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Application of self-organizing maps to the study of U-Zr-Ti-Nb distribution in sandstone-hosted uranium ores☆

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ABSTRACT

This paper presents a novel approach for processing the spectral information obtained from high-resolution elemental mapping performed by means of Laser-Induced Breakdown Spectroscopy. The proposed methodology is aimed at the description of possible elemental associations within a heterogeneous sample. High-resolution elemental mapping provides a large number of measurements. Moreover, typical laser-induced plasma spectrum consists of several thousands of spectral variables. Analysis of heterogeneous samples, where valuable information is hidden in a limited fraction of sample mass, requires special treatment. The sample under study is a sandstone-hosted uranium ore that shows irregular distribution of ore elements such as zirconium, titanium, uranium and niobium. Presented processing methodology shows the way to reduce the dimensionality of data and retain the spectral information by utilizing self-organizing maps (SOM). The spectral information from SOM is processed further to detect either simultaneous or isolated presence of elements. Conclusions suggested by SOM are in good agreement with geological studies of mineralization phases performed at the deposit. Even deeper investigation of the SOM results enables discrimination of interesting measurements and reveals new possibilities in the visualization of chemical mapping information. Suggested approach improves the description of elemental associations in mineral phases, which is crucial for the mining industry.

1. Introduction

This study was performed on the sample of sandstone-hosted uranium ore from Břevniště (north-east part of the Bohemian Cretaceous Basin) deposit which showed exceptional concentrations of uranium, zirconium, and niobium (see Table 1). The study of the spatial abundance of elements and their associations is difficult for these types of ores, due to the relatively small size of mineral phases (in μm), the gel nature of components, or both. Hence the application of conventional instruments for geological analysis, such as optical microscopy, electron microprobe, scanning electron microscopy or X-Ray Fluorescence (XRF), are often limited due to the low-grade ore. In the case of investigated uranium-bearing sandstones, the limiting factors are represented by the size of particles and the colloidal nature of some mineral phases. These methods need extensive sample preparation prior to analysis. However, for direct in-situ or stand-off detection the mentioned methods are not applicable. Analytical method with great potential to satisfy demands discussed above is Laser-Induced Breakdown Spectroscopy (LIBS). LIBS [1,2] is a promising analytical technique with rising popularity in the scientific community. With respect to other analytical techniques (Inductively Coupled Plasma (ICP), XRF, etc.), LIBS has many advantages such as instrumentation robustness, almost no sample preparation, possibility to study samples in solid, liquid and gaseous state of matter, and fine spatial resolution. The last mentioned brings the possibility of elemental mapping [3], shot-to-shot analysis enabling the study of elemental distribution. The spatial resolution can be further enhanced by a special arrangement called double pulse (DP) LIBS [4], which was utilized in this work. The utilization of DP-LIBS enables the usage of lower ablation energy resulting in lower sample damage and smaller crater size retaining the signal intensity. To a certain extent, DP-LIBS compensates for moderate disadvantages of LIBS, such as higher detection limits, lower stability, and moderate repeatability.

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The use of LIBS in the frame of geology has already been described in some works [5,6] concerning for example contaminants in ore analysis [7], in-situ qualitative and quantitative analysis of ores [8] and ore provenance [9]. Moreover, LIBS was, among other techniques, utilized on Mars Science Laboratory Curiosity rover [10], performing extraterrestrial geological analysis of Martian rocks for the distance up to 7 m. The majority of the mentioned geological applications of LIBS utilize one or more Multivariate Data Analysis (MVDA) statistical methods for dimensionality reduction or spectra classification. A comprehensive review by El Haddad [11] describes applications of various MVDA methods to LIBS. With regard to the chemical analysis, MVDA is often called "chemometrics". Since the interest in MVDA is rising, some recent papers discuss the influence of data pre-treatment [12] and outliers identification [13] on the performance of analysis.

The possibility of uranium detection using LIBS brings interesting applications such as process control of nuclear reprocessing plants or inspection of nuclear facilities [14,15]. The most comprehensive study of LIBS applicability for uranium detection is given by Chinni et al. [16], focusing on applications connected with issues of weapons of mass destruction and environmental surveillance. In [16] Chinni et al. calculate the detection limits and its improvements in various LIBS experimental configurations, namely DP technique, analysis under buffer gas or reduced atmosphere, and even stand-off analysis.

The association of elements U-Zr-P-Ti is unique for the origin deposit (Břevniště ore field, Czech Republic). Based on the results of the complete chemical analysis (Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), see Table 1) of powdered fragments of 26 rocks; a single flat sample with the highest content of uranium was prepared for LIBS measurement. Each mentioned element is represented with a large number of lines in LIBS spectrum. Therefore, MVDA can be used for dimensionality reduction or selection of important spectral features.

