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Accuracy and precision of EDS analysis for identification of metal-bearing minerals in polished and rough particle samples

Točnost in natančnost EDS analize pri prepoznavanju mineralov s kovinami v poliranih vzorcih in grobih delcih

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Abstract

The study was carried out in order to estimate reliability of EDS analysis for identification of various natural and anthropogenic metal-bearing phases in polished and rough particle samples of stream sediments. For this purpose, the accuracy and precision of EDS analysis were assessed. Results of the precision measurements showed that the overall relative standard deviation of EDS measurements was 8 % for polished samples and 24 % for rough particle samples and was within acceptable limits for most of major elements and some of the elements present in minor or trace contents in the analysed metal-bearing phases. The random analytical fluctuations were considered negligible and phase compositions could be determined with sufficient reliability in individual grains of each phase. The overall average relative error for all elements amounted to about 12 %, which was within acceptable limits for accuracy in EDS analysis of polished samples. Chemical formulae and identification of mineral species of metal-bearing phases were thus calculated from atomic ratios between constituent elements with sufficient accuracy. A comparison between EDS measurements in polished and rough particle samples using the Welch's t-test showed that about 38 % of studied metal-bearing phases could be identified with sufficient reliability by EDS analysis of rough particle samples. The results of this study demonstrated that elemental composition of metal-bearing phases in polished and rough particle samples was mostly determined with sufficient precision and accuracy using EDS analyses.

Izvleček

Raziskava je bila izvedena z namenom oceniti zanesljivost EDS analize pri identifikaciji raznovrstnih naravnih in antropogenih fazah s kovinami v poliranih vzorcih in vzorcih grobih delcev rečnih sedimentov. V ta namen sta bili ocenjeni točnost in natančnost EDS analize. Rezultati meritev natančnosti so pokazali, da je celotni relativni standardni odklon EDS meritev znašal 8 % za polirane vzorce in 24 % za grobe delce ter je bil znotraj sprejemljivih meja za večino glavnih elementov in nekatere sledne elemente v analiziranih fazah. Naključna analitična nihanja so bila zanemarljiva, tako da je bilo možno z zadostno zanesljivostjo določiti sestavo faz v posameznih kristalnih zrnih. Celotna povprečna relativna napaka za vse elemente je znašala okrog 12 %, kar je bilo znotraj sprejemljivih meja točnosti EDS analize poliranih vzorcev. Kemijske formule in identifikacija mineralnih vrst faz s kovinami so bile z zadovoljivo točnostjo preračunane iz atomskih razmerij med sestavnimi elementi. Primerjava EDS meritev v poliranih vzorcih in grobih delcih z uporabo Welch-evega t-testa je pokazala, da je bilo okrog 38 % faz s kovinami identificiranih z zadostno zanesljivostjo iz analize grobih delcev. Rezultati raziskave so pokazali, da je bila elementarna sestava faz s kovinami v poliranih vzorcih in grobih delcih določena z ustrezno natančnostjo in točnostjo z uporabo EDS analize.

Introduction

In environmental geochemistry, analysed samples or metal-bearing phases are frequently very diverse and may be natural or anthropogenic by origin. This results in limited pre-knowledge of the sample's elemental composition and its identity and thus difficult selection of suitable standards for quantitative EDS analysis. Because suitable standards of natural minerals are often not available for all analysed metal-bearing phases, pre-measured universal fitted standards included in the EDS software are commonly used instead.

Samples of environmental media that are commonly used in environmental geochemistry are usually so friable that their surface morphologies, important for their characterisation, are destroyed during preparation of polished sections. In these cases, samples with rough, randomly oriented surfaces are analysed, which may introduce severe spectral artifacts and interferences due to significant X-ray absorption and fluorescence effects and consequently affects quantification of elements and identification of their mineral species.

Usefulness of fitted-standards EDS analysis for identification and characterisation of minerals in stony meteorites by their stoichiometry calculated from atomic ratios of constituent elements was demonstrated in a study of mineral composition of chondritic meteorite (Miler et al., 2009). Obtained results were the main motive to perform similar study on genetically various metal-bearing phases in stream sediments, which is presented in this paper. The aim of this study was to estimate reliability of EDS analysis for identification of various natural and anthropogenic metal-bearing phases in polished and rough particle samples of stream sediments. The estimation of reliability of EDS analysis was based on assessing (a) precision of EDS analysis of elemental composition in polished and rough particle samples, (b) accuracy of EDS analysis of elemental composition in polished samples and (c) agreement between EDS measurements of constituent elements in polished and rough particle samples. Partial results of the study presented in this paper were also included as a chapter in PhD thesis "Application of SEM/EDS to environmental mineralogy and geochemistry" (Miler, 2012).

Materials and methods

Sample preparation

Stream sediments, collected at different locations along the Meža River and its tributaries and the Drava River in 2005 (Fux, 2007; Fux & Gosar, 2007), were used for this study. Stream sediments were air dried and sieved to a fraction smaller than 0.063 mm, which was considered the most suitable for SEM/EDS analysis, due to its grain size. Polished-sections of individual metal-bearing phases were prepared for EDS analysis by embedding sediments in araldite resin, followed by fine polishing using a diamond suspension fluid and coating with carbon for conductivity (Miler, 2012). Rough particle samples were prepared by mounting sediment particles on a double-sided carbon tape and coating them with a thin layer of gold for conductivity instead of carbon (Miler, 2012) to obtain more detailed morphological features of the particle surface. Gold coating, however, introduces Au characteristic lines and reduces intensities of some light element peaks due to absorption of their characteristic X-rays and may thus influence the EDS analysis.

SEM/EDS analysis

SEM/EDS analysis was carried out in a high vacuum using a JEOL JSM 6490LV scanning electron microscope (SEM) coupled with an Oxford INCA energy dispersive spectroscopy (EDS) system, comprising Oxford INCA PentaFETx3 Si(Li) detector and INCA Energy 350 processing software, at 20 kV accelerating voltage, spot size 50 and 10 mm working distance (Miler, 2012). Each analysed metal-bearing phase was characterised by its chemical composition measured by the EDS point analysis with acquisition times of 30 s for polished samples and 60 s for rough particle samples. Longer times for rough particle samples were chosen in order to improve signal-to-noise ratios and assure sufficient signal for quantification of minor elements (Reed, 2005). Mineral species of 16 analysed metal-bearing phases were assessed by calculating stoichiometric ratios from atomic % of constituent elements, acquired by the EDS analysis (Gonzalez et al., 2007; Vanek et al., 2008), and comparison with atomic proportions of constituent elements in known stoichiometric minerals, obtained from mineral databases (Anthony et al., 2009; Barthelmy, 2010). The software was calibrated for quantification using pre-measured universal standards included in the EDS software, which is a basic standardisation procedure in fitted-standards EDS analysis (Goldstein et al., 2003), referenced to a Co optimisation standard. The correction of EDS data was performed on the basis of the standard ZAF-correction procedure included in the INCA Energy software (Oxford Instruments, 2006).

