

INVESTIGATION OF POTENTIAL OF LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR DETECTION OF SPATIAL DEPOSITION AND μ CT FOR VOLUME DEPOSITION OF CRITICAL METALS IN MINERALS/ORES

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INTRODUCTION

The platinum group metals (PGMs) i.e. platinum, palladium, rhodium, iridium, osmium and ruthenium represent the key materials for automotive exhaust gas treatment. Since currently exist no adequate alternatives, the importance of these metals for automotive industry is steadily rising [1]. Identification of selected metals in real time directly at the deposit sites is nowadays very complicated, especially at locations with extremely harsh climatic conditions and with no access to the local energy sources, such as Talnakh deposit, Siberia, Russia. Especially the spatially resolved chemical measurements so called chemical images or compositional maps which can be utilized for instance for interpretation of ore formation history in mineralogy it is complicated to do out of laboratory.

One of the most promising methods, which is nowadays under rapid research in the field of mobile chemical analysis, is Laser-Induced Breakdown Spectroscopy (LIBS). LIBS is a simple atomic emission spectroscopy technique capable of real-time, essentially non-destructive determination of the elemental composition of samples of any state of matter (solid, liquid, or gas) with a great potential for chemical mapping [2]. Recently, LIBS potential has been well publicized when selected for Mars exploration [3]. In order to obtain volume information about

the samples, the μ CT station has been employed, which in combination with LIBS brings the information about the 3-dimensional spatial distribution and amounts of selected metals in the sample volume.

Both LIBS and μ CT have already been developed as mobile devices demonstrating a great potential of these methods for in situ analysis.

The process of verification of LIBS and μ CT as useful techniques for in situ mineral analysis and rare ores localization, respectively, was performed in following steps. Firstly, verification of LIBS in laboratory conditions by table top setup on polished samples prepared for reference technique (Tescan Integrated Mineral Analyzer) was realized. The chemical maps of different elements were compared with TIMA pictures. It was established that the spatial distribution of each element from LIBS chemical map is in agreement with the spatial distribution of corresponding minerals in TIMA pictures. It was established that particular elements corresponding to particular minerals have the same spatial distribution in LIBS chemical maps as in TIMA pictures. Then the tomograms were compared with LIBS chemical maps. The cut $1 \mu\text{m}$ under the polished sample surface was selected. The results from both LIBS and μ CT were combined to prepare 3D chemical map of the sample.

SAMPLES

Unique Talnakh PGE-Cu-Ni sulfide deposit is located in the northwest flank of the Triassic basalt trap formation of Siberia. All metals entered the basalts owing to a remobilization (recycling) of ore elements. The discovery of the Talnakh deposits with high-grade sulfide ores confined to the base of Early Triassic thin (150 m in average) sill-shaped bodies of the giant Siberian traps significantly influenced concepts of the origin of magmatic copper-nickel ores. Intensive attention from the world's leading scientists to the Talnakh and spatially and temporally associated Norilsk deposit is due to uniquely giant sizes of ore bodies; their assumed association with the young Mesozoic Basalt Traps; and the fact that all other large known deposits of copper-nickel and platinum ore deposits in the world are much more older and associated with giant Proterozoic ultramafic-mafic intrusions. The discovery of a new type of ore deposits not only changed the situation in the world's mineral markets, but also strongly improved the understanding of magmatic sulfide ore formation. If the hypothesis of a genetic link between ore formation and the trap rocks is correct, similar deposits may be discovered in all continents affected by the global Mesozoic trap magmatism or all other planets where huge trap magmatism occurred during its evolution history.

