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THE FIRST APPLICATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY: A FAST-ANALYTICAL TECHNIQUE IN TARGETED SEARCH FOR ELEMENTS IN GEOLOGICAL SAMPLES FROM DEEP BOREHOLES IN LATVIA

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Laser-induced breakdown spectroscopy (LIBS) provides a rapid, cost-effective, and extra-sensitive analysis of geological samples to make preliminary conclusions about the presence of valuable elements up to the trace levels in the ore. We present the first results of a highly sensitive qualitative analysis of the core samples of geological ore from two boreholes in Latvia (Staicele 1, from a depth range of 794–802 m, and Garsene (Subate) 2A, from a depth range of 1102–1103 m) using LIBS. Our measurements using this technique confirmed the high iron content and indicated traces of rare and high in-demand metals (such as Ti, V, Co, Sm, etc.) in the sample from Staicele, renewing interest in studying boreholes across Latvia. The presented pilot studies demonstrated effectiveness and unique possibility in performing a very sensitive and time-saving qualitative analysis of the composition of samples of ores from the old but still valuable borehole cores by using the LIBS method. We compare these measurements with other methods of sample analysis.

Keywords: *Deep boreholes, geological samples, laser-induced breakdown spectroscopy, valuable elements in the ore.*

1. INTRODUCTION

Mineral magnetite $Fe^{2+}Fe_2^{3+}O_4$ is the main compound of iron ores. Magnetic anomalies caused by magnetite iron ores have been known in Latvia for a long time. They were identified in the northern, southern, and central parts of the country in several studies in the 1960s and described in the book [1]. Gneiss with a high content of magnetite was firstly discovered within a borehole at Staicele, in the northern part of the magnetic belt crossing Latvia in a north-south direction [2], [3].

Staicele and Garsene (Subate) deposits are located in the Latvian–East Lithuanian (LEL) tectonic block (Fig. 1) that consists of gneisses, schists, and amphibolite and includes numerous magnetic anomalies [3], [4]. The concentration of metal ores took place during the metamorphism. In total, more than 26 billion tons of iron ore reserves have been estimated across the country [5]. In the 1980s, costly drillings were carried out and core samples of iron ore from wells were collected and studied. Iron-rich ores were formed in the Proterozoic by deposition of iron compounds on the sea floor after which they were metamorphosed. During their formation the some ores (i.e., Garsene deposit, Sample #2) were enriched during underwater volcanism [5].

The additional value of iron ores deposits is presence of metals and other elements, i.e., manganese, cobalt, phosphorus, etc. in concentrations raising interest owing to steady progress in extraction technologies [6]. The use of advanced methods of materials analysis is a way to determine the iron content and to reveal the traces of the rare and high-demand metals.

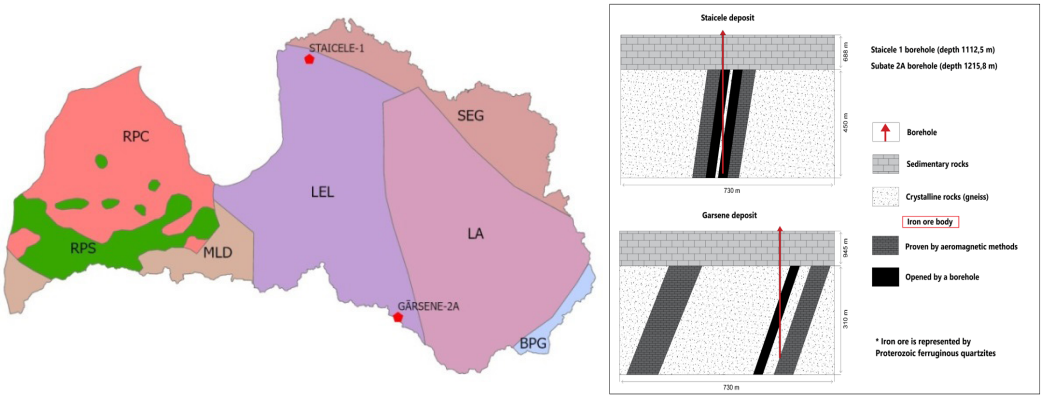

Fig. 1. Locations of the examined iron ore deposits and geological structure of ferruginous quartzite deposits.