Precision

Precisions of EDS analyses of rough particle and polished samples were assessed for constituent elements in 16 different metal-bearing phases. The upper precision threshold level for EDS analysis of polished samples was set at ≤ 12 % relative, which is in accordance with accepted precision levels for fitted standards EDS analysis (Statham, 2002). Since no reported data on precision levels for EDS analysis of rough particle samples were found, the precision threshold level was adapted from the accepted precision for standardless EDS analysis (Statham, 2002) and was arbitrarily set at ≤ 30 % relative. EDS data sets consisted of 20 replicate measurements made at random locations on each metal-bearing grain. The precisions of EDS measurements of element contents in metal-bearing phases were expressed as Relative Standard Deviations (RSD):

$$RSD\ (\%) = \left(\frac{\sigma^{at}}{X_{av}}\right) \cdot 100\%$$

where σ^{at} is standard deviation of replicate measurements (in at%), X_{av} is mean content of constituent element (in at%).

Compositional homogeneity

Compositional homogeneity of metal-bearing phases in polished sections was assessed by determining scatter in intensity (number of counts) of spectrum peaks of constituent elements, not corrected for background, obtained by analyses of random points on a metal-bearing phase. The level of homogeneity was expressed as (Goldstein et al., 2003):

$$Homogeneity\ (\%) = \frac{3 \cdot \sqrt{\overline{N}}}{\overline{N}} \cdot 100\%$$

where $\overline{N}$ is mean uncorrected intensity (number of counts) in spectrum peaks of constituent elements.

Criterion for homogeneity is that the scatter in number of counts should be within limits of $\overline{N} \pm 3 \cdot \sqrt{\overline{N}}$ (Goldstein et al., 2003; Reed, 2005).

Accuracy

Theoretical accuracy for EDS analysis of metal-bearing phases was also assessed. The upper accuracy threshold level for EDS analysis of metal-bearing phases in polished samples was set at ≤ 25 % relative to the composition of fitted standards, which is in accordance with the accepted accuracy for standardless quantitative analysis of flat-polished bulk samples using fitted standards procedures (Newbury, 1998; Goldstein et al., 2003). EDS measurements were carried out at 20 random locations on surface of each grain. Accuracy of EDS analysis of element contents in metal-bearing phases were estimated by calculation of relative error:

$$Relative\ error\ (\%) = \frac{|X_{av} - X_{st}|}{X_{st}} \cdot 100\%$$

where X_{av} is mean content of constituent element in analysed metal-bearing phase (in at%), X_{st} is content of constituent element in known stoichiometric mineral (in at%).

Comparison of mean element contents in polished and rough particle samples (Welch's t-test)

Mean element contents in metal-bearing phases in polished and rough particle samples were compared using Welch's t-test at the 95 % confidence level, since the population variances and number of measurements were mostly unequal in both samples. The following equation was used:

$$t = \frac{\overline{X}_1 - \overline{X}_2}{S_{\overline{X}_1 - \overline{X}_2}}$$

where

$$S_{\overline{X}_1 - \overline{X}_2} = \sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}$$

Welch-Satterthwaite equation was used for the calculation of degrees of freedom (d.f.):

$$d.f. = \frac{\left(\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}\right)}{\frac{S_1^4}{n_1^2 \cdot (n_1 - 1)} + \frac{S_2^4}{n_2^2 \cdot (n_2 - 1)}}$$

Where $\overline{X}_1$ and $\overline{X}_2$ are mean element contents (in at%) in analysed metal-bearing phases in rough particle and polished samples, respectively, s_1^2 and s_2^2 are variances in rough particle and polished samples, respectively and n_1 and n_2 are number of measurements in rough particle and polished samples, respectively.

Results and discussion

Precision of EDS analyses of metal-bearing phases in polished and rough particle samples

The EDS microanalysis depends on several variable factors, such as the number of detected characteristic X-rays emitted from constituent elements in a sample and effects of spectral interferences and spectral background. These factors may vary from analysis to analysis. Other factors that also influence the analysis are related to sample preparation and elemental composition of the sample. Precision was determined in order to assess repeatability of measurements, thus taking into account all deviations that arise due to variations in compositional homogeneity of analysed phases and random nature of X-ray generation and emission. Precisions of EDS analyses of constituent element contents were calculated for different metal-bearing phases and are given in Table 1.

The precision measurements in polished samples showed that EDS relative standard deviations (RSD) were within acceptable limits for quantitative EDS analysis (< 12 %) for 85 % of all measured elements in 16 analysed phases, while they exceeded the upper limit value for 15 % of all elements. The average RSD amounted to 3 % for elements within acceptable limits and 34 % for elements that exceeded the upper limit value. The precision was in acceptable limits for all major constituent elements, while it exceeded the upper limit values for 73 % of minor or trace elements. The average RSD was thus 3 % for major constituent elements and 27.2 % for minor or trace elements. High RSD values for minor and trace elements were ascribed to inhomogeneous distribution of these elements throughout analysed phases.

Tab. 1. Elemental composition of 16 metal-bearing phases in rough particle and polished sediment samples coated with carbon, determined by EDS analysis; n - number of measurements on individual grains, (X_{av} (at%)) - mean elemental composition with standard deviation in atomic %, Acq. t. - spectrum acquisition time, Level of homogeneity (%) - level of compositional homogeneity of phases (lower values suggest higher degree of homogeneity), Peak intensity - intensity of X-ray lines. Upper values of precision threshold level were arbitrarily set at ≤ 12 % for polished and at ≤ 30 % for rough particle samples.

Tab. 1. Elementarna sestava 16 kovinskih faz v grobih delcih in poliranih vzorcih sedimentov naparjenih z ogljikom, določena z EDS analizo; n - število meritev na posameznih zrnih, (X_{av} (at%)) - aritmetična sredina elementarne sestave s standardnim odklonom v atomskih %, Acq. t. - čas zajema spektra, Level of homogeneity (%) - stopnja homogenosti sestave faz (nižje vrednosti pomenijo višjo stopnjo homogenosti), Peak intensity - intenziteta linij rtg-žarkov. Izbrana mejna vrednost natančnosti je ≤ 12 % za polirane vzorce in ≤ 30 % za grobe delce.