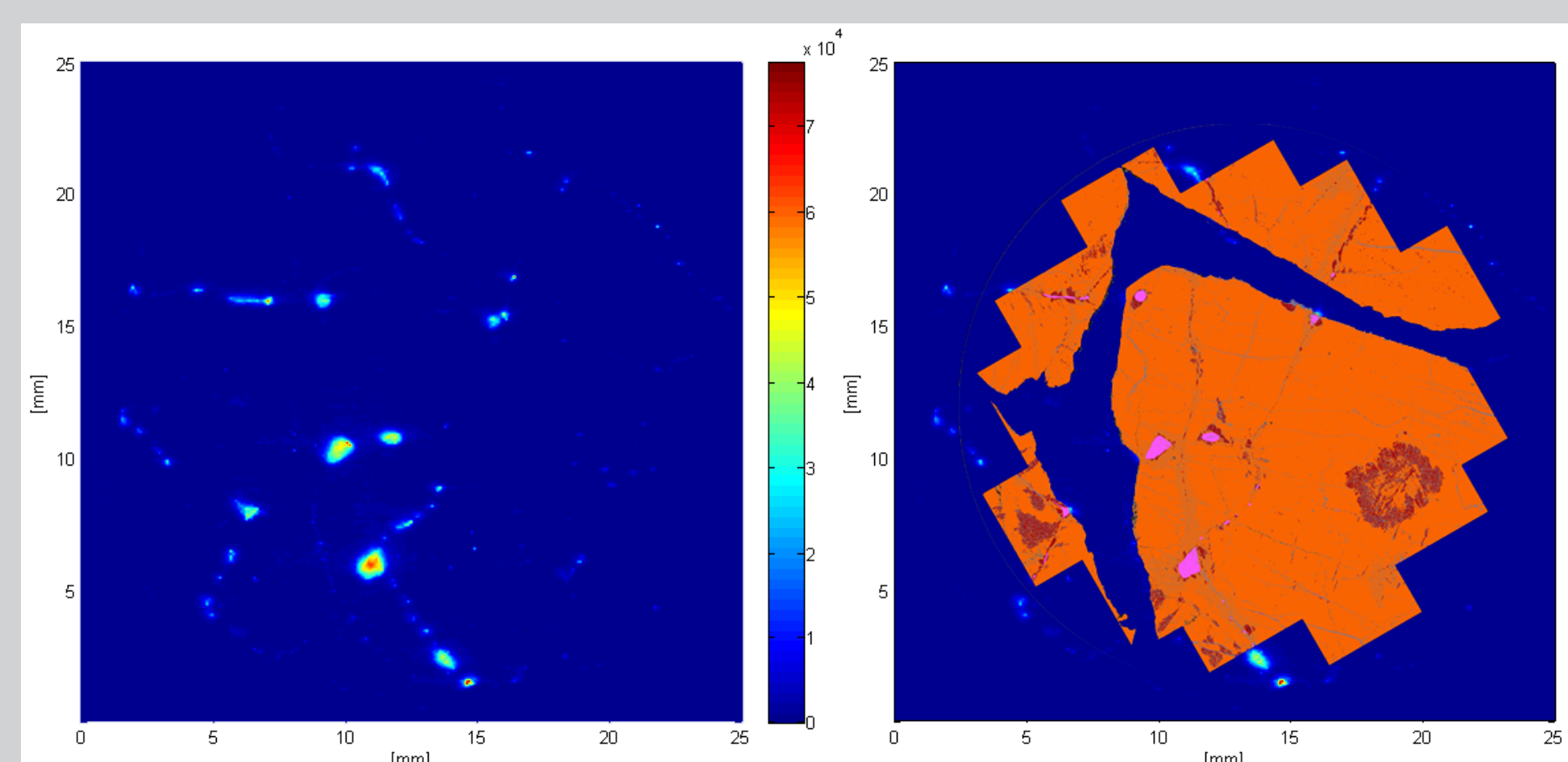


FIG. 3 EXAMPLE OF CHEMICAL MAPS OBTAINED VIA LIBS (LEFT SIDE) AND TIMA (RIGHT SIDE). THE SIZE AND ORIENTATION WAS ADJUSTED IN ORDER TO COMPARE BOTH LIBS AND TIMA IMAGES. IN LIBS CHEMICAL MAPS THE COLOR CORRESPONDS TO RELATIVE CONTENT OF LEAD. IN TIMA IMAGES DIFFERENT COLOR CORRESPONDS TO SPECIFIC MINERALS (SEE FIG. 1-2).