Left panel: locations of the studied iron ore deposits – Staicele-1 and Garsene (Subate)-2A and the disposition of the crystalline basement tectonic complexes of Latvia (modified after [3] and [4]): RPC – Kurzeme Pluton Central part – rapakivi granites; RPS – South Kurzeme Pluton South – anorthosites and gabbro-norites; MLD – Mid Lithuanian Domain (West Lithuanian Granulite Belt); LEL – Latvian–East Lithuanian gneiss and amphibolite block; SEG – South Estonian (Estonian-Latvian) granulite belt; LA – Latgalian granite and gneiss block; BPG – Belarus–Podlasie granulite belt.

Right panel: geological structure of ferruginous quartzite deposits – Staicele (according to Staicele 1 exploration borehole) and Garsene (Subate) (according to Subate 2A exploration borehole) in LEL tectonic domain of northern and southern zones (modified after [5] by D. Vorobyov interpretation).

This article presents the results and preliminary conclusions of the pilot studies of elemental composition of two samples of magnetite ores obtained in the 1980s from the boreholes at Staicele and Garsene (Fig. 1, left panel) using the most advanced and sophisticated current method available: laser-induced breakdown spectroscopy (LIBS). The data were compared with results obtained by other methods of material analysis: X-ray diffractometry (XRD), energy-dispersive X-ray fluorescence (EDXRF), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX). Core samples were obtained from deposits at drilling depths of up to 1 km and deeper (Fig. 1, right panel). The full collection of materials is located in the core sample storage facility at Gardene (at the Latvian Environment, Geology and Meteorology Centre in the municipality of Dobele).

2. EXPERIMENTAL ARRANGEMENTS AND DESCRIPTION OF SAMPLES

LIBS is a sophisticated spectrometric technique [7] applicable to the direct, highly sensitive, and non-destructive spectral analysis of objects of various origins (interacting only with hundreds of ng to a few μg of the sample material). It is used to measure the concentration of macro- and micro-components in solid, liquid, and air samples. The advantage of the method is a relatively simple experimental setup, which includes a laser, a focusing system, a detector, a spectral device, and a data processing system (Fig. 2), and an exceptional ability to indicate the presence of very small concentrations of elements in the sample. Samples for use in the LIBS method of analysis are quick to prepare and enable spectral recording and simultaneous spectral identification [8].

The method is based on the study of the emission spectrum from the plasma induced by a highly energetic, short laser pulse focused on the surface of the sample. The spectral emission characteristics from laser-induced plasma produced on the surfaces of selected samples are analysed in the UV to near-infrared spectral regions.

The experimental procedure is as follows. Laser pulses (HP), with a duration of 150 ps at the wavelength λ=1064 nm and with energies E_{HP} = 15 mJ, were focused using a silica glass lens (L) with a focus of 300 mm. The time delay between the laser pulse and the registration of spectra (integration time T_{int}=1 μs) was controlled by a trigger signal (TS). The delay was fixed at 200 ns to reduce the influence of the continuous plasma emissions at the early stages of laser-induced plasma formation. The spectra were registered using the collecting optics (CO), spectrometer (SP), and iCCD camera.

Laser-induced ablation forms a crater on the sample surface with a typical diameter of 30–400 μm. Laser plasma can be created at any point of any material regardless of its aggregate state. The ablation of atoms from the surface of the sample is induced by a laser pulse for a few tens of nanoseconds, heating the targeted point on the sample surface resulting in electron temperatures of the plasma up to 10 eV and ensuring the excitation of resonance spectra of atoms and even ions of elements present in the sample [9]. It is possible to study a composition (up to trace level) of a very wide range of completely different materials (various gaseous mixtures, metals, alloys, organic samples, geological ores, and minerals, etc.) [10]. As it has been mentioned above, an addi-

tional advantage of LIBS technology is the possibility to perform a fast analysis of the composition of elements in various places of borehole core samples for a highly sensitive search for the inclusions of exotic elements. Particularly, LIBS is considered to be practically indispensable for the detection of light elements such as lithium and beryllium, which are problematic for other spectroscopic methods [11].

