpreted as those ore minerals than can originate from Pb-Zn poor ore waste deposits and separation tailings (technogenic source) and from natural weathering of ore outcrops (geogenic source). Technogenic heavy metal-bearing phases are characterized by complex chemical composition and distinctive morphology, especially spherical shape, which indicate that they derive from high-temperature technogenic processes in iron- and steel-based metallurgical industry [12, 14]. Associations of geogenic heavy metal-bearing accessory and common rock-forming mineral phases are compositionally relatively simple minerals with mostly preserved crystal structure whose origin is natural weathering of metamorphic and carbonate bedrock.

4. Conclusions

Combination of SEM and EDS proved to be very useful as independent analytical method for identification of heavy metal-bearing phases in stream sediments and their characterisation according to their source and genesis.

Basic problems in EDS analyses of heavy metal-bearing mineral phases occur in: (a) identification and quantification of light elements in compounds with heavy metals due to absorption of their X-rays by heavy metals, (b) distinction of some of heavy metal-bearing minerals due to peak overlaps caused by the closeness of X-ray lines of constituent elements, which are within the energy resolution of the EDS, and (c) quantification of X-ray spectra, obtained from unpolished samples. Electron beam overlaps due to small grain size also need to be considered. These problems were more or less successfully solved and heavy metal-bearing mineral phases were successfully identified.

Heavy metal-bearing phases in investigated stream sediments of the Meža River, its tributaries and the Drava River were successfully identified and characterized according to their source and genesis by means of SEM/EDS. Heavy metal-bearing phases were apportioned to three groups, geogenic/technogenic, technogenic and geogenic, respectively, which are characterized by different associations of heavy metal-bearing phases.

SEM/EDS thus provides invaluable information on mineralogy and morphology of heavy metal-bearing phases, which are important for source apportionment and the assessment of stability, solubility and bioavailability of heavy metals from heavy metal-bearing phases.

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