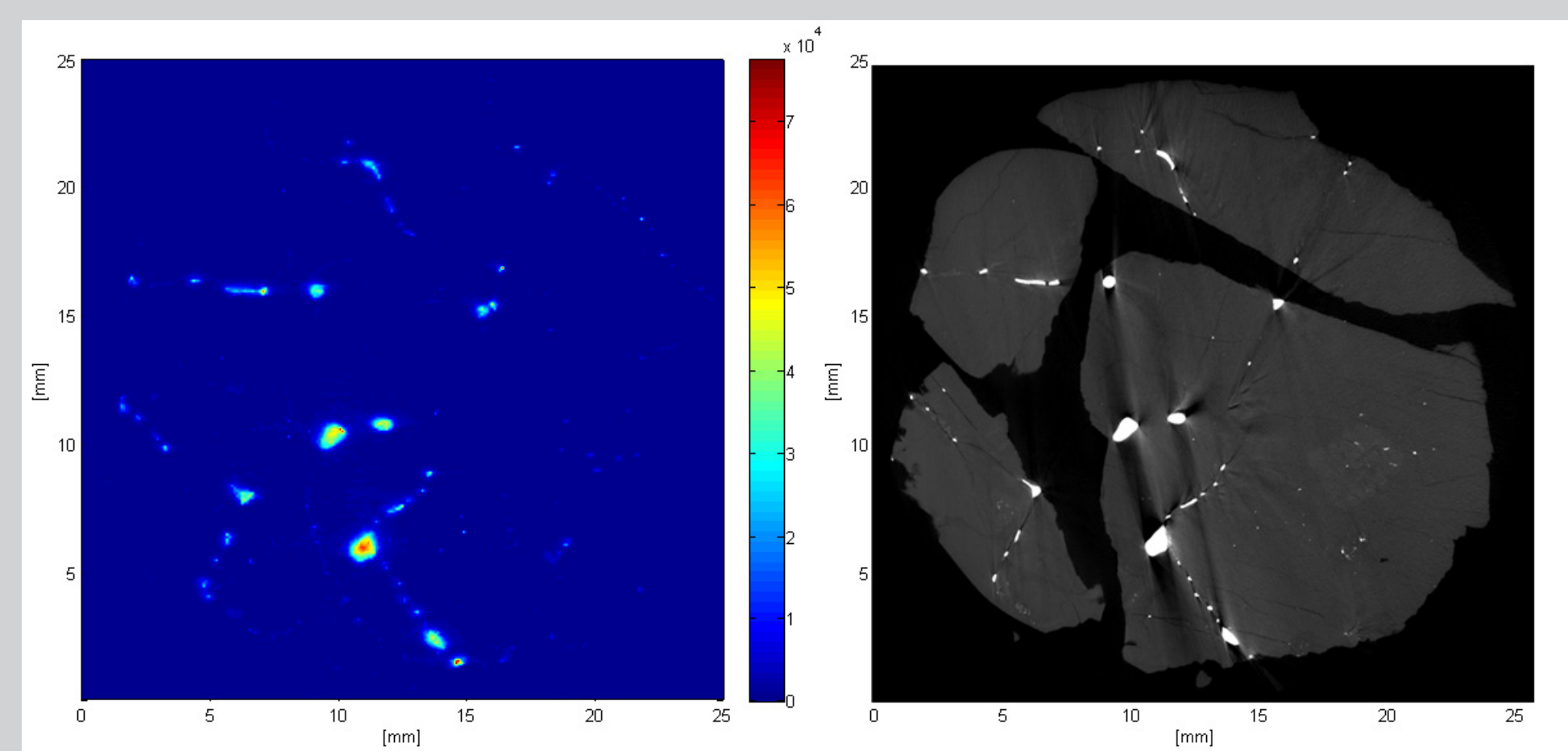


FIG. 4 CHEMICAL MAP OF LEAD (LEFT SIDE) AND TOMOGRAM. THE ORIENTATION AND SIZE WAS ADJUSTED FOR EASIER COMPARISON. THE SPOTS ON THE TOMOGRAM WITH HIGHER CONCENTRATION OF Pb ARE WHITE.

