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Chemical mapping of mine waste drill cores with laser-induced breakdown spectroscopy (LIBS) and energy dispersive X-ray fluorescence (EDXRF) for mineral resource exploration



Kerstin Kuhn^{a,*}, Jeannet A. Meima^a, Dieter Rammlmair^a, Christian Ohlendorf^b

^a Federal Institute for Geosciences and Natural Resources (BGR), Stilleweg 2, 30655 Hannover, Germany

^b University of Bremen, GEOPOLAR, Celsiusstraße FVG-M, 28359, Bremen, Germany

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ABSTRACT

Resource estimation for metals in mine tailings and ore deposits requires many samples, usually in the form of drill cores. In order to detect zones of metal enrichment or depletion as well as different lithological zones in such cores, two different core scanning methods were tested on three drill core metres from tailings of a former Pb-Zn mine to obtain chemical information. The results provide an objective basis for further sub-sampling of the taken drill cores and help reduce the amount of samples and therefore the costs for further investigations. For the determination of element concentrations a prototype of a core scanner working with laser-induced breakdown spectroscopy (LIBS) was tested and the results were compared to data from a commercially available ITRAX core scanner, working with energy-dispersive X-ray fluorescence (EDXRF). Apart from a smooth surface, no complex sample preparation was necessary. Peak intensities of selected elements determined by the two scanners were calibrated by means of linear regression (LR) and partial least squares (PLS) regression with respect to bulk geochemical wavelength-dispersive XRF (WDXRF) analysis results of representative core samples. The application of PLS compensates for matrix effects in LIBS and EDXRF and improves prediction accuracy for most elements, compared to LR. In general, prediction ability of PLS models is slightly higher for EDXRF results than for LIBS. The advantage of the LIBS core scanner is the high spatial resolution and the ability to create two-dimensional (2D) element distribution images as well as phase or mineral distribution maps of the drill core at larger scales. Within the analysed tailing cores metal-rich layers with concentrations up to a maximum of 2.2% Pb + Zn + Cu, could be detected by both core scanning methods. Since these layers are not visible by the human eye, the used core scanning methods are appropriate methods for mineral exploration.

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1. Introduction

Recovery of metals from mine waste gets more and more important. The lower energy consumption compared to primary mining and the additional usage of residues like quartz could make a recovery profitable. Furthermore, from an ecological point of view, mine waste remediation costs could be minimised.

Tailings are residues from ore processing which includes size reduction as well as a mineral separation by flotation. The layered tailing ponds show grain sizes from sand to clay. Tailings are characterised by a strong heterogeneity due to separation processes during deposition, due to different rock sources during ore processing, periodically moving spigot points, as well as alteration processes after deposition.

Therefore, the metal distribution also is vertically and laterally heterogeneous within the tailing material and a set of drill cores is necessary to characterise a pond. Statistical sub-sampling of these drill

* Corresponding author. *E-mail address:* kerstin.kuhn@bgr.de (K. Kuhn). cores for geochemical and mineralogical investigations will create a huge amount of samples which will cost a lot of time and money.

An element screening method for fast detection of zones with element enrichment or depletion will reduce the amount of subsamples and generate a basis for selective sampling. With such a method it is possible to detect and choose end-members, rather than mixtures, of different zones within a tailing site for further analysis.

Current core logging techniques include porosity logging (bulk density), multi-sensor core logging (gamma ray attenuation, P-wave velocity, magnetic susceptibility, electrical resistivity, spectrophotometry, natural gamma), digital imaging and non-imaging optical systems, Xray computed tomography (3D X-radiography of sediments), magnetic resonance imaging, and confocal macro-/microscopy with laser imagery (Rothwell and Rack, 2006; St-Onge et al., 2007).

For element mapping there are only a few techniques, such as natural gamma radiation (Blum et al., 1997), X-ray fluorescence spectral scanning (Croudace et al., 2006; Jansen et al., 1998; Rodriguez et al., 2012), imaging spectroscopy (Clark, 1999; Clark and Roush, 1984; Goetz and Wellman, 1984), as well as laser-induced breakdown spectroscopy (Bolger, 2000). Whereas natural gamma-ray spectrometry allows estimation of K, U and Th concentrations (Blum et al., 1997; St-Onge et al., 2007), X-ray fluorescence is able to detect a wide range of elements from Al to U (St-Onge et al., 2007). Especially for element screening of marine and lacustrine sediment cores X-ray fluorescence core scanning is very common (Francus et al., 2009; Ohlendorf et al., 2014; Rothwell et al., 2006; St-Onge et al., 2007; Thomson et al., 2006). There are also some commercial EDXRF devices on the market, which perform 2D chemical mapping (Melcher et al., 2006; Rammlmair et al., 2001; Rammlmair et al., 2006; Rodriguez et al., 2012; Shanahan et al., 2008). However, we are not aware of any device, which can analyse metre-long cores. Investigations of base and trace metal mineralisation in rocks by EDXRF were published e.g. by Melcher et al. (2006); Rammlmair et al. (2006); Rodriguez et al. (2012), and Zuo (2013). LIBS is able to detect almost all elements, depending on the experimental setup. It is often used in material science, but relatively unknown in geosciences (Harmon et al., 2009). Chemical mapping with LIBS is reported from only a few research groups (e.g. Bolger, 2000; McMillan et al., 2014; Novontý et al., 2008; Yoon et al., 1997).

Within this study, we generate two-dimensional element maps of three drill core metres, from a Pb–Zn-tailing of the Maubacher Bleiberg deposit by a prototype of a LIBS core scanner. Results are compared with one-dimensional element profiles generated with an ITRAX[™] core scanner using the X-ray fluorescence technique.

Due to matrix effects, influencing the LIBS and EDXRF intensities, the results of both core scanning methods are semi-quantitative (Croudace et al., 2006; Harmon et al., 2009; Krasniker et al., 2001; Rothwell and Rack, 2006; Tucker et al., 2010). Chemical matrix effects can occur in the LIBS plasma, when a species, present in the sample, inhibits the ionization of another species of much lower ionization potential (Eppler et al., 1996; Harmon et al., 2009). Physical matrix effects, caused by changing material properties like crystallinity and transmissibility of the minerals, grain size, surface texture, water content, as well as textural and porosity changes, coherence, and indurations, or presence of organic matter, will have a direct effect on the degree of laser energy coupling (Harmon et al., 2009; Miziolek et al., 2006) or have an impact on the production and detection of fluorescent radiation (Loewemark et al., 2011; Rothwell and Rack, 2006; St-Onge et al., 2007).