By utilizing Principal Component Analysis in one of our previous studies [17] we have shown that chemical composition can be estimated from the variability in the dataset. Moreover, it has been demonstrated that utilization of a subset of original data as an input to the MVDA algorithm leads to identical results, for the case of heterogeneous datasets.

This paper shows a novel approach to study and visualize elemental association of complex geological samples by the implementation of self-organizing maps (SOM). SOM was applied on a shot-to-shot analysis of the datasets acquired by LIBS technique introduced in [17]. Hereinafter we refer to the simultaneous presence of spectral lines of different elements within a respective single spectrum as an elemental association in the interaction region.

2. Methods

2.1. Self-organizing maps

SOM is a type of artificial neural network trained to produce low-dimensional, discretized representation of the input data. SOM utilized in this work were introduced by Tuevo Kohonen [18] and are often called accordingly – Kohonen maps. SOM consist of so-called neurons or nodes. Each neuron is represented as the vector of weights (of the same length as the input data; in our case the wavelengths of emission spectra) and the position in a map space. The map space is initially organized in either rectangular or hexagonal grid. Afterward, the neuron map is trained according to the input data which results in changes of weights and positions in the map space.

SOM training is an iterative process, where SOM is adapting to the input data. At each iteration, a single object (in our case a single spectrum) is taken from the input data, and its distance to all neurons is calculated (in our case Euclidean distance in the multidimensional space formed by the spectral variables under study). The closest neuron is considered as the winning neuron (called the best matching unit (BMU)), and its internal weights are adjusted accordingly to the input object. Moreover, the neighborhood (in most cases the closest 4 to 8 neurons) of the winning neuron is also adjusted, but with lower weights. The rate of adjustments is decreasing with the rising iteration number, and the training continues until a number of iterations reach previously stated high number. The training procedure is sometimes called competitive-cooperative training, where competitive part of training is the determination of winning node and cooperative part of training is the adjustment of neighboring neurons. The SOM was, in our case, trained with a representative subset of 1000 spectra on a rectangular grid with 30 × 30 neurons (a square grid with a comparable number of neurons and number of spectra in a representative subset).

3. Experimental setup

3.1. Sample

Břevniště deposit is one of the uranium deposits of sandstone type situated within ore district and the geological structure called the Stráž block [19] (in the area of northern part of the Bohemian Cretaceous Basin, Czech Republic). Unique association of elements U-Zr-P-Ti characterizes the ore field and forms mostly fine-grained mineralization located in the Cenomanian sediments (especially sandstones and siltstones) [20]. These host rocks are composed mainly of quartz, clay matrix and accessory minerals (such as oxides, sulfides or carbonates). The mineralization is a result of an incursion of ore-forming solutions into intergranular spaces or its interaction with clay matrix in pores among quartz grains. Specific nature of this deposit resides in the occurrence of uraniferous hydrozircon and leucoxenes *s.l.* (alteration products and mixtures of Fe-Ti oxides) and partial colloidal to meta-colloidal nature of ore minerals [21].

The sample studied by the LIBS was a small flattened piece of sandstone cemented with Araldite epoxy, for the detailed description of the preparation process we refer to our previous work [17]. Prior to the flattening and cementing, approximately 30 g of sample were crushed and pulverized into very fine powder using an agate mill for

Table 1
Comparison of U, Zr, Nb and major oxides contents in studied uranium ore, with the average contents in sandstones from another U-deposit (but in the same uranium-bearing region) and outside the ore field. Values in the brackets indicate, how many times is a concentration of a given elements higher at the Břevniště deposit.

Element locality	U [ppm]	Zr [ppm]	Nb [ppm]	TiO_2 [wt%]	Fe_2O_3 [wt%]	P_2O_5 [wt%]
Břevniště[a]	3838.0	¿50,000.0	3424.0	0.10	1.41	0.91
Osečná-Kotel[b]	202.3 (19×)	210.1 (238×)	6.4 (535×)	0.23 (0.4×)	1.43 (1×)	0.07 (13×)
Outside ore-bearing area[c]	2.3 (1670×)	100.0 (500×)	6.0 (570×)	0.10 (1×)	0.84 (2×)	0.02 (46×)

Notes:
[a] Average contents of the investigated sample.
[b] Sandstone-hosted U-deposit within the North Bohemian Cretaceous Basin, CZ [22,23].
[c] Average contents in sandstones outside the ore-bearing area (within Bohemian Cretaceous Basin, CZ) [24,25].