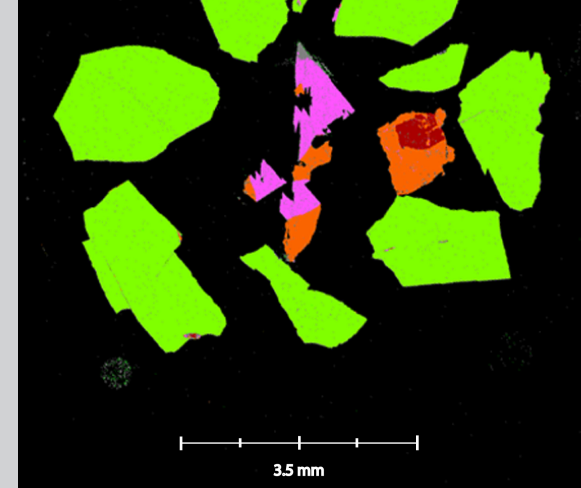
RESULTS AND DISCUSSION

LIBS RESULTS VALIDATION

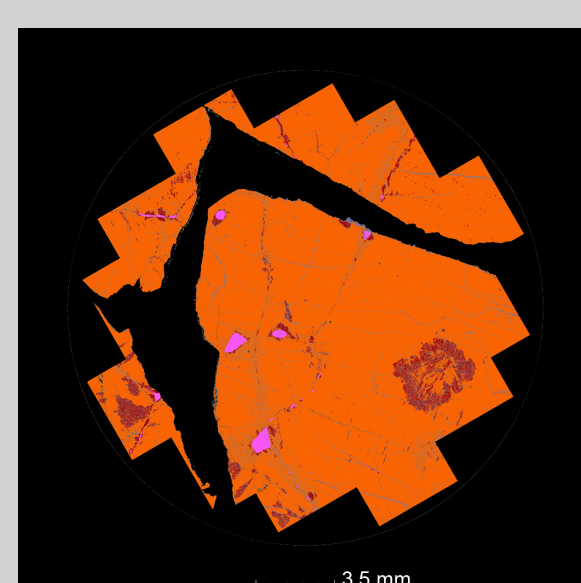
In order to examine the capability of LIBS for high-resolution chemical mapping, the area of $25 \times 25 \text{ mm}^2$ was sampled with the spatial resolution of $100 \mu\text{m}$. In the first step, the resulting chemical maps were compared with the pictures obtained via TIMA. Special attention was paid to the spatial deposition of individual minerals and corresponding elements within the sample. After resizing and rotation of the chemical maps, respectively TIMA pictures, it is clearly visible that the elements corresponding to individual minerals have the same spatial deposition within the sample Fig. 3. The rescaled TIMA pictures were placed into the coordinate system of LIBS pictures for easier comparison. In the Fig. 3 there is for the illustration chemical map of lead and TIMA pictures. The mineral description and the chemical formula of TIMA pictures is on Fig. 1 and Fig. 2.

In the Fig. 4 there are the chemical maps of lead (left side) and the tomogram (right side) – the plane $1 \mu\text{m}$ under the sample surface - depicted. The size and the orientation of pictures were adjusted for easier comparison. The white spots represent places with higher density of mineral. On the basis of the spatial distribution of these spots it is supposed on Galenit (white spots) and Pentlandite (grey spots).

FIG. 1 IMAGE OBTAINED FROM TIMA - SEPARATED SPERRYLITE GRAINS



SPERRYLITE PtAs_2
GALENA PbS
PENTLANDITE $(\text{Fe,Ni})_9\text{S}_8$
CHALKOPYRITE CuFeS_2



FERRO-ACTINOLITE $\text{Ca}_2\text{Fe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
GALENA PbS
PENTLANDITE $(\text{Fe,Ni})_9\text{S}_8$
CHALKOPYRITE CuFeS_2