	Rough particle sample		**Polished sample**			
Element	**X_{av} (at%)**	**Precision (RSD %)**	**X_{av} (at%)**	**Precision (RSD %)**	**Level of homogeneity (%)**	**Peak intensity**
Ba-S-O	**n=8, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	74.08 ± 5.03	6.79	70.55 ± 0.95	1.35	7.57	1572.5
S	14.00 ± 2.29	16.39	15.23 ± 0.47	3.08	7.75	1498.4
Sr	0.28 ± 0.21	**73.52**	0.98 ± 0.11	11.26	20.62	211.7
Ba	11.63 ± 2.68	23.07	13.24 ± 0.58	4.37	8.59	1220.9
Ti-O	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	74.85 ± 5.68	7.59	72.06 ± 0.63	0.88	11.42	689.9
Ti	25.15 ± 5.68	22.58	27.94 ± 0.63	2.26	5.13	3423.0
Fe-Ti-O	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	78.04 ± 3.92	5.02	66.74 ± 0.68	1.02	10.28	851.2
Ti	11.53 ± 1.60	13.86	16.96 ± 0.35	2.09	7.16	1757.1
Mn	0.58 ± 0.39	**67.52**	0.90 ± 0.18	**20.59**	32.39	85.8
Fe	9.86 ± 2.40	24.38	15.40 ± 0.46	2.97	9.89	920.6
Ca-Ti-Si-O	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	72.58 ± 3.09	4.26	69.39 ± 0.74	1.07	7.68	1526.2
Al	0.67 ± 0.17	25.89	0.79 ± 0.11	**13.73**	15.92	355.1
Si	9.79 ± 0.96	9.85	11.13 ± 0.28	2.54	4.98	3623.6
Ca	8.64 ± 1.04	12.05	9.72 ± 0.29	2.96	5.56	2909.9
Ti	8.33 ± 1.34	16.11	8.97 ± 0.26	2.93	6.71	1996.5
Zr-Si-O	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	71.41 ± 2.48	3.47	71.05 ± 0.86	1.22	9.73	950.0
Si	13.92 ± 1.10	7.90	14.10 ± 0.44	3.09	5.97	2521.3
Zr	14.68 ± 1.45	9.88	14.85 ± 0.48	3.27	5.88	2599.5
Ce-P-O	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	71.61 ± 6.10	8.51	72.20 ± 0.60	0.83	7.74	1500.6
P	15.22 ± 2.84	18.63	15.58 ± 0.39	2.50	8.40	1274.8
La	3.77 ± 0.95	25.28	3.12 ± 0.18	5.85	16.81	318.5
Ce	6.98 ± 1.78	25.55	6.39 ± 0.29	4.54	12.80	549.5
Nd	2.12 ± 0.63	29.59	2.38 ± 0.22	9.33	14.11	451.9
Th	0.30 ± 0.32	**104.63**	0.38 ± 0.39	**101.84**	25.65	136.8
Pb-(C)-O	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	85.88 ± 2.73	3.17	78.63 ± 0.68	0.86	13.18	517.8
Pb	14.13 ± 2.73	19.30	21.37 ± 0.68	3.17	21.42	196.2
Zn-S	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
S	54.28 ± 2.27	4.19	52.91 ± 0.68	1.29	5.26	3252.9
Zn	45.52 ± 2.44	5.37	46.65 ± 0.67	1.45	10.47	821.2
Cd	0.20 ± 0.42	**211.93**	0.44 ± 0.24	**55.25**	30.37	97.6
Zn-(C)-O	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	82.08 ± 2.63	3.21	74.40 ± 0.67	0.90	7.55	1579.8
Zn	17.92 ± 2.63	14.69	25.60 ± 0.67	2.61	12.39	586.4

Tab. 1 (continued)

	Rough particle sample		Polished sample			
Element	**X_{av} (at%)**	**Precision (RSD %)**	**X_{av} (at%)**	**Precision (RSD %)**	**Level of homogeneity (%)**	**Peak intensity**
Fe-S	**n=8, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
S	68.57 ± 3.06	4.46	68.83 ± 0.28	0.41	3.70	6561.9
Fe	31.43 ± 3.06	9.73	31.17 ± 0.28	0.90	8.07	1383.5
Pb-Mo-O	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	83.01 ± 4.49	5.41	71.72 ± 1.39	1.94	13.59	487.6
Mo	9.19 ± 2.46	26.71	14.97 ± 0.80	5.33	5.71	2757.2
Pb	7.80 ± 2.07	26.50	13.31 ± 0.67	5.05	24.45	150.6
Pb-Zn-V-O	**n=6, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	76.68 ± 3.59	4.68	61.88 ± 3.45	5.58	13.79	473.4
V	7.53 ± 1.21	16.10	12.53 ± 1.19	9.50	12.23	601.5
Zn	7.38 ± 1.54	20.82	12.76 ± 1.37	10.74	19.56	235.4
Pb	8.42 ± 1.51	17.96	12.84 ± 1.00	7.76	26.18	131.3
Zn-Si-O	**n=8, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	73.13 ± 5.84	7.99	64.91 ± 0.67	1.03	7.79	1484.3
Si	10.45 ± 1.43	13.65	12.16 ± 0.16	1.35	9.21	1060.0
Zn	16.42 ± 4.52	27.54	22.93 ± 0.64	2.79	11.85	641.3
Pb-S	**n=7, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
S	55.70 ± 1.38	2.47	54.27 ± 0.58	1.07	4.83	3850.6
Pb	44.30 ± 1.38	3.10	45.73 ± 0.58	1.27	18.53	262.1
Fe-Si	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
Si	33.85 ± 1.92	5.66	27.20 ± 0.45	1.64	7.98	1413.9
Fe	66.15 ± 1.92	2.90	72.80 ± 0.45	0.61	6.10	2417.5
Fe-O (Pb,Zn)	**n=10, Acq. t.=60 s**		**n=20, Acq. t.=30 s**			
O	73.19 ± 5.93	8.11	71.43 ± 2.81	3.94	6.05	2459.5
Si	2.64 ± 1.15	**43.74**	0.92 ± 0.20	**21.27**	23.04	169.6
Ca	1.31 ± 0.61	**46.09**	0.38 ± 0.08	**20.01**	30.39	97.5
Fe	19.84 ± 4.25	21.41	26.23 ± 2.61	9.95	7.38	1654.0
Zn	1.77 ± 1.22	**69.31**	0.53 ± 0.13	**23.71**	54.96	29.8
Pb	1.27 ± 0.77	**60.87**	0.50 ± 0.08	**16.76**	71.11	17.8

values exceeding upper limits are in bold

However, since minor and trace elements produce low intensity spectral lines, their RSD values may also result from poor counting statistics. The lowest average RSD values calculated for all constituent elements in each individual phase were obtained for Fe-S, Fe-Si, Pb-S, Ti-O and Zn-Si-O, and the highest for trace element containing Ce-P-O, Zn-S and Fe-O (Pb,Zn), in which the RSD upper limit value of 12 % was exceeded. The RSD values for all measured elements ranged from 0.4 % to 101.8 %, with an average of 8 %, which was well within the acceptable limits.