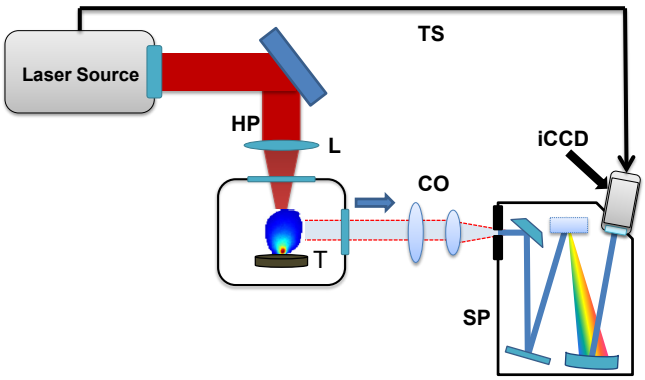

Fig. 2. Experimental scheme for LIBS. Laser source – 150 ps pulses at 1064 nm, TS – a trigger signal from a laser source, HP – a heating pulse, L – 300 mm focusing lens, T – a target, SP – a spectrometer, CO – collecting optics, iCCD – detector (intensified CCD camera).

Samples collected for analysis were the rare and unique geological materials from the boreholes in Latvia's two largest and most promising deposits – Staicele and Garsene. Each of these two fields has one geological exploration well: named Staicele 1 (at Staicele) and Subate 2A (1979) (at Garsene). The analysed geological materials were taken from the core samples at certain depths, i.e., from the layers of the deposits with the richest magnetite content.

Traces of some elements, such as cobalt, titanium, vanadium, etc., are currently becoming critically important for the EU industry. Particularly, the mass fraction of V_2O_5 reached 0.2 %, as it was determined during the studies performed by the aforementioned instrumentation at the Faculty of Chemistry of the University of Latvia. Staicele iron deposit ores (Sample #1 from a depth range of 794–802 m) have the same history but, in addition, contain a relatively high amount of manganese (the mass fraction of MnO reaches 6.65 %).

3. RESULTS OF LIBS MEASUREMENTS

LIBS measurements were carried out to study the elemental composition of the ore from the Staicele deposit (Sample #1) where the main mineral is magnetite. For the analysis of the selected sample, the laser beam was pointed at the zone with the largest area of magnetite to initiate and study ablation plasma. Table 1 presents the data from the LIBS analysis of Sample #1, comprising a complete list of all elements found in the spectra of LIBS based on the spectra of the studied sample (Fig. 3). These results include the common and intense resonance spectra lines of core elements (iron, manganese, and silicon), as well as the presence of atomic resonance lines of many other elements, including rare earth elements at trace levels, which are important for the industry [12].

Table 1. Elements Detected by the LIBS Method in a Sample of Magnetite Matrix #1 from the Staicele Deposit Evidenced by their Main Resonance Lines

Element	Wavelength, nm	Element	Wavelength, nm
Rb	354.115	Ca	393.366
Fe	355.492	Ca	396.846
Cr	357.868	Tb	400.547
Pm	374.586	Ga	403.298
U	375.834	Mn	404.135
Cr	381.543	Tc	404.911
Fe	382.444	Mn	405.554
Ho	382.927	Th	405.925
Tc	383.282	V	406.392
In	383.465	Fe	407.173
Tm	383.820	Mn	407.941
Mg	383.829	Co	411.877
Pr	384.659	Gd	413.228
Dy	386.880	Mo	414.355
Th	388.691	Gd	426.012
Si	390.552		

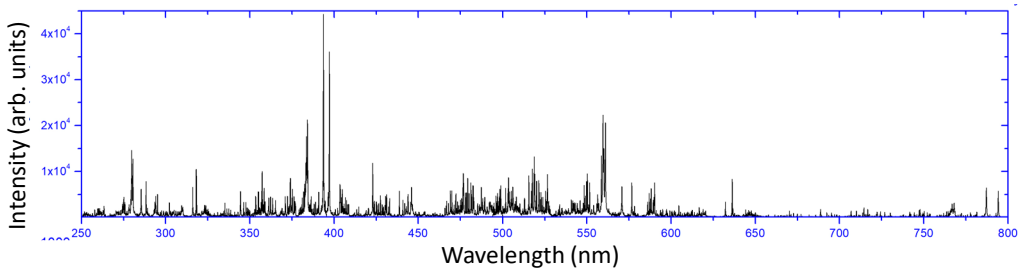

Fig. 3. Example of LIBS plasma emission of Sample #1 (magnetite matrix from the Staicele deposit) recorded 200 ns after ablation by 150 ps laser pulse. The intense lines represent the atoms of the main components in the sample. The interpretation of the spectrum in the region of 354–427 nm is given in Table 1.