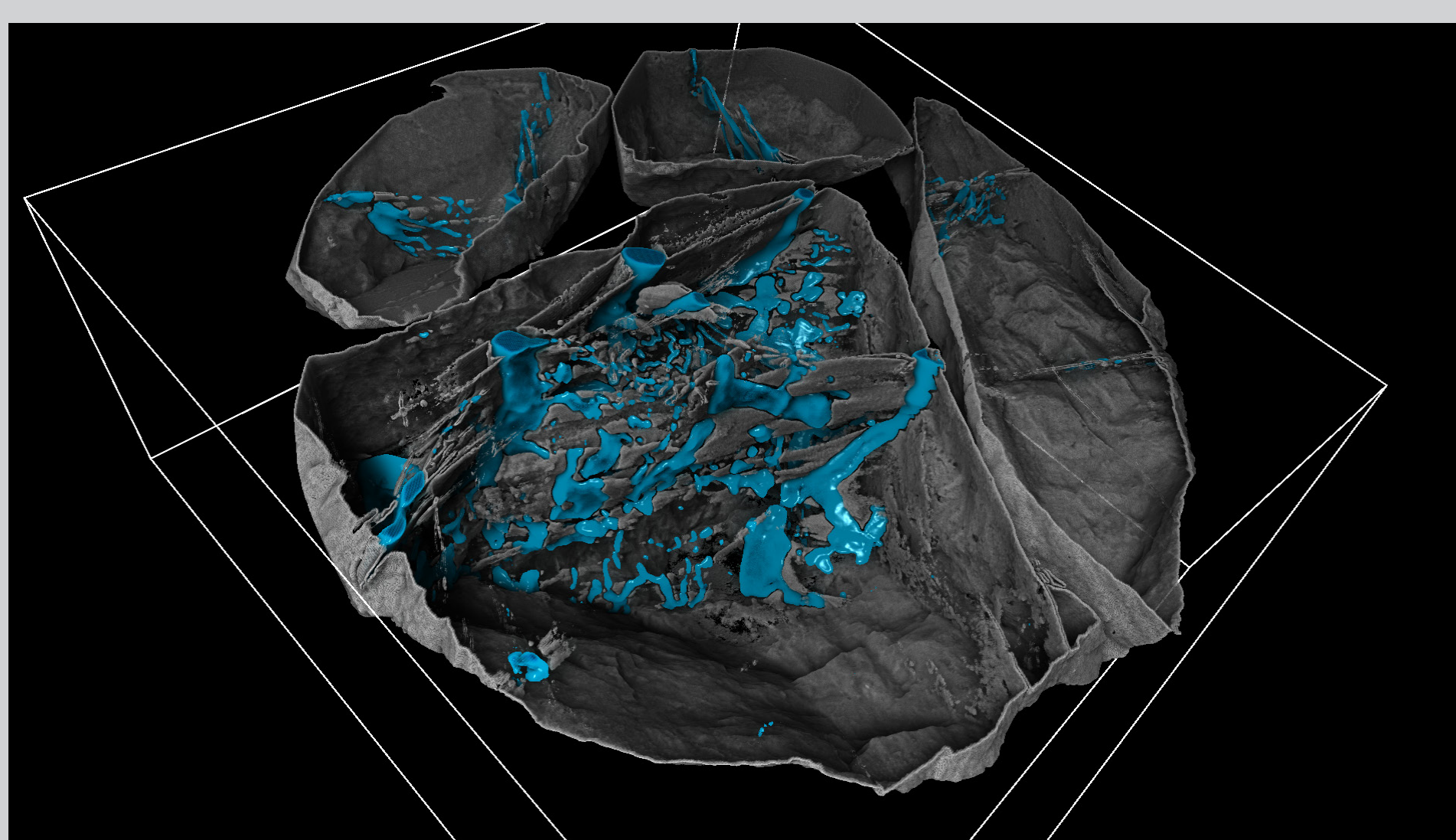


FIG. 5 SPATIAL DEPOSITION OF GALENA IN THE VOLUME OF THE SAMPLE.