Precision was also calculated for elements in 16 phases identified in rough particle samples (Table 1). The RSD values were below the upper limit value for EDS analysis of rough particle samples, set at 30 %, for 85 % of all measured elements in all analysed phases, while they exceeded the upper limit value for 15 % of all elements. The precision was within acceptable limits for all major constituent elements, while it exceeded the upper limit values for 73 % of elements present in phases in minor or trace contents. These results were in good agreement with those of EDS analysis of polished samples. The average RSD for major constituent elements in these phases was 12.2 %, which is well below the upper limit value for EDS analysis of rough particle samples. However, the average RSD for minor and trace constituent elements was 68.9 %. The lowest average RSD values for all constituent elements were calculated for Pb-S, Fe-Si, Zr-Si-O, Fe-S and Zn-(C)-O, while they exceeded the upper limit value of 30 % in phases containing trace elements, such as Ce-P-O, Zn-S and Fe-O (Pb,Zn). The RSD values for all elements including major, minor and trace elements ranged from 2.5 % to 211.9 %, with an average of 24 %.

Most of RSD values for minor and trace elements exceeded the upper limit values in both polished and rough particle samples. The exceptions were Sr in Ba-S-O, for which RSD upper limit was exceeded in rough particle samples, and Al in Ca-Ti-Si-O, where RSD limit for Al was exceeded in polished samples.

RSD values were generally much higher and much more variable in rough particle samples than RSD for elements in polished samples. The main reason for such differences in RSD values are geometry effects, arising during rough particle EDS analysis due to surface morphology and orientation of particle surfaces. Comparison between ratios of RSD values for individual phases in rough particle and polished samples showed greatest differences for Zn-Si-O, Ti-O and Fe-S, while the best correspondence was observed for Ce-P-O, Pb-Zn-V-O and also Pb-S, Fe-O (Pb,Zn), Zr-Si-O and Ca-Ti-Si-O.

Precision measurements thus showed that the overall repeatability of EDS analyses of polished and rough particle samples, under applied analytical conditions, was within acceptable limits for all major elements and smaller part of the elements present in minor or trace contents in analysed metal-bearing phases. This indicated that the random analytical fluctuations were mostly negligible and that composition of phases could be determined with sufficient reliability in individual grains of each phase.

Compositional homogeneity of metal-bearing phases in polished samples

Compositional homogeneity provides information on the degree of element distribution in an analysed phase. Homogeneity of chemical composition of analysed metal-bearing phases affects the repeatability of EDS analysis. For this reason, homogeneity of analysed grains in polished samples was assessed. Calculated levels of compositional homogeneity (in %) of different metal-bearing phases are given in Table 1.

Levels of compositional homogeneity ranged between 3.7 % and 71 % with an average value of 14.3 %, which considerably exceeded the desired homogeneity level of < 1 %, according to Goldstein et al. (2003). The results of the homogeneity test were generally in agreement with precision RSD values for elements in different phases, however these relations seemed to be more complicated in more complex phases, especially those containing minor and trace elements, which is mostly due to low number of counts in spectrum peaks and consequently higher counting errors. Less complex metal-bearing phases, such as Fe-S, Fe-Si and Zr-Si-O exhibited the most homogeneous compositions, while Fe-O (Pb,Zn) was the least homogeneous phase, primarily on the account of minor and trace elements. The calculated average level of homogeneity for major constituent elements was about 10 % and for minor and trace elements 30.5 %. This could suggest that elements present in a phase in minor or trace contents are generally distributed more heterogeneously than major constituent elements. However, the calculated level of homogeneity for minor and trace elements could also be ascribed to low intensities of their spectra and counting errors. Zn and Pb were the most common elements that occurred either as major constituents or as minor and trace elements. The average level of homogeneity for Zn and Pb when they occurred as major elements was 18 %, but when they were present in minor contents, the homogeneity level was above 63 %. There were also some exceptions. The distributions of Pb and Zn in Pb-Zn-V-O, Pb-C-O, Pb-Mo-O and Pb-S were inhomogeneous despite the fact that Pb and Zn occurred as major elements.

Where precision and homogeneity coincided, repeatability of measurements depended on the distribution of constituent elements. In 8 phases (Ba-S-O, Pb-C-O, Zn-S, Zn-C-O, Fe-S, Zn-Si-O, Pb-S and Fe-Si) distributions of constituent elements agreed with calculated RSD values, while in 4 phases (Ti-O, Zr-Si-O, Pb-Mo-O and Pb-Zn-V-O) the repeatability of measurements could not be explained by compositional homogeneity. Since determination of compositional homogeneity is based on measuring the intensities of uncorrected element peaks, it is directly subjected to various factors related to spectra acquisition conditions. The result of homogeneity test thus depended, besides on distribution of constituent elements, also on the quantity of contaminant gases, adsorbed on the surface of the phase, ratio between the volume of the analysed phase and the electron beam interaction area, on signal variations and instrumental factors and also intensity of spectral lines. The latter usually occurred due to changes in SEM/EDS operating conditions, such as the intensity of electron beam and drift of the sample position.

Mineral composition of metal-bearing phases and accuracy of their identification

Because suitable standards of natural minerals were not available, the accuracy was used to define the degree of concordance between elemental compositions of analysed individual metal-bearing phases with corresponding stoichiometric mineral species obtained from mineral databases (Anthony et al., 2009; Barthelmy, 2010).

Accuracies were obtained by comparing elemental composition of measured phases to the elemental composition of corresponding minerals. Elemental compositions of most common metal-bearing phases and their possible corresponding mineral analogues and relative errors of EDS analysis of constituent element contents are given in Table 2.

The EDS relative errors were within acceptable limits (< 25 %) for 90 % of all measured elements in 16 analysed phases and exceeded the upper limit value for 10 % of all elements. The average relative error for elements within acceptable limits was 8.6 % and 45.1 % for elements above the limit, which are values presented in bold in Table 2. The overall average relative error for all elements in all phases, relative to the underlined mineral analogues in Table 2, ranged from 0.2 % to 69.2 % and amounted to 12.3 %, which was within acceptable limits for accuracy in quantitative EDS analysis. The calculated overall relative error was relatively high mostly because some of analysed metal-bearing phases contained minor and trace elements, whose contents are usually extremely variable and may substitute for major constituent elements in analysed phases and their mineral analogues. Furthermore, contents of

Tab. 2 Comparison between elemental composition of metal-bearing phases in carbon-coated polished sediment samples and elemental composition of corresponding stoichiometric minerals; (X_{av} (at%)) - mean elemental composition of 20 measurements in atomic %, (X_{st} (at%)) - elemental composition of stoichiometric mineral, (Rel. err. (%)) - relative error in %; (+) - positive values, (-) - negative values. Elemental composition of stoichiometric minerals, except those marked with *, was obtained from mineral databases (Anthony et al., 2009; Barthelmy, 2010) and recalculated to atomic %, considering only elements that were also identified in analysed phases. Upper value of accuracy threshold level was set at ≤ 25 %.