Analysis of the spectra obtained from Sample #1 evidenced the presence of the traces of various lanthanides, such as Gd (gadolinium), Tb (terbium), Dy (dysprosium), Pr (praseodymium), Tm (thulium), Ho (holmium), and Pm (promethium). Resonance lines of the atoms of actinides, e.g., U (uranium), Th (thorium), and Tc (technetium), were also present in the spectra. Tc (technetium) is formed due to the radiative decay of radioactive U (uranium) and Th (thorium) isotopes. The presence of Mo (molybdenum), Co (cobalt), V (vanadium), Ga (gallium), In (indium), Cr (chromium), and Rb (rubidium) is evidenced by the typical atomic spectra of the elements mentioned.

The presence of the main components (Fe, Mn, and Si) in the Staicele samples, as well as small amounts of a few other elements (particularly rare earth elements), was also confirmed by other methods. For comparison with our LIBS measurements of Sample #1 resulting in the identification of a large list of elements, we present the results obtained by other methods, leading

to the identification of the presence of only a few elements with low concentrations. The measurements using SEM-EDX were carried out by targeting micro-inclusions in the studied samples differing from the main ore mass by visual signs (colour, lustre, fracture, cleavage), which are rather difficult to diagnose by the XRD method.

XRD and EDXRF were made available at the Faculty of Chemistry of the University of Latvia and the Assay Office of Latvia to analyse the elemental content and other characteristics of the two samples and compare them with the LIBS experiment. X-ray diffraction diagram of two studied samples of magnetite ore confirmed the presence of magnetite (Fig. 4).

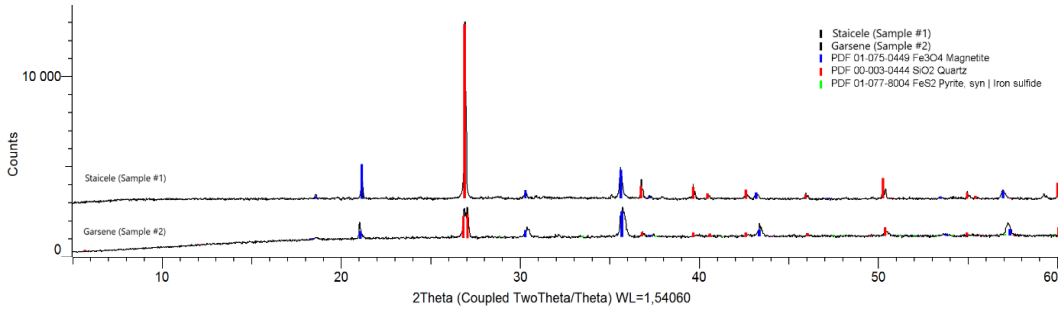

Fig. 4. X-ray diffraction diagram of two studied samples of magnetite ore confirming the presence of magnetite. Further studies of the samples were carried out precisely in the magnetite matrix of the samples.

The elemental qualitative analysis was performed using the EDXRF method. From the comparison of the results of the EDXRF method with the XRD data, it can be concluded that the iron in the samples is in the form of magnetite and pyrite (FeS_2).

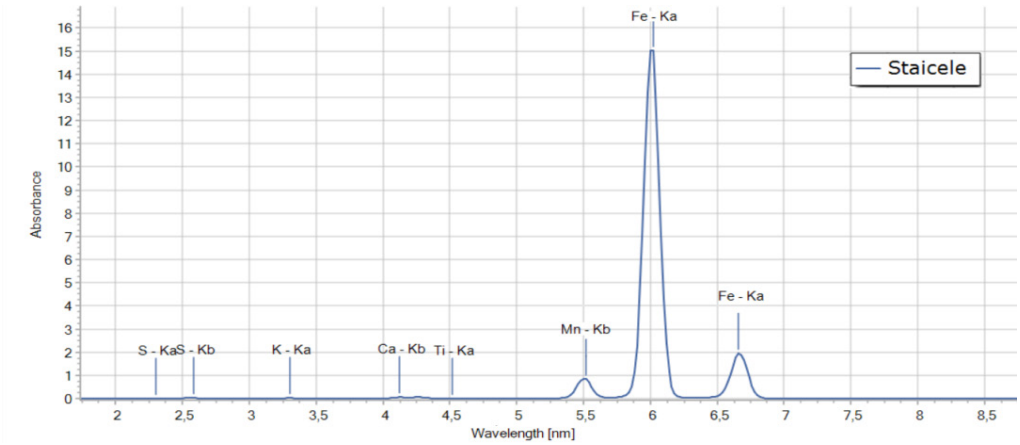

Fig. 5. Example of EDXRF results of Sample #1 from Staicele deposit, which shows a high content of iron in the sample, as well as the impurities of other elements, which are in the form of micro-inclusions of minerals in the studied ore matrix.