Therefore, the emission intensity of one element measured in two different matrixes does not necessarily represent the real element concentration, and a simple linear correlation of element intensity and real element concentration is not possible. Standard univariate calibration techniques are not adequate, since many calibration curves, one for each matrix, are necessary (Harmon et al., 2009; Tucker et al., 2010). Thus, the multivariate PLS regression algorithm was used in this study for quantification of element concentration for all materials. PLS is often used for calibration of chemical and geophysical parameters of spectra and a variety of studies have successfully applied PLS to LIBS spectral data (Amador-Hernández et al., 2000; Clegg et al., 2009; Labbé et al., 2008; Luque-García et al., 2002; Martin et al., 2005; McMillan et al., 2014; Ortiz et al., 2004; Tucker et al., 2010; Yaroshchyk et al., 2012). Quantitative ITRAX X-ray microanalysis of natural samples are usually done by "XRF fundamental parameters" calculations, but this assumes compositional and physical homogeneity for the measured samples (Croudace et al., 2006). Semi-quantitative results, with certain errors referring to the application to heterogeneous samples, appear to be acceptable for many users, since they are mainly interested in distribution patterns. Multivariate analyses for quantification of EDXRF core scanner data are not very common.

For application in mineral resource exploration, element concentrations should be determined as precisely as possible. In this context we investigate, whether a supplementary multivariate calibration on basis of calibration samples can improve the accuracy of quantification.

We choose PLS, since it is an appropriate method that can cope with numerous X-variables, which are often correlated and simultaneously model several response variables, Y (Wold et al., 2001). Like other multivariate methods, it is less sensitive to noise, can cope with spectral interferences and can model non linear behaviours. Since PLS uses the information contained in both, X and Y variables to fit the model, by switching between both matrices iteratively to find the relevant PLS components (latent variables), it often needs fewer components then other methods to reach an optimal solution. Detailed information of the PLS regression and its applications are given in Geladi and Kowalski (1986), Höskuldsson (1988), Naes and Martens (1985), Sirven et al. (2006); Wold et al. (1984, 2001), and Yaroshchyk et al. (2012).

The goal of this study is to evaluate advantages as well as disadvantages of the LIBS and ITRAX core scanners for resource exploration. To document this, zones of metal enrichment (Pb, Zn, Cu, Ni, Co) are determined and information about the texture of the mineralisation and the lithological structure of the layered material shall be gained.

2. Materials and methods

2.1. Samples

The investigated drill cores were derived from a 43-year-old Pb–Zntailing site, called Beythal (Fig. 1). The tailing site is located about 20 km east of Aachen (Germany) and contains flotation residues from the now inactive open cast mine Maubacher Bleiberg. The deposit was mined for lead (about 2.5%) and zinc (about 0.8%, Schachner, 1961). The flotation residues were deposited in the time interval 1950 to 1969. Beythal covers an area of about 45 ha and contains about 3.7 Mio m³ of mine waste (Reicherter and Klitzsch, 2010).

The tailing material is characterised by layers of sand as well as mixtures of silt and clay. It mainly consists of quartz and phyllosilicates with an illite–muscovite composition. Also minor amounts of carbonates such as dolomite, Mn–Fe-dolomite, ankerite, and siderite as well as a variety of accessory minerals were detected.

For this study, three consecutive drill core metres were analysed, each of them with a length of 1 m and a diameter of 5 cm. The cores were taken from a depth of about 7 to 9 m below surface. The plastic liners were split into halves and the sediment was allowed to dry at room temperature. If necessary, the surface was smoothed.

2.2. LIBS experiments

2.2.1. LIBS fundamentals

In LIBS, a very short duration laser pulse is optically focused to a small spot on the sample surface generating a plasma that vaporizes a small amount of sample material. Initially, ionization is high and the optical plasma emission is characterised by an intense continuous background and emissions from ions (Cremers and Radziemski, 2006). As electron-ion recombination proceeds, neutral atoms, and then molecules form. The plasma expands and cools and the atoms and molecules emit light at their characteristic wavelengths. The obtained emission spectrum is, therefore, characteristic for the elemental composition of the sample. Delaying the spectral acquisition a few us after the laser pulse allows the broadband emission to subside and the elemental fluorescence to be observed (Body and Chadwick, 2001). Each firing of the laser produces a single LIBS measurement. Usually the signals from many laser plasmas are added or averaged to increase accuracy and precision and to average out non-uniformities in sample composition (Miziolek et al., 2006).

2.2.2. LIBS core scanner measurements

Element mapping of the drill core sections was performed by a prototype LIBS core scanner manufactured by LTB Berlin, which is operated in our working group. It is applicable for point measurements, 1D profiles and 2D scans. Fig. 2 shows the experimental LIBS set-up used in this work.



Fig. 1. Picture of the studied tailing Beythal (source: Bündnis 90 die Grünen). The tailing pond is located in western Germany, near Aachen (red circle in small picture, source: www.worldofmaps.net). The location of the analysed drill core is marked by a red star.

The specifications of the used LIBS core scanner are summarized in Table 1. During mapping, the laser is moved over the sample via a computer-controlled biaxial translation stage. The translation stage is driven automatically via a stepper motor controlled by the LIBS software "Sophi" and is stopped for every measurement. The LIBS core scanner is able to map an area of 1 m by 2.5 cm with a user-defined step size. In order to reduce the duration of the measurements and the amount of spectra, the studied cores were mapped within an area of about 1 m by 1 cm and with a step size of 400 μ m. The measurement grid consisted of 25 spectra along the y-direction and according to the length of the core metre, between 2478 and 2490 spectra along the x-direction. At each grid point five laser shots were fired and emission intensities were accumulated in one spectrum. This resulted in approximately 62,000 spectra per core metre.

Measurements were run directly on the dried core surface under ambient atmosphere at atmospheric pressure. To prevent the production of bigger particle clouds, an exhaust system was installed close to the sample surface. This prevented plasma formation inside the cloud as well as sediment deposition on the rest of the sample.

The splitted cores show some surface morphology in the range of 2 mm. Furthermore, deep shrinkage cracks occur in the clay, which are caused by drying of the material. However, since the laser focal length covers a large zone, the plasma is generated even beyond the optimal focus point.

For every element there is an optimal experimental set-up for LIBS analysis. The main parameters for adjusting measurements are the delay time between laser pulse and the read out of the CCD, the number of laser shots that are accumulated for one measurement, and the laser



Fig. 2. Picture and schematic diagram of the experimental setup of the used LIBS core scanner. Original LIBS spectrum with 36,400 support points between 285 and 964 nm.