Tab. 2 Primerjava elementarne sestave kovinskih faz v poliranih vzorcih sedimentov naparjenih z ogljikom in elementarno sestavo možnih stehiometričnih mineralov; (X_{av} (at%)) - aritmetična sredina elementarne sestave 20 meritev v atomskih %, (X_{st} (at%)) - elementarna sestava stehiometričnega minerala v atomskih %, (Rel. err. (%)) - relativna napaka v %; (+) - pozitivne vrednosti, (-) - negativne vrednosti. Elementarna sestava stehiometričnih mineralov, razen tistih označenih z *, je bila povzeta iz podatkovnih baz mineralov (Anthony et al., 2009; Barthelmy, 2010) in preračunana v atomske %, glede na elemente določene v analiziranih fazah. Izbrana mejna vrednost točnosti je ≤ 25 %.

	Phase	**Stoichiometric mineral**		**Stoichiometric mineral**	
Element	**X_{av} (at%)**	**X_{st} (at%)**	**Rel. err. (%)**	**X_{st} (at%)**	**Rel. err. (%)**
	Ba-S-O	**Barite**			
O	70.55	66.66	5.83 (-)	n.d.	n.d.
S	15.23	16.67	8.66 (+)	n.d.	n.d.
Sr	0.98	n.d.	n.d.	n.d.	n.d.
Ba	13.24	16.67	20.54 (+)	n.d.	n.d.
Σ Ba,Sr	14.22	16.67	14.69 (+)	n.d.	n.d.
	Ti-O	**Rutile-anatase-brookite**			
O	72.06	66.68	8.08 (-)	n.d.	n.d.
Ti	27.94	33.32	16.16 (+)	n.d.	n.d.
	Fe-Ti-O	**Ilmenite**		**Pseudorutile**	
O	66.74	60.00	11.23 (-)	64.29	3.81 (-)
Ti	16.96	20.00	15.20 (+)	21.42	20.81 (+)
Mn	0.90	n.d.	n.d.	n.d.	n.d.
Fe	15.40	20.00	23.00 (+)	14.29	7.78 (-)
Σ Fe,Mn	16.30	20.00	18.51 (+)	14.29	14.06 (-)
	Ca-Ti-Si-O	**Sphene**			
O	69.39	62.82	10.45 (-)	n.d.	n.d.
Al	0.79	2.57	**69.21** (+)	n.d.	n.d.
Si	11.13	12.82	13.20 (+)	n.d.	n.d.
Ca	9.72	12.18	20.19 (+)	n.d.	n.d.
Ti	8.97	9.61	6.65 (+)	n.d.	n.d.
Σ Al,Ti	9.76	12.18	19.83 (+)	n.d.	n.d.
	Zr-Si-O	**Zircon**			
O	71.05	67.80	4.80 (-)	n.d.	n.d.
Si	14.10	16.95	16.80 (+)	n.d.	n.d.
Zr	14.85	15.25	2.66 (+)	n.d.	n.d.
	Ce-P-O	**Monazite**		**Rhabdophane**	
O	72.20	66.66	8.30 (-)	71.43	1.08 (-)
P	15.58	16.66	6.49 (+)	14.29	9.08 (+)
La	3.12	4.17	**25.24** (+)	3.57	12.78 (+)
Ce	6.39	8.34	23.37 (+)	10.72	**40.39** (+)
Nd	2.38	3.33	**28.73** (+)	n.d.	n.d.
Th	0.38	0.83	**54.54** (+)	n.d.	n.d.
Σ La,Ce,Nd,Th	12.26	16.67	**26.47** (+)	14.29	14.21 (+)
	Pb-(C)-O	**Cerussite**		**Hydrocerussite**	
O	78.63	75.00	4.85 (-)	72.72	8.12 (-)
Pb	21.37	25.00	14.54 (+)	27.28	21.66 (+)

Tab. 2 (continued)

	Phase	**Stoichiometric mineral**		**Stoichiometric mineral**	
Element	**X_{av} (at%)**	**X_{st} (at%)**	**Rel. err. (%)**	**X_{st} (at%)**	**Rel. err. (%)**
	Zn-S	**Sphalerite**			
S	52.91	51.29	3.16 (-)	n.d.	n.d.
Zn	46.65	48.71	4.23 (+)	n.d.	n.d.
Cd	0.44	n.d.	n.d.	n.d.	n.d.
Σ Zn,Cd	47.09	48.71	3.33 (+)	n.d.	n.d.
	Zn-(C)-O	**Smithsonite**		**Hydrozincite**	
O	74.40	75.00	0.81 (+)	70.59	5.39 (-)
Zn	25.60	25.00	2.43 (-)	29.41	12.94 (+)
	Fe-S	**Pyrite-marcasite**		**Pyrite***	
S	68.83	66.67	3.24 (-)	68.25	0.84 (-)
Fe	31.17	33.33	6.47 (+)	31.75	1.82 (+)
	Pb-Mo-O	**Wulfenite**			
O	71.72	66.66	7.59 (-)	n.d.	n.d.
Mo	14.97	16.67	10.20 (+)	n.d.	n.d.
Pb	13.31	16.67	20.16 (+)	n.d.	n.d.
	Zn-Si-O	**Hemimorphite**		**Willemite**	
O	64.91	62.50	3.85 (-)	57.15	13.58 (-)
Si	12.16	12.50	2.69 (+)	14.28	14.83 (+)
Zn	22.93	25.00	8.29 (+)	28.57	19.75 (+)
	Pb-Zn-V-O	**Descloizite**			
O	61.88	62.50	1.00 (+)	n.d.	n.d.
V	12.53	12.50	0.21 (-)	n.d.	n.d.
Zn	12.76	12.50	2.06 (-)	n.d.	n.d.
Pb	12.84	12.50	2.71 (-)	n.d.	n.d.
	Pb-S	**Galena**			
S	54.27	50.00	8.54 (-)	n.d.	n.d.
Pb	45.73	50.00	8.54 (+)	n.d.	n.d.
	Fe-Si	**Gupeiite**			
Si	27.20	25.00	8.80 (-)	n.d.	n.d.
Fe	72.80	75.00	2.93 (+)	n.d.	n.d.
	Fe-O (Pb,Zn)	**Goethite-lepidocrocite**		**Bernalite**	
O	71.43	66.67	7.14 (-)	75.00	4.76 (+)
Si	0.92	n.d.	n.d.	1.75	**47.54** (+)
Ca	0.38	n.d.	n.d.	n.d.	n.d.
Fe	26.23	33.33	21.30 (+)	22.25	17.90 (-)
Zn	0.53	n.d.	n.d.	0.50	6.55 (-)
Pb	0.50	n.d.	n.d.	0.50	0.24 (-)
Σ Fe,Zn,Pb	27.27	33.33	18.20 (+)	23.25	17.28 (-)