The spectrum (Fig. 5) clearly shows that the EDXRF confirmed the presence of the elements, which, in addition to manganese and titanium, can be contained in other associated minerals – ingrowths, e.g., pyrite and various other silicates.

Other minerals, for example, annite - $KFe^{2+}_3(AlSi_3O_{10})\ (OH)_2$), from the biotite group, and almandine - $Fe^{2+}_3Al_2(SiO_4)_3$] rarely found in samples are also the sources of iron. These minerals are found in small quantities, but still can be sources of other "exotic" elements available to advanced extraction methodologies despite small concentrations in the mineral (Fig. 5, Table 2). The largest contributor of iron to the ore is magnetite, which was confirmed in the previously presented spectra and ensured its strong magnetism.

Table 2. Elements Detected by the EDXRF Method in the Samples of the Magnetite Matrix #1 and Matrix #2 from the Staicele and Garsene Deposits

Oxide of element	Sample #1 (Staicele)	Sample #2 (Garsene)
	W, %	
Si_O2	51.9	35.6
Fe_2O_3	36.0	52.4
MnO	5.17	0.03
Al_2O_3	5.01	3.49
MgO	-	3.43
CaO	1.03	1.94
K_2O	0.65	0.17
TiO_2	0.19	-
SO_3	0.09	-
P_2O_5	-	2.72
V_2O_5	-	0.197
Y_2O_3	-	0.008
CuO	-	0.023

The EDXRF data (Table 2) contain information about the elements that were not diagnosed with LIBS (potassium, titanium). This difference is explained by the fact that the EDXRF method analyses the larger surface of the sample. At the same time, its definition boundary is much smaller than that of LIBS, so the data 1 and 2 of Table 2 are distinguishable. In this case, EDXRF shows the main chemical composition of the analysis zone. Meanwhile, LIBS shows the part of the same zone with the presence of elements that EDXRF cannot determine.

The ablation spectra of the geological core sample (#2) from Garsene were measured and compared with the ablation spectra of a pure iron sample (see the recordings of spectra in Fig. 6). This was carried out using pulse energy of 17–20 mJ, pulse duration of 28 ps, an integration time of 2 s, and a delay of 1 sec between the heating pulse and the ICCD gate.

Sample #2 came from a geological core at a drilling depth of 1102–1103 m. Sample #2 appears to be a shiny black mass of magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$) with yellow scar inclusions. Weak yellow inclusions may comprise pyrite (FeS_2), pyrrhotite (Fe_7S_8), or troilite (FeS). The remarkable content of Co, Mn, and several other elements was foreseen earlier based on general considerations and literature data [6].

The black curves in the recorded LIBS plasma spectra of Sample #2 in Fig. 6 are the non-calibrated experimental data. The red, green, and blue curves are taken from the NIST data [13]. The atomic spectrum of Fe from the NIST tables was compared with the LIBS plasma spectra of Sample #2 and the highest purity Fe sample.

The spectra obtained from highest purity Fe show relatively good coincidence with NIST data for Fe I and Fe II, evidencing the proper calibration of our spectrometer. The spectrum of Sample #2 coincides well with the spectra of atomic Fe I and Fe II of an elemental sample of Fe, which means that Sample #2 was predominantly iron.

In contrast to Sample #1, we were unable to find the resonance lines of other metals, even at a trace level. Such a result can be explained by the fact that the position of target ablation in LIBS analysis was located in a crystal of pure magnetite. This is valuable information from a mineralogical point of view, emphasising the advantage of using LIBS in a geological sample analysis.