Table 1	
Specifications of the LIBS core scanner	

Laser	Nd:YAG Q-switched laser
Wavelength	1064 nm
Pulse width	11 ns
Energy	maximum of 55 mJ/pulse
Repetition rate	20 Hz
Spot size	200 µm
Spectrometer Spectral range Spectral resolution	Echelle spectrometer 285–964 nm R = 10,000 (resolution: 0.29–0.96 nm)
Detector Resolution	CCD 1024 \times 256 pixel

energy. Tests for optimising the measurement parameters were done on homogenized, pressed and loose materials from the same tailing. The results showed, that a delay time of 1.5 to 1.7 μ s worked best for most elements and for the clay- and the sand-sized material. For the core mapping a delay time of 1.5 μ s was chosen. The best compromise between high LIBS intensities and a crater depth in the loose sand of not more than 2 mm were reached with five laser shots accumulated. Laser energy was set to 55 mJ, which is the highest energy that can be reached with our system.

2.3. EDXRF experiments

For verification of the LIBS data, the results are compared with data obtained by EDXRF. For these measurements an ITRAXTM XRF core scanner (Cox analytical systems) operated at GEOPOLAR (University of Bremen) was used. The ITRAXTM XRF core scanner is a flat-beam X-ray fluorescence scanner that uses an intense non-destructive micro X-ray beam for scanning core surfaces. According to the used flat-beam optical system, 1D element profiles with a spatial resolution in x-direction of 50, 100 or 200 μ m are generated (Croudace et al., 2006; Rammlmair et al., 2001; St-Onge et al., 2007). Standard systems operate with a resolution of 100 or 200 μ m.

Element profiles can be obtained for a maximum core length of 180 cm. Croudace et al. (2006) gives a detailed description of the technical details of the ITRAXTM core scanner.

EDXRF scanning of the 1 m cores from Beythal was performed with a 3 kW molybdenum target tube operating at 30 kV and 40 mA. The X-rays are focused by means of a proprietary flat-beam optical device generating a 20 × 0.2 mm rectangular beam with its long axis perpendicular to the sample main axis x (Croudace et al., 2006). However, the used evacuable cone in front of the detector has an entrance window of 8×0.2 mm and therefore the real sampling area is slightly larger than 8×0.2 mm. Step size in the x-direction was set to 200 µm with a count time per step of 7 s plus 1.7 s deadtime. X-ray fluorescence was detected with a 1024 channel silicon drift detector (SDD) with a resolution of 140 eV for Mn K α .

2.4. Bulk chemical analyses

The results of the two scanning methods were compared and validated to 78 bulk quantitative chemical analyses. Element concentrations were obtained by wave length dispersive X-ray fluorescence (WDXRF). The analyses were performed by means of two wavelength dispersive sequential spectrometers (Philips PW1480 and PW2400) with a Cr and Rh tube, respectively. Measurements were done on fused glass discs, which were produced from subsamples of optically homogeneous zones of the cores (each 2 to 6 cm³).

The total sulphur content of the samples was analysed by combustion Infrared Detection analysis with a LECO CS 230 analyser. Thereto, the samples were heated to 2000 °C and the released sulphur dioxide was measured by an IR detection system.

2.5. Quantitative analyses

2.5.1. Data processing

For all of the approximately 62,000 LIBS spectra per core metre, a background subtraction was done by the LIBS software "Sophi".

Within this study the elements Pb, Zn, Cu, Ni, Co, Si, Al, K, Na, Ca, Mg, Fe, Mn, Ti, Ba, and S were investigated. Out of the large number of emission lines characterising LIBS spectra of heterogeneous rock and sediment samples, several lines were chosen, that are not disturbed by interferences with other element emission lines. Furthermore, the shape of these element peaks was checked for the two different matrixes (sand, silt to clay) in order to get an indication, whether they might be influenced by saturation phenomena at high element concentrations or by background noise at low concentrations. A good verification of the chosen emission lines for each element but from different emission lines, should strongly correlate to each other. For every element, two to three emission lines, meeting all demands, were chosen for this study (Table 2).

For chemical mapping all original spectra were reduced to these wavelengths, by calculating peak area integrals, with peak widths of 0.1 nm, from each of the 47 emission lines. Further data processing includes individual normalisation of each wavelength channel to the integrated total energy of that spectrum. This normalisation to total intensity shall compensate for subtle variations in laser power (Body and Chadwick, 2001; Tucker et al., 2010). Additionally, spectra with total spectral energies greater or smaller than two standard deviations from the mean total energy of all spectra, referring to the same calibration or validation sample, were considered as outliers and excluded from the spectral data set. Investigations of rejected spectra indicated that they originate from deep shrinkage cracks in silt and clay or from failure measurements with no signals apart from the background. Prior to the quantification, the spectral data were centred to the mean value.

For visualization of the pre-processed data, the peak area values were transformed into 8 bit grey value images each representing a 2D mapping of one element.

The EDXRF scanning with the ITRAX core scanner resulted in about 5000 spectra per core metre. By the aid of standard fitting procedures implemented in the Q-Spec spectral analysis software, individual elemental peak areas were extracted from the spectrum. Thereto, the sum-spectrum was fitted to a XRF fundamental parameters model and the fit was optimized by minimising the mean square error. With the optimized fit, the individual EDXRF raw-spectra for each iteration process were re-evaluated with a maximum of 100 iterations per spectrum in an automated batch procedure. Element data are expressed as counts (cts) and were calculated from peak area integrals of element

Table 2	
Wavelengths of the used LIBS emission	lines.

Element	
	Spectral line (nm)
Pb	405.7807, 363.9568, 368.3462
Zn	481.053, 472.215, 330.258
Cu	327.396, 324.754
Ni	352.454, 351.505, 345.847
Со	340.512, 352.981, 351.264
S	921.2865, 922.8092, 923.7538
Ba	614.1713, 553.5481, 712.0331
Si	390.5523, 288.158, 298.7645
Ti	364.268, 365.35, 308.802
Al	394.40058, 309.28386, 396.152
Fe	404.5813, 385.9911, 358.119
Mn	403.076, 403.449, 322.809
Mg	382.93549, 517.268, 383.8292
Ca	430.253, 647.166, 649.378
Na	819.4824, 588.995, 589.5924
K	693.877, 404.414, 404.721

specific regions of interest. The multivariate PLS Regression was applied to mean-centred data, as it was done for the LIBS results.