n.d. - not determined
*values of reference standards measured by EDS analysis
underlined data were used in calculation of average relative errors
values exceeding upper limits are in bold

some of these elements in certified minerals were not provided in mineral databases and thus they could not be included in calculation of relative errors. On the basis of their elemental composition, mineral species of all analysed metal-bearing phases were designated with sufficient accuracy. The relative error for those phases ranged from 1.5 % to 24.4 % with an average amounting to 10.3 %, which was within acceptable limits. The best results were obtained for Pb-Zn-V-O and Zn-C-O, while the highest relative errors were observed for more complex metal-bearing phases containing variable minor and trace elements, such as Ce-P-O and Ca-Ti-Si-O. Obtained results also showed that EDS analysis of polished samples provided data with sufficient accuracy for calculation of chemical formulae of metal-bearing minerals based on the atomic ratios between constituent elements but not their absolute contents. The atomic ratios between light elements and other constituent elements in most of analysed metal-bearing phases, however, were always somewhat higher than the ratios in corresponding stoichiometric minerals, although relative errors for light elements, especially O, were generally low and mostly well within the acceptable limits. Average relative errors calculated for light elements were biased negatively (Table 2), while they were positively biased for metals. This confirmed that measured contents of light elements were generally higher than those in stoichiometric minerals and measured contents of metals were mostly lower than in stoichiometric minerals. This was ascribed to the fact that quantification of light elements in EDS analysis is strongly subjected to matrix effects (Oxford Instruments, 2006). Thus, matrix corrections and consequently errors in quantification are always much greater for light elements.

Elemental composition and calculated relative errors for constituent elements in Ba-S-O showed good agreement with barite stoichiometry. High relative error was observed for Ba, which is most probably due to minor contents of Sr substituting for Ba in barite (Brower, 1973), forming a solid solution between barite and celestine. For this reason and since contents of Sr were not given for stoichiometric barite, the sum of Ba and Sr was also considered in calculation of relative error and mineral formula, which provided much better results. By chemical composition and calculated relative errors for constituent elements, Ti-O corresponded best to TiO_2 (Table 2), which has several natural mineral polymorphs: rutile, anatase and brookite and a few anthropogenic forms differing by their oxidation states and atomic coordination. These, however, could not be distinguished from each other merely on the basis of EDS analysis. According to its elemental composition, analysed Fe-Ti-O has two possible mineral analogues, ilmenite and pseudorutile. Based on calculated relative errors, Fe-Ti-O agreed better with pseudorutile, however the ratio between Ti and Fe showed good correspondence with ilmenite. Moreover, minor content of Mn, which was measured in Fe-Ti-O and also applied to calculation of Ti/Fe ratio, is consistent with ilmenite of metamorphic origin (Cassidy et al., 1988). Elemental composition of Ca-Ti-Si-O corresponded in stoichiometry well to mineral sphene, which was also confirmed by relative errors calculated for major constituent elements, with the exception of Al, which is a minor element substituting for Ti in sphene. Contents of major constituent elements in Zr-Si-O corresponded only to mineral zircon. The calculated relative errors were well within accepted limits, but reached the highest values for Si although atomic ratios between Zr and Si agreed well with zircon stoichiometry. Elemental composition of Ce-P-O, obtained by EDS analysis, corresponded to two possible Ce-bearing mineral series according to data in mineral databases (Anthony et al., 2009; Barthelmy, 2010); monazite and rhabdophane. Mean relative errors were greater for Ce-monazite than for Ce-rhabdophane. However, much better agreement with monazite was observed for major constituents Ce and P. Moreover, Ce/P atomic ratio and presence of Th and Nd, which are very variable trace elements in Ce-monazite (Barthelmy, 2010), conformed better in stoichiometry to Ce-monazite rather than Ce-rhabdophane (Table 2). Compositionally, Pb-C-O agreed with minerals cerussite and hydrocerussite (Table 2). However, calculation of relative errors and O/Pb atomic ratio confirmed that the analysed Pb-C-O is cerussite. Elemental composition of Zn-S and stoichiometric ratio between Zn and S, corresponded very well to mineral sphalerite (Table 2) and so did the calculated relative errors. Minor contents of Cd were also detected in Zn-S, which is in agreement with the fact that Cd frequently occurs as a trace element in Zn ore minerals (Štrucl, 1984). Considering its elemental composition, Zn-C-O could correspond to two possible Zn-bearing carbonate minerals; smithsonite and hydrozincite (Table 2). Though, atomic ratios between O and Zn and calculated relative errors were consistent with stoichiometric smithsonite. Relative errors and atomic ratios between Fe and S corresponded to stoichiometry of pyrite or marcasite (Table 2). For comparison, a polished pyrite standard was also analysed with EDS analysis and the results showed perfect match. However, based solely on EDS analysis it is impossible to determine whether analysed Fe-S is either pyrite or marcasite. Constituent elements in Pb-Mo-O were difficult to identify due to overlaps between the S Kα (2.307 keV), Pb Mα (2.342 keV) and Mo Lα (2.293 keV) energy lines, which are below the energy resolution of the EDS, thus Pb-Mo-O could easily be mistaken for Pb-S-O. There is also no difference in Mo/O atomic ratios in wulfenite and S/O in anglesite. The peak overlaps were resolved by comparing acquired spectra with synthesized spectra of possible minerals with ideal compositions and presence of Mo was also confirmed by exciting its non-overlapping high-energy X-ray lines at 30 kV accelerating voltage. The obtained elemental composition and relative errors for Pb-Mo-O, which were in acceptable limits, corresponded well to wulfenite. Analysed Zn-Si-O has two possible mineral analogues; hemimorphite and willemite. The calculated atomic ratios and relative errors indicated that Zn-Si-O agreed best with mineral hemimorphite. According to mineral databases (Anthony et al., 2009; Barthelmy, 2010), descloizite was the only possible analogue containing elements that were also present in the analysed Pb-Zn-V-O. Atomic ratios and relative errors showed that in stoichiometry Pb-Zn-V-O perfectly corresponded to mineral descloizite, although the measured O contents were slightly lower than in stoichiometric descloizite. Pb-S corresponded to mineral galena, which was also confirmed by calculated relative errors and atomic ratios. However, measured contents of S were somewhat higher than in stoichiometric galena, while Pb contents were consequently somewhat lower. The calculated relative errors and atomic ratios between constituent elements in analysed Fe-Si corresponded in stoichiometry perfectly to mineral gupeiite. Natural occurrences of gupeiite are very rare in nature though and may be either of extraterrestrial or anthropogenic origin (Reller et al., 2000). Fe-O (Pb,Zn) corresponded to three different mineral species, goethite or lepidocrocite and bernalite according to its elemental composition. Since Pb and Zn may also substitute for Fe in goethite and lepidocrocite, a sum of Fe, Pb and Zn was also considered in the calculation of relative errors. Si and Ca, which were also identified in analysed Fe-O (Pb,Zn), most probably co-precipitated with Fe-O (Pb,Zn). Relative errors calculated for constituent elements showed best agreement between the chemical composition of Fe-O (Pb,Zn) and mineral bernalite. However, considering the fact that O contents, obtained by EDS analysis, are commonly a little bit higher than those in stoichiometric minerals, it could be assumed that the mineral analogue of Fe-O (Pb,Zn) was more probably goethite or lepidocrocite and not bernalite. In addition to that, bernalite is considered a very rare mineral.