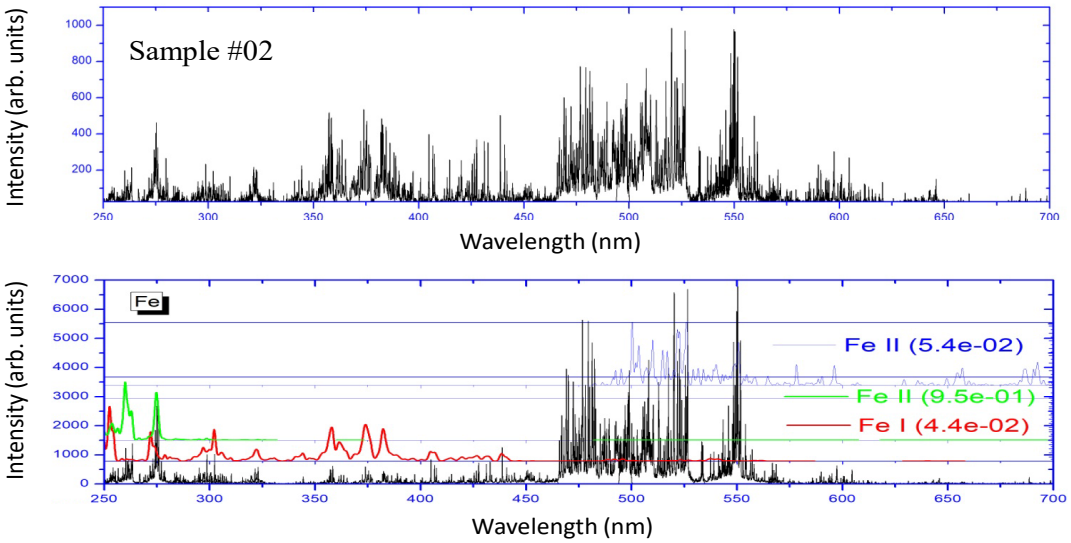

Fig. 6. Upper panel: LIBS of Sample #2 from the Garsene – Subate 2A (1979) borehole. Bottom panel: spectrum of pure iron measured using LIBS. Blue, green, and red spectra are taken from [13] for the iron atoms and ions.

4. DISCUSSION AND CONCLUSION

These pilot studies demonstrated the value and need for further applications of the LIBS technique in studies of Latvian geology, among others, intending to dis-

cover economically usable metal ores in crystalline basement rocks at depths ranging from 300–1900 m [4]. The data of XRD were included for comparison with the results obtained using LIBS. Repeated analyses were carried out to confirm the conclusions made using the LIBS. XRD method showed the main mineralogical composition of the studied zone within the detection limits of 0.5%. This made it possible to show the main mineralogical composition excluding microinclusions of other minerals, since this method does not allow studying such small inclusions. Therefore, SEM-EDX was used to recognise microinclusions. This allowed confirming the mineralogy described in previous studies. We did not carry out detailed studies using above methods while considering it sufficient to describe the data in the form of mentioning the minerals without attaching the spectrum to each inclusion, since in this article we were concentrated on the studies of LIBS.

We also included the results of the EDXRF of our samples. The analysis was performed in the same place as LIBS, but the results still differed slightly due to the specifics of these two methods. Due to the fact that the area for EDXRF is larger, a slightly different result is obtained due to the fact that more magnetite matrices with microinclusions of other minerals fall into the analysis area. The advantage is that EDXRF confirms both the presence of the main elements that are part of the minerals diagnosed by the XRD method and those found by the LIBS method. Meanwhile, LIBS in turn shows the content of other useful elements reliably detected by this method, while EDXRF cannot show the content of these elements. Therefore, it is possible to predict the prospects for the use of ores from these two deposits using LIBS. The locations of the deposits are shown in the schematic geological map (Fig. 1), drawn on the basis of the data available in the literature. In Western Latvia, where the basic intrusions are located, the presence of various metals, including precious metals, is possible. The LIBS method could be particularly useful in studies of such deposits.

In conclusion, our studies have shown that the LIBS methodology has the unique ability to conduct sensitive, efficient, not time-consuming qualitative investigations of ore compositions. In the case of core Sample #1 from Staicele, the LIBS technique demonstrated the ability to identify tiny amounts of priceless substances that should be considered for extraction. The presence of Mo, Co, V, Ga, In, Cr, and Rb, and traces of several lanthanides including Gd, Tb, Dy, Pr, Tm, Ho, and Pm (as well as the actinides U, Th, and Tc) were discovered and compared to past examinations.

The results of the study of core Sample #2 by the LIBS method, demonstrated a high iron content and the presence of silicone-based minerals. The presence of iron was confirmed by other techniques that were earlier applied to this sample. Iron was indicated as the second element after silicon at a mass fraction reaching 37 %. The important finding during the application of LIBS technologies in the case of the core sample from Garsene (Sample #2) is a confirmation of the absence of other metals and rare elements identified in the core sample from Staicele (Sample #1), even at a trace level, providing the important information for eventual planning on future exploitation of relevant ores. Our pilot studies, using LIBS methods, show the possibility to obtain promising and remarkable added value, in the case of comprehensive renewed studies of already existing geological borehole core samples related to geology and prospective industrial extraction of various components as well.

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