In order to check the necessity of a multivariate calibration, linear regression analyses were carried out.

2.5.2. Partial least squares (PLS) regression

In our application, the X-variables of the predictor matrix consist of average peak areas from either optical element emission intensities (LIBS) or fluorescence radiation (EDXRF). For that purpose, average spectra were calculated from all LIBS or EDXRF spectra (reduced to 47 and 14 element-characteristic wavelengths, respectively) obtained from the same regions where the subsamples for WDXRF measurements were taken from (rectangles of about 1 to 2 cm by 1 cm). Depending on the size of these subsamples, each average spectrum was calculated from about 625 to 1250 single LIBS spectra, or 50 to 150 single EDXRF spectra. The Y-variables of the response block include element concentrations of the same sample area, measured by WDXRF.

Please note, since Na and Mg cannot be detected under ambient atmosphere by the used ITRAX core scanner (Mo-tube, Rothwell and Rack, 2006), only intensities from the other 14 elements were used for the X-matrix. Nevertheless, the Y-matrix consists of 16 element concentrations, including Na and Mg. Sodium and Mg concentrations are predicted based on inter-element correlations. However, due to other mineral phases or alteration processes, these correlations might be disturbed for some layers and therefore predicted concentrations have to be considered with caution. The selection of appropriate training samples for the PLS model is therefore essential.

Altogether 78 average spectra (described as samples further on in the text) with corresponding WDXRF element concentrations distributed over all three drill cores were used to calibrate and validate the PLS models for LIBS and EDXRF. In order to test the prediction capability of the PLS model, the sample set was split into a training set and a test set. Thereto, a principal component analysis (PCA) was done on the Xmatrix and several samples with the highest, lowest, as well as intermediate scores for the most important principle components (PC) were selected. These samples span the concentration range and were taken for model calibration (training set, n = 39) using the leave-one-out cross-validation method. The rest of the dataset has been utilized for validation of the PLS model by a regression and contained 39 samples, too (test set).

Calibration of the PLS model and prediction of element concentrations was performed by the software package Unscrambler (CAMO Software) using the NIPALS PLSR algorithm (Nonlinear Iterative Partial Least Square Regression).

According to the results of Tucker et al. (2010), compositions of the WDXRF training and test samples for the main rock forming elements, bound to oxides, were input as weight % oxides and not as atomic fractions. Only the investigated base metals and the trace element Ba, as well as S (measured with LECO) remain as atomic fractions. Accordingly, all predicted concentrations of the major rock components are returned as wt.% oxide.

The selection of the number of latent variables, required for the construction of a calibration model, was done by selecting the local minima of RMSEP (root-mean-square error of prediction) for the training set and the test set. Additionally, the prediction performance for all individual spectra of the drill cores was taken into consideration. In order to avoid sub- or overfitting of the model for some elements, the Y-variables were split and 11 different PLS models were calibrated. While for elements like Pb, Zn, Cu, Si, Fe, Mn, S, and Ba a PLS model with only that single Y-variable reveals best results (PLS type I), other correlating elements can be combined to groups (PLS type II) without increasing RMSEP or decreasing R² (square of correlation coefficient for validation). These three groups consist of Ni + Co, $Al_2O_3 + TiO_2 + K_2O + Na_2O$, and MgO + CaO.

2.5.3. Spatially resolved analyses

Finally, the PLS regression models, which were calibrated by averaged spectra of larger areas were used to predict element concentrations for all pre-processed LIBS and EDXRF spectra of the drill core. The generated spatially resolved data sets with predicted concentrations instead of intensities, were then transformed into grey value pictures, or plotted as a graph. Of course, the predicted concentrations have to be regarded with care, since single spectra of a heterogeneous material are used. Compared to the averaged spectra, which were used for calibrating the PLS, single spectra are characterised by a stronger variability of element concentrations (higher number of extreme values). Therefore, prediction of element concentrations, which are higher or lower than concentrations of the calibration samples, implies more uncertainties, since for these concentration levels the model extrapolates.

2.6. Classification methods

On basis of the 2D spatially resolved element images generated by the LIBS scanner, a classification with the focus on the lithological composition of the tailings was performed. The spectral angle mapper (SAM) algorithm is a supervised classification method for hyperspectral images that determines the spectral similarity between two spectra by calculating the angle between the spectra and treating them as vectors in a space. Classification is based on end member spectra, which were extracted from the images. For further information please refer to Kruse et al. (1993). Classification analyses were done by the hyperspectral image processing and analysis software package ENVI.

Furthermore, the post-classification approach majority analyses was applied on the classification image produced by SAM. With this method, spurious pixels within a large single class are changed to the respective class.

3. Results and discussion

3.1. Quantitative analyses by linear regression

Quantitative PLS analyses were done on the basis of internal reference samples, taken from the tailing cores, and measured by WDXRF. A statistic compendium of the bulk chemical WDXRF analysis can be found in Table 3.

As already mentioned before, LIBS spectra are influenced by matrix effects. For the investigated tailings, most of the elements are strongly influenced by the matrix of the tailing material. Only for Cu these effects seem to be minor important. Thus, simple linear regression (LR) of Cu intensities shows a coefficient of linear regression ($r^2 = 0.71$) which is much higher than most other elements ($r^2 = 0.07$ to 0.51, Table 4). The most substantial matrix effects are caused by the different materials sand and silt/clay. Especially in the sandy material, these effects are strong. This is probably caused by the transparency of quartz, the main constituent of the sandy material. Krasniker et al. (2001) demonstrated the linear decay of plasma energy and spectral intensities with increasing sand percentages for major and minor soil constituents (20–90% sand content). The laser light, that encounters the optically transparent and hardly evaporated quartz, passes through the particle with some losses and is able to penetrate deep into the sample, where it contributes to the formation of large craters (Krasniker et al., 2001). The energy, which is captured inside the quartz, is lost regarding the plasma formation. However, matrix related effects also occur in different layers of the fine-grained material.

In contrast to LIBS, the modelling of the EDXRF spectra by the fundamental parameter approach can reduce the influence of the sand and silt/clay matrix. However, the quality of the processed EDXRF spectra differs from element to element. For the elements Pb, Zn, Cu, Fe₂O₃, SiO₂, and K₂O, EDXRF results correlate well with element concentrations of the reference samples (Table 4, Fig. 3). This is expressed by r²-values

Table 3

Statistic compendium of the bulk chemical analysis done with WDXRF and in the case of sulphur with LECO. Total iron is calculated as Fe₂O₃.