Comparison between elemental compositions of metal-bearing phases in rough particle and polished samples

Identification of phases in rough particle samples is considered difficult and unreliable mostly due to sample geometry effects and matrix correction, which are not suited to rough surface analyses (Reed, 2005). To assure that EDS measurements of phases in rough particle samples are reliable and representative, a comparison between average contents of elements in phases in rough particle samples and average element contents in polished samples was made using Welch's t-test and calculating the X_{av}^{u}/X_{av}^{p} ratio. The results of this comparison are presented in Table 3.

Welch's t-test was carried out in order to show differences in elemental composition of metal-bearing phases measured in rough particle and polished samples. The t-test showed that there were no statistically significant differences between mean element contents in 6 metal-bearing phases (Ti-O, Zr-Si-O, Ce-P-O, Zn-S, Fe-S and Pb-S) measured in rough particle

Tab. 3. Comparison between elemental composition of metal-bearing phases in rough particle and polished sediment samples; n - number of measurements on different grains, (X_{av}^{u} (at%)) - mean elemental composition of rough particle samples with standard deviation in atomic %, (X_{av}^{p} (at%)) - mean elemental composition of polished samples in atomic %.

Tab. 3. Primerjava med elementarno sestavo kovinskih faz v grobih delcih in poliranih vzorcih sedimentov; n - število meritev na različnih zrnih, (X_{av}^{u} (at%)) - aritmetična sredina elementarne sestave grobih delcev s standardnim odklonom v atomskih %, (X_{av}^{p} (at%)) - aritmetična sredina elementarne sestave poliranih vzorcev v atomskih %.

	Rough particle sample	**Polished sample**	**Comparison**		
Element	**X_{av}^{u} (at%)**	**X_{av}^{p} (at%)**	**Welch's t-test**		**X_{av}^{u}/X_{av}^{p} ratio**
Ba-S-O	**n=8**	**n=10**	**t (0.05,22) = 2.074**		
O	74.08 ± 5.03	70.25 ± 0.31	**2.150**	**different**	1.05
S	14.00 ± 2.29	15.38 ± 0.19	1.693	equal	0.91
Sr	0.28 ± 0.21	0.61 ± 0.45	2.010	equal	0.46
Ba	11.63 ± 2.68	13.76 ± 0.47	**2.213**	**different**	0.85
Ti-O	**n=10**	**n=10**	**t (0.05,30) = 2.042**		
O	74.85 ± 5.68	72.82 ± 0.78	1.123	equal	1.03
Ti	25.15 ± 5.68	27.19 ± 0.78	1.123	equal	0.93
Fe-Ti-O	**n=10**	**n=10**	**t (0.05,17) = 2.110**		
O	78.04 ± 3.92	68.46 ± 1.32	**7.326**	**different**	1.14
Ti	11.53 ± 1.60	15.98 ± 0.62	**8.211**	**different**	0.72
Mn	0.58 ± 0.39	0.82 ± 1.01	0.698	equal	0.71
Fe	9.86 ± 2.40	14.74 ± 1.08	**5.860**	**different**	0.67
Ca-Ti-Si-O	**n=10**	**n=10**	**t (0.05,9) = 2.262**		
O	72.58 ± 3.09	69.28 ± 0.58	**3.315**	**different**	1.05
Al	0.67 ± 0.17	0.65 ± 0.45	0.073	equal	1.02
Si	9.79 ± 0.96	11.04 ± 0.18	**4.003**	**different**	0.89
Ca	8.64 ± 1.04	9.89 ± 0.27	**3.698**	**different**	0.87
Ti	8.33 ± 1.34	9.14 ± 0.45	1.810	equal	0.91
Zr-Si-O	**n=10**	**n=10**	**t (0.05,6) = 2.447**		
O	71.41 ± 2.48	70.43 ± 0.61	1.220	equal	1.01
Si	13.92 ± 1.10	14.35 ± 0.26	1.209	equal	0.97
Zr	14.68 ± 1.45	15.23 ± 0.44	1.153	equal	0.96

Tab. 3 (continued)