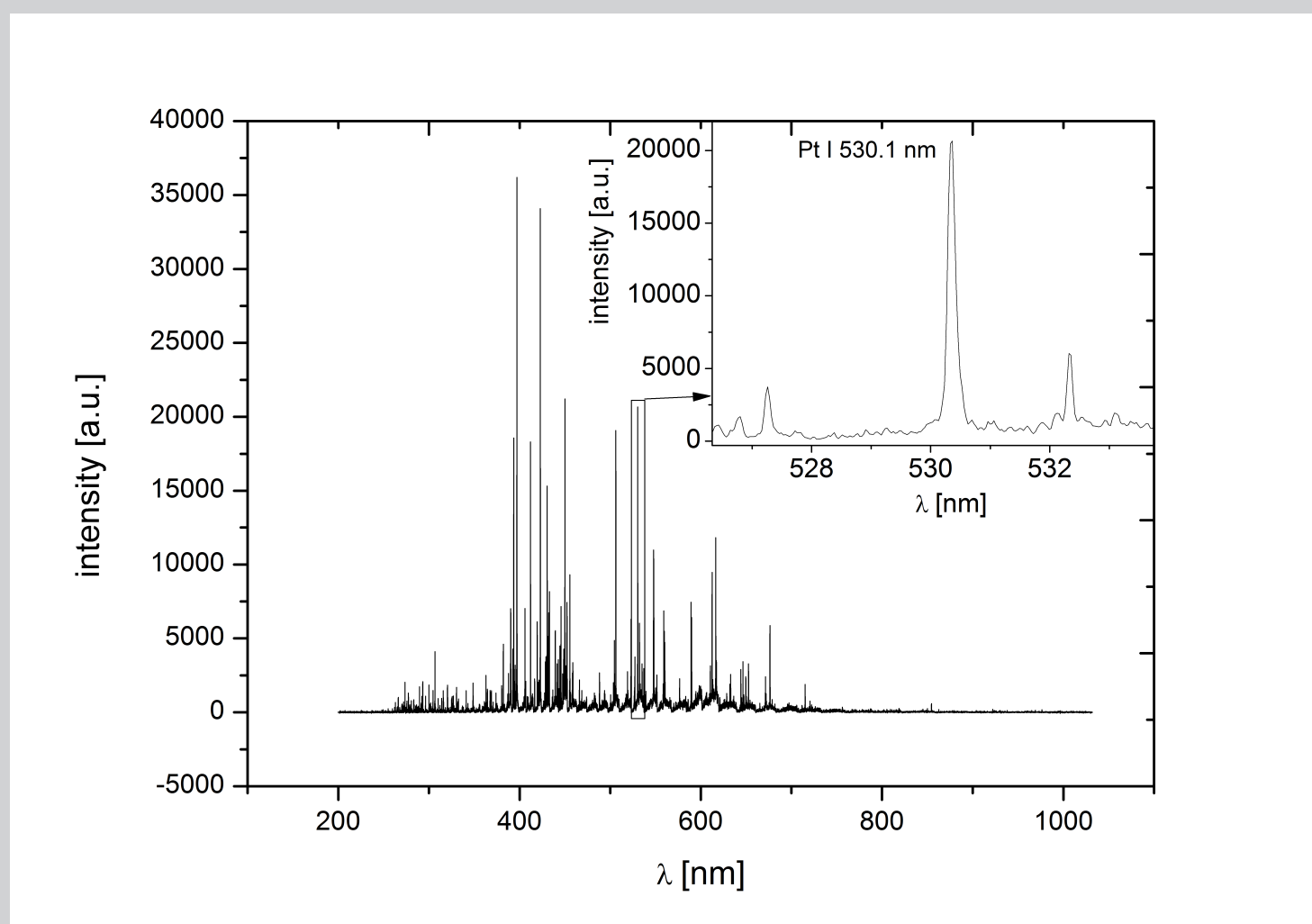


FIG. 6 TYPICAL LIBS SPECTRUM OF SPERRYLITE OBTAINED VIA STAND-OFF LIBS WITH ENLARGED AREA WITH SPECTRAL LINE OF PLATINUM.

Since the position of each mineral in the 2-dimensional tomogram is determined, it is then possible to prepare 3-dimensional chemical map of mineral distribution in the sample volume Fig 5.

STAND-OFF MEASUREMENTS

In the last step, a couple of measurements using so called stand-off LIBS were performed to prove the capability of LIBS to detect selected metals in minerals for larger distances (in our laboratory conditions the distance was limited to 6.2 m). Special emphasis was put on the capability of stand-off LIBS to detect sperrylite as a potential source of platinum. Fig. 6 shows typical spectrum obtained via stand-off LIBS. High signal to noise ratio of Pt spectral line proves the ability of stand-off LIBS to detect Sperrylite even for higher distances. In the frame of ongoing research the upgrade of the experimental setup is planned, which will combine both detection for higher distances and high resolution mapping. This will be allowed using the custom software capabilities and 2-axes motorized rotation of the detection.