	Pb (ppm)	Zn (ppm)	Cu (ppm)	Ni (ppm)	Co (ppm)	Ba (ppm)	S _{total} (%)	SiO ₂ (%)	TiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	MnO (%)	MgO (%)	CaO (%)	Na ₂ O (%)	K ₂ O (%)	LOI (%)
Sand(n=29)																	
Mean	404	2032	35	146	57	61	0.30	88.25	0.24	2.71	0.97	0.14	1.13	1.80	0.02	0.59	3.09
Median	385	2071	32	132	55	65	0.29	88.69	0.24	2.65	0.92	0.13	1.07	1.76	0.02	0.58	2.94
Min	267	1528	15	105	36	30	0.26	83.05	0.22	2.21	0.81	0.10	0.87	1.36	0.01	0.48	2.37
Max	700	2913	101	262	93	96	0.42	90.44	0.31	3.64	1.53	0.22	1.70	2.73	0.04	0.80	4.53
Stdev	100	322	17	39	13	21	0.04	1.69	0.02	0.27	0.16	0.03	0.22	0.36	0.01	0.06	0.58
Silt/clay $(n = 49)$																	
Mean	2411	2305	91	232	137	210	0.44	73.08	0.48	10.84	2.38	0.16	1.41	2.10	0.09	2.28	5.38
Median	1945	1753	81	235	134	211	0.37	73.34	0.48	10.81	2.34	0.15	1.35	2.03	0.09	2.26	5.22
Min	859	908	33	155	70	144	0.22	66.64	0.39	6.67	1.90	0.09	1.07	1.54	0.04	1.46	4.43
Max	9493	11,980	262	342	207	271	1.22	78.46	0.57	14.44	3.15	0.26	1.98	3.21	0.12	3.02	6.61
Stdev	1575	1819	45	33	24	33	0.20	2.48	0.04	1.62	0.29	0.03	0.20	0.35	0.02	0.34	0.55

Stdev: standard deviation, LOI: loss on ignition at 1030 °C.

of the LR model of >0.73. Whereas differences between predicted and reference concentrations for Pb, Zn, and Cu probably result from the low number of calibration samples with high metal concentrations (Fig. 3), the other elements show some differences within certain matrices. For K, these differences occur mainly in the sandy material, whereas Fe and Si show divergences in some fine-grained layers. Stronger matrix effects seem to influence the elements Ni, MnO, S, TiO₂, and CaO ($r^2 = 0.12$ to 0.67).

Cobalt, Ba, and Al_2O_3 concentrations are near the detection limits and therefore signals are very noisy. However, in contrast to Co and Ba with no distinct distribution patterns, Al_2O_3 distribution patterns fit quite well to WDXRF concentrations. Aluminium is the element with the lowest atomic number detectable by the ITRAX scanner (Mo-tube) and measurements are often compromised by attenuation of excited X-rays in the air gap between the X-ray detector and the core surface (Rothwell and Rack, 2006).

Despite fundamental parameter analyses, matrix effects still occur for a variety of elements measured with the ITRAX scanner and therefore, spectra calibration by a multivariate method seems to be appropriate not only for the LIBS data, but also for the ITRAX data.

Table 4

The prediction performance of the linear regression (LR) models and the PLS regression models for LIBS and ITRAX core scanner data. The coefficient of linear regression r^2 , the coefficient of multiple correlation R^2 , as well as the root mean square error of prediction refer to the test set, which was used for model evaluation. Please note, that MgO and Na₂O is not detectable by the ITRAX scanner (n.d.).

	LR model LIBS	PLS model LIBS			LR model EDXRF	PLS mod	del EDXRF		
	r ²	RMSEP (%)	R ²	Latent variables	r ²	RMSEP (%)	R ²	Latent variables	
SiO ₂	0.18	1.93	0.93	8	0.88	1.76	0.94	3	
Fe_2O_3	0.01	0.23	0.90	8	0.89	0.15	0.96	3	
Al_2O_3	0.01	1.17	0.92	8	0.37	0.82	0.96	6	
K ₂ O	0.26	0.25	0.91	8	0.88	0.18	0.96	6	
Na ₂ O	0.23	0.01	0.85	8	n.d.	0.01	0.89	6	
TiO ₂	0.48	0.04	0.92	8	0.67	0.02	0.96	6	
Ba	0.07	0.003	0.89	8	0.05	0.002	0.90	6	
Pb	0.41	0.08	0.72	4	0.91	0.05	0.89	3	
Zn	0.51	0.06	0.65	6	0.79	0.04	0.82	3	
Cu	0.71	0.003	0.61	4	0.73	0.002	0.76	7	
Со	0.43	0.002	0.72	8	0.13	0.002	0.81	7	
Ni	0.49	0.003	0.57	8	0.18	0.003	0.60	7	
S	0.31	0.12	0.60	5	0.13	0.10	0.68	2	
MnO	0.14	0.02	0.36	4	0.19	0.02	0.44	7	
MgO	0.22	0.16	0.49	4	n.d.	0.13	0.63	9	
CaO	0.22	0.27	0.36	4	0.12	0.24	0.47	9	

3.2. Quantitative analyses by PLS regression

The evaluation of the PLS models was performed by means of 39 independent test samples. In order to show the predictive ability of the models, the statistical parameters R^2 (square of correlation coefficient for validation) and RMSEP (root-mean-square error of prediction) were used (Table 4).

It turned out that, depending on the element, the optimal number of latent variables of the PLS models varied between 4 and 8 for LIBS data and between 2 and 9 for the EDXRF data. As already highlighted by previous studies (Tucker et al., 2010; Yaroshchyk et al., 2010; Yaroshchyk et al., 2012), the models calculated from pre-processed average LIBS spectra have lower root mean square errors of calibration and validation compared to models created with unprocessed average spectra.

Assuming, that there is no bias in the models, the RMSEP represents the standard deviation of the differences between predicted and observed values. For both core scanners, the elements can be assigned to three different groups showing similar prediction qualities of the corresponding PLS model. The first group comprises the compounds/ elements SiO₂, Fe₂O₃, Al₂O₃, K₂O, Na₂O, TiO₂, and Ba, which are bound within the main siliceous matrix minerals guartz, illite-muscovite, chlorite, and to a minor extend in feldspar and rutile/anatase. Iron is bound to a minor extend in carbonates and sulphides (e.g. siderite, ankerite, pyrite, bravoite, chalcopyrite, sphalerite), too. Mineralogy was verified by means of transmitted and incident light optical microscopy, scanning electron microscopy and microprobe analyses. The element concentrations of the first group plot within two clouds in the measured vs. predicted scatter plots, since concentrations differ quite strong between the fine-grained clay/silt-matrix and the coarse-grained sand matrix (Fig. 3). Within the same lithological unit, variations are low. The PLS predicted element concentrations of the validation samples show a strong correlation to the WDXRF concentrations. Thus, R²_{test set}-values are very high and vary between 0.96 and 0.89 for the ITRAX core scanner, and between 0.93–0.85 for the LIBS core scanner.