	Rough particle sample	**Polished sample**	**Comparison**		
Element	**X_{av}^{u} (at%)**	**X_{av}^{p} (at%)**	**Welch's t-test**		**X_{av}^{u}/X_{av}^{p} ratio**
Ce-P-O	**n=10**	**n=10**	**t (0.05,34) = 2.032**		
O	71.61 ± 6.10	72.68 ± 0.74	0.551	equal	0.99
P	15.22 ± 2.84	15.38 ± 0.33	0.171	equal	0.99
La	3.77 ± 0.95	3.14 ± 0.43	1.897	equal	1.20
Ce	6.98 ± 1.78	6.27 ± 0.24	1.235	equal	1.11
Nd	2.12 ± 0.63	2.23 ± 0.22	0.538	equal	0.95
Th	0.30 ± 0.32	0.29 ± 0.28	0.060	equal	1.03
Pb-(C)-O	**n=10**	**n=10**	**t (0.05,8) = 2.306**		
O	85.88 ± 2.73	78.57 ± 0.85	**8.092**	**different**	1.09
Pb	14.13 ± 2.73	21.43 ± 0.85	**8.092**	**different**	0.66
Zn-S	**n=10**	**n=10**	**t (0.05,6) = 2.447**		
S	54.28 ± 2.27	53.62 ± 0.68	0.890	equal	1.01
Zn	45.52 ± 2.44	46.39 ± 0.68	1.076	equal	0.98
Zn-(C)-O	**n=10**	**n=10**	**t (0.05,7) = 2.365**		
O	82.08 ± 2.63	76.49 ± 0.80	**6.419**	**different**	1.07
Zn	17.92 ± 2.63	23.51 ± 0.80	**6.419**	**different**	0.76
Fe-S	**n=8**	**n=10**	**t (0.05,10) = 2.228**		
S	68.57 ± 3.06	69.12 ± 1.02	0.488	equal	0.99
Fe	31.43 ± 3.06	30.88 ± 1.02	0.488	equal	1.02
Pb-Mo-O	**n=10**	**n=10**	**t (0.05,24) = 2.064**		
O	83.01 ± 4.49	71.70 ± 1.78	**7.410**	**different**	1.16
Mo	9.19 ± 2.46	15.15 ± 0.94	**7.166**	**different**	0.61
Pb	7.80 ± 2.07	13.15 ± 0.94	**7.456**	**different**	0.59
Pb-Zn-V-O	**n=6**	**n=4**	**t (0.05,11) = 2.201**		
O	76.68 ± 3.59	60.78 ± 0.40	**10.762**	**different**	1.26
V	7.53 ± 1.21	13.06 ± 0.23	**10.889**	**different**	0.58
Zn	7.38 ± 1.54	12.86 ± 0.57	**7.967**	**different**	0.57
Pb	8.42 ± 1.51	13.31 ± 0.30	**7.687**	**different**	0.63
Zn-Si-O	**n=8**	**n=4**	**t (0.05,37) = 2.026**		
O	73.13 ± 5.84	65.87 ± 1.36	**3.338**	**different**	1.11
Si	10.45 ± 1.43	12.12 ± 0.13	**3.301**	**different**	0.86
Zn	16.42 ± 4.52	22.01 ± 1.39	**3.204**	**different**	0.75
Pb-S	**n=7**	**n=8**	**t (0.05,4) = 2.776**		
S	55.70 ± 1.38	54.50 ± 1.05	1.886	equal	1.02
Pb	44.30 ± 1.38	45.50 ± 1.05	1.886	equal	0.97
Fe-Si	**n=10**	**n=4**	**t (0.05,43) = 2.016**		
Si	33.85 ± 1.92	28.59 ± 1.96	**4.564**	**different**	1.18
Fe	66.15 ± 1.92	71.41 ± 1.96	**4.564**	**different**	0.93
Fe-O (Pb,Zn)	**n=10**	**n=10**	**t (0.05,33) = 2.035**		
O	73.19 ± 5.93	71.00 ± 0.76	1.153	equal	1.03
Si	2.64 ± 1.15	0.92 ± 0.43	**4.421**	**different**	2.87
Ca	1.31 ± 0.61	0.35 ± 0.15	**4.906**	**different**	3.81
Fe	19.84 ± 4.25	25.73 ± 1.91	**4.002**	**different**	0.77
Zn	1.77 ± 1.22	1.37 ± 0.64	0.901	equal	1.29
Pb	1.27 ± 0.77	0.64 ± 0.45	**2.237**	**different**	1.99

and polished samples. This indicated that these phases could be identified with sufficient reliability using the data obtained by EDS analysis of rough particle samples. For other 6 phases (Pb-C-O, Zn-C-O, Pb-Mo-O, Pb-Zn-V-O, Zn-Si-O and Fe-Si), there were significant differences in element contents obtained from polished and rough particle samples. In 4 phases (Ba-S-O, Fe-Ti-O, Ca-Ti-Si-O and Fe-O (Pb,Zn)), which are among the most complex phases according to their elemental composition, t-test showed significant differences mostly for major constituent elements, while for most of minor and trace elements no significant differences were observed. The differences between contents of constituent elements measured in rough particle and polished samples were ascribed to geometry effects due to the surface morphology and orientation of particle surfaces, to variations in analytical conditions and homogeneity level of individual phases.

The comparison using X_{av}^{u}/X_{av}^{p} ratios showed that contents of light and some other non-metallic elements (O, Si, P and S) in most of metal-bearing phases measured in rough particle samples were generally higher than those measured in polished samples, while contents of metals, especially Ti, Fe, Zn and Pb, were mostly lower in rough particle than in polished samples. These ratios were quite different in Ce-P-O and Pb-S, in which contents of metals were higher and contents of light elements were lower in rough particle samples. In other metal-bearing phases, the X_{av}^{u}/X_{av}^{p} ratios were relatively constant and did not change considerably from phase to phase. They appeared to be mostly independent of different combinations of elements but were dependent on their contents. Thus, in more complex phases, such as Fe-O (Pb,Zn), contents of minor and trace elements were higher in rough particle samples, while in simple phases, such as Zn-S, Pb-S, Ti-O and Fe-S, better ratios between element contents were observed. In metal-bearing phases, in which elements were present as major constituents, the X_{av}^{u}/X_{av}^{p} ratios were lower than 1. However, when they occurred as minor or trace elements, the X_{av}^{u}/X_{av}^{p} ratios became more variable and were generally higher than 1. Thus, the X_{av}^{u}/X_{av}^{p} ratios for major constituent light elements ranged between 0.86 and 1.26, with an average value of 1.04 ± 0.10. The average values of X_{av}^{u}/X_{av}^{p} ratios for major constituent metals were 0.80 ± 0.16 and 1.53 ± 1.06 for metals and light elements present in minor or trace contents in analysed metal-bearing phases.

EDS measurements of rough particle samples thus proved as sufficiently reliable for identification of most of analysed natural and anthropogenic metal-bearing phases, as compared to EDS analysis of polished samples. However, all established characteristics, relations between elements and phases and X_{av}^{u}/X_{av}^{p} ratios need to be considered in calculation of mineral formulae and identification of metal-bearing phases.

Conclusions

The results of this study demonstrated that elemental and mineral compositions of metal-bearing phases in polished and rough particle samples were mostly determined with sufficient precision and accuracy using EDS analyses. Precision measurements showed that the overall average repeatability of EDS analyses under applied analytical conditions amounted to 8 % for polished samples and 24 % for rough particle samples, which was within acceptable limits for most of major elements and some of the elements present in minor or trace contents in the analysed metal-bearing phases. The random analytical fluctuations were considered negligible and phase composition could be determined with sufficient reliability in individual grains of each phase. The homogeneity test showed that metal-bearing phases with minor or trace elements were least homogeneous. The precisions were thus explained by homogeneity level of constituent element distributions throughout phases for 50 % of all analysed phases. The overall average relative error for all elements amounted to about 12 %, which was within acceptable limits for accuracy in quantitative EDS analysis. This allowed calculation of chemical formulae and identification of mineral species of metal-bearing phases based on atomic ratios between constituent elements, determined with sufficient accuracy. All analysed individual phases were thus identified with sufficient accuracy. A comparison between average contents of elements in rough particle and polished samples (the X_{av}^{u}/X_{av}^{p} ratio) showed that the ratios were mostly constant in different phases and depended on atomic number and contents of constituent elements. Light elements and trace metals thus have higher ratios than major metals. However, the t-test showed that only about 38 % of studied metal-bearing phases could be identified with sufficient reliability using the data obtained by EDS analysis of rough particle samples, while for 62 % of phases mineral composition could not be reliably determined. EDS measurements of rough particle samples were sufficiently reliable for identification of most of analysed natural and anthropogenic metal-bearing phases, however, relations between elements and phases and X_{av}^{u}/X_{av}^{p} ratios needed to be considered in calculation of mineral formulae and identification of metal-bearing phases in rough particle samples.

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