CONCLUSIONS

In this work we demonstrated the capability of LIBS for the detection of selected metals in geological samples. Moreover, we showed that it is possible to prepare multi-elemental chemical map of selected elements with relatively high spatial resolution ($100 \mu\text{m}$) and that the detection of metals

EXPERIMENTAL METHODS

TESCAN INTEGRATED MINERAL ANALYZER (TIMA)

There has to be chosen a reference technique to LIBS, which complies with certain conditions – a well-described industrial device, which is able analyze minerals in acceptable time, and it has to be well-tested on various samples. As the best option Tescan Integrated Mineral Analyzer (TIMA) was selected.

TIMA combines Back-scattered electron spectroscopy (BSE) and Energy-dispersive X-ray spectroscopy (EDX) data for automatic measurement of mineral abundance, mineral liberation and association, particle and grain sizes and bright particles on multiple samples of grain mounts, thin sections or polished sections. TIMA can find its application in ore characterization, search for precious metals and rare earth minerals, remediation and many other areas.

TIMA has been tested and used for the examination of various samples. Using scanning electron microscope together with various detectors enabled identification of the mineral species in detail and at the same time it is a powerful tool for broadening the knowledge of ores and ore deposits in general. Additionally, TIMA allows high speed automatic data acquiring and processing at the same time, thereby it offers various types of analyses depending on required results.

LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

The beam of ablation laser was directed normal to the surface sample by mirrors and focused onto the sample surface by a 30 mm focal length glass triplet. The beam of the second laser was directed parallel to the sample surface to the plasma using mirrors and focusing lens of 40 mm focal length. The setup is composed of two Q-switched Nd:YAG lasers both operating at 10 Hz. LQ 529a (SOLAR, BY) Fig. 1.1 operated at the second harmonic (532 nm) with the pulse width $\sim 10 \text{ ns}$ was used as the ablation source and Brilliant B (Quanteq, FR) Fig. 1.7 at first harmonic (1064 nm) with the pulse width $\sim 6 \text{ ns}$ was used for reheating the plasma. The energy of primary/ablation laser pulse was 30 mJ per pulse and the energy of secondary/re-excitation laser pulse was 110 mJ per pulse.

The sample was mounted on the stage with precision movements ($2 \mu\text{m}$ resolution) inside the ablation chamber (Tescan a.s., CZ). The ablation spot was targeted and controlled by a CCD camera placed outside of the ablation chamber.

The LIBS plasma radiation was collected with UV-NIR achromatic collimating mirror system, the CC52 (ANDOR, UK) Fig. 1.4 and transported by the fiber optic system ($25 \mu\text{m}$ in diameter) onto the entrance of spectrometer in Echelle configuration (ME5000, Mechelle, ANDOR, UK) Fig. 1.5. As the detector ICCD camera (iStar 734i, ANDOR, UK) Fig. 1.6 was employed.

μ CT

The μ CT analysis of this sample was performed using GE phoenix|x-ray tomography system |tome|x s, equipped with a 240 kV / 320 W maximum power microfocus X-ray tube. To achieve the smallest tube spot size it was necessary to keep as small X-ray energy as possible. For this reason, no filter was installed in the beam path. The μ CT scan was carried out at 220 kV and 65 μA acceleration voltage and X-ray tube current, respectively. With such energy the tube spot size was $14.3 \mu\text{m}$. The linear voxel size of obtained volume was $14.8 \mu\text{m}$. At an integration time of 1000 ms, 2400 projections were taken over 360° . The images were projected onto high contrast digital array detector DXR250 with 2048×2048 pixel, $200 \times 200 \mu\text{m}$ pixel size. The μ CT scan was carried out in the air-conditioned X-ray cabinet (21°C).

The tomographic reconstruction was realized using datos|x 2.0 3D computed tomography software. The 2D-cross section visualizations were performed with VG Studio MAX 2.1 software and 3D visualizations with volume exploration and presentation tool Drihti.

may be performed for larger distances.

To prove the LIBS capability for multi-elemental chemical mapping, the chemical map of the area of $25 \times 25 \text{ mm}^2$ was prepared on the samples measured with special mineral analyzer TIMA and the results were compared. Special attention was focused on the spatial distribution of minerals and elements, respectively.

For obtaining the information about 3-dimensional spatial distribution of selected metals in the ore volume, the chemical maps were combined with tomograms.

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