The metals Pb, Zn, Cu, Co, Ni and the element S belong to the second group, whose PLS models have moderate $R^2_{test set}$ -values between 0.72 and 0.57 for the LIBS scanner and between 0.89 and 0.60 for the ITRAX scanner. All of these elements are bound in different ore minerals and their alteration products, and they are characterised by nugget formation. Additionally, these minerals show a non-uniform distribution, with enrichments in only a few layers within the three drill cores. Therefore, calibration and validation samples with high concentrations are rare and have a strong influence on the model (Fig. 3). More calibration and validation samples with high metal concentrations would improve the PLS model.

The last group of elements include CaO, MgO, and MnO. PLS models of these elements are characterised by the lowest $R^2_{test set}$ -values

varying between 0.49 to 0.36 for the LIBS scanner and 0.63–0.44 for the ITRAX scanner. The three elements are bound to different carbonates, which occur in the tailing material. These carbonates are calcite $(CaCO_3)$, dolomite $(CaMg(CO_3)_2)$, ankerite $(Ca(Fe, Mg, Mn)(CO_3)_2)$, and subordinately siderite $(FeCO_3)$ as well as mixtures of these minerals. Just like the sulphides, these minerals are minor components within the tailings and show variable distributions as well as nugget effects. Further reasons for the low PLS prediction abilities of both methods, beside the nugget effect, could not be identified.

While both chemical screening methods represent near-surface sampling techniques, a 3D object with a volume of at least 3 cm³ was analysed by WDXRF. Therefore, bulk chemical WDXRF results represent average concentrations covering large volumes. For elements that show nugget effects, it is more difficult to obtain representative WDXRF measurements. This might be reflected by the lower correlation coefficients of the second and third group.

For all elements, the prediction capability of the PLS regression models generated from ITRAX intensities is better than from LIBS intensities. This is not surprising, since energy-dispersive XRF and wavelength-dispersive XRF, which was used for calibration of the PLS model, are quite similar techniques compared to LIBS.

Furthermore, both core scanners have different sampling statistics. On the one hand, the sample area of the ITRAX scanner is slightly larger, with 1.6 mm² (8 mm \times 0.2 mm), compared to 0.8 mm² for one LIBS row $(0.03 \text{ mm}^2 \times 25 \text{ sampling points})$. On the other hand EDXRF scanners are characterised by element specific excitation response volumes which are increasing with atomic number of the element. Wilhelms-Dick et al. (2012) published extrusion depths for the Avaatech EDXRF core scanner of up to several hundreds of microns. In porous materials, the fluorescence X-ray extrusion depth for heavy elements (e.g. Fe, Co, Ni, Cu, Zn, Pb) should be even higher and amount to 1 mm. The LIBS scanner performs point-sampling measurements with a diameter of approximately 200 µm and a crater depth ranging between a view micrometre until several hundred of microns, according to the material and the number of laser shots. For the tailings, analysed with five laser shots, sampling depth is smaller than 100 µm. Although LIBS craters are larger in sandy material, a lot of the material is thrown out and not ablated. Due to the smaller sampling volume, element concentrations vary substantially, depending on the mineral ratio ablated by the laser beam. Very fine-grained clay material provides the best statistical results since thousands of grains are ablated. The homogeneously distributed pores have probably a moderate effect on the ablation depth and signal intensity. On the other hand coarser, sand dominated material might provide single crystals and/or large pores within the focus area

A further point that derogates prediction quality for the LIBS scanner results are subtle variations in LIBS intensities between the 25 measured rows (y-direction), due to the calibration of the LIBS spectrometer after every measured row in x-direction. These calibrations were done, since LIBS measurement time of one core metre took about 20 h and the shifting of the spectrometer should be prevented. By installing the spectrometer to an enclosure with constant temperatures, calibration during measurement would not be necessary for future measurements. Although pre-processing procedures could not eliminate the intensity shifts from spectrometer calibration, the influences of these shifts are reduced by averaging many spectra of a larger area (according to the WDXRF sample area) for each PLS calibration sample.

3.3. Spatially resolved geochemistry of the tailing material

Based on the PLS regression models, spatially resolved element concentrations of the three drill core metres were predicted by regression. Fig. 4 shows the predicted concentrations of one drill-core metre for both methods in comparison to WDXRF bulk chemical results. For a better comparison with the 1D graph of the ITRAX scanner, the LIBS concentration matrix was reduced to one dimension by averaging the concentrations of the 25 sampling spots in y direction.

For both methods, PLS regression compensates matrix effects to a large extend, leading to a good correlation of element distribution patterns and WDXRF results. Although, element concentrations have to be regarded carefully as the model extrapolates especially very high concentrations, they fit very well to WDXRF results. Due to the correlation of Na and Mg with other elements, element concentrations of these elements can be predicted by PLS even though the ITRAX core scanner cannot detect them. Although prediction ability of the LIBS and the EDXRF PLS models for Mg, Ca, and Mn are quite low for the test set, correlation patterns with WDXRF results are good (Fig. 4). However, similar to CaO and MnO which are also bound to carbonates, the predicted concentration patterns of the EDXRF data are quite noisy. The choice of less latent variables for the PLS models would smoothen the graphs, but also lead to mismatches for some layers. For Co and Ni, predicted concentrations from EDXRF intensities also reveal noisy signals, but with lower amplitude than for CaO, MnO, and MgO.

In summary, both methods provide a good basis to image element distribution patterns along drill cores. Furthermore, predicted element concentrations are consistent with WDXRF concentrations. By means of these distribution patterns, inter-elemental correlations can be identified and information about lithology and mineralisation of the tailing material can be drawn.

3.4. Lithology of the tailing material

Inter-element correlations can be gathered from 1D element graphs as well as from 2D maps (Figs. 4 and 5). The advantage of spatially resolved mapping, generated by the LIBS Scanner, is the possibility to detect structures within the material. By means of hyperspectral classification methods, like SAM, a classification of the results is possible. For very coarse-grained rocks or ore, this could be a mineral classification. In the case of fine-grained tailings, the resulting classification image does not represent a mineral distribution map, since grain sizes of the tailing material are smaller than diameter of the LIBS laser. It rather can be seen as a lithological distribution image, indicating the spatial distribution of quartz-, phyllosilicate- or carbonate-rich layers.

The layers with sand-sized tailing material mainly consist of quartz grains and can easily be perceived by the human eye. Within the core logging results, these areas are characterised by the highest Si contents. In the classification map, quartz-rich layers are coloured in red (Fig. 5). However, there are also minor contents of phyllosilicates and carbonates, occurring as disseminated mineral grains or in very thin layers. These structures are visible in almost all element distribution maps.

Within the silt- and clay-sized material, the classification map reveals different lithological layers, which are not distinguishable on a photograph. In an optical image of the drill core, the different layers have quite similar colours. Additionally, colours of some layers, which were located at the tailing surface for a longer period, have changed by secondary oxidation processes. The main siliceous matrix of the fine-grained material consists of clay-sized phyllosilicate minerals and minor amounts of quartz, feldspar residues and rutile/anatase. Zones with the highest content of these minerals are reflected by high concentrations of Al₂O₃, Fe₂O₃, K₂O, Na₂O, TiO₂ and Ba and represent most of the fine-grained material (blue colours within the lithological classification map, Fig. 5). The Si concentrations of the fine-grained layers can be considered as a combination of Si bound to quartz and Si bound to phyllosilicates and feldspar. Due to the strong variation of the quartz content within the fine material, there is no obvious correlation to the phyllosilicate distribution.

Some 2–10 cm thick layers with higher contents of carbonate minerals occur within the sand and the silt- to clay-sized parts (yellow to green colours within the classification map, Fig. 5B). In these layers, CaO, MgO, and MnO concentrations are up to twice as high as in the

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Fig. 3. Comparison of predicted concentrations versus reference concentrations (WDXRF) for both core scanner data. For the ITRAX scanner prediction results of the LR models as well as of the PLS models are shown. Predicted concentrations of the LIBS scanner derive from PLS. The training set is represented by open circles, and the closed circles represent the test set. The line shows the regression curve of the training set. Analysed elements, which are not shown in this figure (group 1: Fe₂O₃, Al₂O₃, K₂O, Ba; group 2: Zn, Ni; group 3: MgO, MnO) have similar correlation patterns like the displayed elements of the same group.

other layers and can reach up to 3% CaO, 2% MgO and 0.3% MnO. The enrichment of carbonates in some layers could ether derive from sorting during material transport, when filling the pond or indicate that these residues derive from ore material, which had higher contents of carbonates.

3.5. Mineralisation of the tailing material

Concentrations of economically interesting metals, like Pb, Zn, Cu, Co and Ni, within the analysed mining residues are not equally distributed, but enriched in certain layers. This can be caused by sedimentation processes during injection of the slurry from (different) spigot points, as well as by the deposition of different residues from different ore processing steps. Furthermore, weathering of the waste material can lead to depletion or enrichment of metals in certain zones.

Due to the small grain sizes of the material and the mixture with other minerals, layers enriched in metals cannot be detected by eye, but with both core scanners. For the analysed drill cores, all metal-rich layers occur in the fine-grained parts of the tailings. The thickness of these layers varies between 0.5 and 4 cm.

For Pb, Zn, and Cu, maximum concentrations occur between 785 and 789 cm sediment depth (Figs. 4 and 5). Average bulk chemical concentrations of that sediment section amount 0.95% Pb, 1.20% Zn, and 262 ppm Cu. A calculation of average metal concentrations for different layers by the PLS predicted concentrations is not advisable, since PLS models extrapolate when predicting concentrations from single spectra. Further small-scaled reference samples from metal-enriched layers and maybe from pure calibration minerals would be necessary to improve PLS models. Because of the low number of metal-rich layers within the three analysed drill core metres, these samples have to be taken from other cores.

Lead, Zn, and Cu show the same zones of enrichment and depletion indicating similar ore processing steps of galena (PbS), sphalerite ((Zn, Fe)S), and chalcopyrite (CuFeS₂). Sulphur also correlates with Zn, Pb, and Cu, which points to the common occurrence within sulphide minerals and secondary formed gypsum, whereby the sulphur derives from the sulphide alteration. Mineralogical investigations showed that most of the galena is altered to cerussite, a Pb-carbonate (PbCO₃). Whereas Pb- and Cu-bearing minerals have mostly higher contents in the fine-grained material, the Zn-bearing mineral sphalerite occurs in the fine- and coarse-grained material in equal amounts (Fig. 4). Nevertheless, the main zones of Zn enrichment are located in the fine-grained parts and correlate to the strongest Pb- and Cu-enrichment zones. In the sandy material, as well as in silt- to clay-sized layers with lower metal concentrations, the metal-bearing minerals are randomly distributed. Bright spots within the 2D maps of the LIBS core scanner (Fig. 6) illustrate this. Within the fine-grained material with high metal concentrations, the metal-bearing minerals form layers, which can be observed in the maps as bright bands (Figs. 4 and 5).

Nickel and Co do not correlate with Pb, Zn, and Cu (Figs. 4, 5). Although concentrations for both metals vary along the drill cores, they do not show distinctive enrichment zones, as it is the case for Pb, Zn, and Cu. The strong correlation between Ni und Co is due to the occurrence within the same mineral bravoite $((Fe_{0.7}Ni_{0.2}Co_{0.1})S_2)$, a variety of pyrite. The beautifully zoned bravoite from the Maubacher Bleiberg deposit, where these ore processing residues come from, is very famous and can contain Ni and Co concentrations up to 25% and 14%, respectively (Vaughan, 1969). The fine-grained material in general contains more Co and Ni compared to the sand-sized material (Fig. 4). The relatively low variability in the Co- and Ni-concentrations within the fine-grained material probably result from a homogenous distribution of that mineral within the ore, and the fact that the Bravoite was not extracted from the Maubacher ore. Maximum concentrations occur at 778–782 cm depth with bulk concentrations of 342 ppm Ni, and 207 ppm Co.

The layers with the highest Co and Ni contents are generally characterised by high carbonate contents (Figs. 5 and 6).

Based on the investigated three core metres, the base metal concentrations within the tailing material are too low for a profitable re-use of the material. This is consistent with WDXRF analyses, which were done for further drill cores taken from other areas of the tailing site.

3.6. Comparison of LIBS and EDXRF

Within our study, both core scanners reveal sufficiently precise results for our application. However, both methods have their advantages and disadvantages. The main advantage of the LIBS core scanner is the high spatial resolution in x- and in y-direction of the analysis which enables the construction of two-dimensional element distribution images, as well as mineral/lithological distribution maps. This is helpful especially for irregularly structured or cross-bedded samples.

However, the bigger sample area of the EDXRF scanner can be an advantage, when horizontal layered cores are analysed and a better statistical coverage is needed.

Another advantage of the EDXRF technique is that it is nondestructive, except for subsequent luminescence dating (Davids et al., 2010). The laser from LIBS leaves behind minor destructions because it generates craters, ranging between several µm in the clay material and up to 1 mm in the sand. The remaining surface consists of molten material and has to be scraped in case of further analysis.

Although smooth surfaces are required for both techniques, they can cope with certain surface roughness. The ITRAX core scanner is equipped with a laser triangulation system, which enables the system to keep always the same distance between the detector and the sample surface. However, strong roughness differences within a narrow space cannot be followed by the measurement unit and a signal would be strongly weakened in such sections. In case of LIBS, some surface roughness is tolerated, due to a high depth of focus. The used drill cores showed variations in height of up to 2 mm (except for drying cracks) and no systematic errors depending on the surface morphology could be recognized.

Both core screening methods work best for dry samples since increasing water concentrations lead to lower signals (BUBLITZ et al., 2001; ESELLER et al., 2010; RAMMLMAIR et al., 2001). However, Bublitz et al. (2001) showed that for soil samples water contents up to 6% even increased LIBS emission intensities. Higher water concentrations lead to decreasing LIBS signals. Effects on emission due to water can also be observed for X-ray fluorescence. In a long-term experimental setup at sediment columns, which were stepwise saturated with water, Rammlmair et al. (2001) showed that for the EDXRF geoscanner (prototype of ITRAX core scanner from Cox) attenuation due to the water content is strong for light elements but less for heavy metals.

While the EDXRF technique is able to detect elements with an atomic number greater than 12, i.e. Al to U (Croudace et al., 2006), the LIBS technique is able to detect almost all elements. However, the number of elements, detectable by LIBS, strongly depends on the experimental setup, particularly the wavelength range and resolution of the spectrometer as well as the used measurement parameters. Therefore, LIBS is most efficient when the setup und the parameters are adapted to the sample matrix and the elements, which should be determined. The more elements should be measured, the more difficulties arise to detect all elements with a good precision.

Big challenges of LIBS analytics include quantification of the LIBS spectra which show a high amount of element emission lines with much interference. For the EDXRF technique, one should be aware of diffraction peaks which can occur in sand-sized material. This may lead to misinterpretation of occurring elements or distort element concentrations.

Measurement times of both scanners are highly variable depending on the statistical coverage needed. For the ITRAX scanner, measurement time and step size in the long direction (x) can be changed. The measurements in this study took about 12 h per drill core metre. For the used prototype LIBS core scanner, measurement time can be influenced by the step size in both x- and y- direction. The shown LIBS measurements were taken with 25 rows in ydirection and therefore took about 20 h per drill core metre. Since the scanner is not designed for fast measuring, the limiting factor is the time for reading/exporting spectra from the CCD, which are three spectra per second as well as the traversing time of the motorized stage. For both core scanners technical modifications would enable for shorter measurements.



Fig. 4. Comparison of element concentrations predicted by PLS (grey lines), and element concentrations analysed by WDXRF (black spots). The upper graphs contain LIBS results and the lower graphs EDXRF results. For a better comparison of the 2D LIBS mapping results with the 1D ITRAX element profiles, spectra from the y-direction were averaged to yield a single spectrum per depth. Due to strong correlations, Pb distribution patterns are representative also for Cu and S; Co also for Ni; Al₂O₃ also for K₂O, TiO₂, Na₂O, as well as Fe₂O₃; and MgO also for CaO and MnO.



Fig. 5. *A*: Spatially resolved element maps of one drill core metre measured with the LIBS core scanner. The predicted concentrations after PLS regression were transformed into grey value pictures. Bright colours reflect high and dark colours low concentrations. *B*: Lithological classification image generated by SAM and majority analyses on basis of the LIBS maps. C: RGB image reflecting the distribution of Pb + Zn + Cu-rich layers and Ni + Co-rich layers. Please note, the vertical stripe patterns, which occur in some maps, refer to artefacts, caused by calibration of the LIBS spectrometer, after every measured row in x-direction.

4. Conclusions

Within this study, two core scanning methods were applied to obtain chemical information for drill cores from tailing material of a former Pb–Zn-deposit.

- Whereas the LIBS core scanner is characterised by higher spatially resolved measurements and the opportunity to provide 2D element maps, the ITRAX core scanner utilises a wider sample area and delivers 1D element profiles of drill cores. For both core scanning methods, the intensities of some of the analysed elements are affected by matrix-effects, whereby element intensities measured with LIBS are more often altered, especially in the sandy parts.
- Therefore, the application of PLS regression turned out to clearly improve results for both core scanners because it compensates for most of the matrix effects. The validation results of the PLS model show, that the ITRAX core scanner yields slightly better correlation to bulk chemical WDXRF concentrations and lower standard deviations. Due to inter-elemental correlations, PLS regression can also be used to predict concentrations for elements, which are characterised by weak signals or cannot be measured at all (e.g. EDXRF Al, Co, Ba, Na, Mg).
- The distribution patterns of predicted element concentrations for whole drill cores are almost similar for both core scanners and show very good correlation to WDXRF concentrations. By means of the maps that were possible with the LIBS core scanner, conclusions

about the mineral distribution can be drawn. According to the spot size, mineral or lithological distribution maps can be generated by classification algorithms. The smaller the spot size, the more accurate the mineral distribution map. However, small sample areas also lead to inferior statistical coverage, when calculating average concentrations for whole layers.

 Using an ITRAX or LIBS core scanner, zones with elevated metal concentrations can be detected and conclusions about the lithological succession can be drawn. Especially for drilling campaigns with many cores, both screening methods deliver a good basis for selective subsampling. In consequence, the amount of sub-samples and therefore costs for further investigations can be reduced when these scanning techniques are applied.

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Fig. 6. Spatially resolved LIBS maps showing element distribution patterns of one segment within the silt/clay layers (left side, depth: 762–767 cm) and one segment within the sand (right side, depth: 700–705 cm), each about 5 cm long. Please note, the horizontal stripe patterns, which occur for some elements, refer to artefacts, caused by calibration of the LIBS spectrometer, after every measured row in x-direction.

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