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Laser-induced breakdown spectroscopy to detect critical raw-materials in rocks and minerals

Janna Lappalainen

Author Janna Lappalainen	
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Supervisor Jussi Leveinen	
Thesis advisor(s) Ilkka Laine, Luis Huaman, Nicolas Barban	
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Abstract

In today's society, the demand for certain metals continues to grow, but their limited availability poses challenges. The European Union (EU) has identified a group of critical raw materials that are essential for the economy, technology, and the environment. These materials are highly relevant, and research aimed at improving their detection and availability is significant.

This thesis focuses on the use of Laser-Induced Breakdown Spectroscopy (LIBS) in the detection of critical raw materials in rocks and minerals. LIBS is an analytical technique that enables the determination of the elemental composition of a given sample. This work consists of a literature review and an experimental section. Initially, general theory related to rocks and minerals is discussed. Additionally, EU's critical raw materials, including rare earth elements and nickel, are introduced. In the third subsection, the LIBS process and its advantages and challenges, both in general terms and in a geological context, are examined. The experimental section details how LIBS technology can be used to detect nickel metal in a rock sample.

The central result of the experiment was the successful detection of nickel in the rock sample. The work shows that LIBS performs well at a general level in identifying different elements, but it faces challenges related to the reliability and precision of the analysis. By focusing on addressing these challenges, LIBS technology may have the potential to play a broader role in geological research in the future.

Keywords Laser-induced breakdown spectroscopy, LIBS, Metals, Rare earth elements, Nickel, Rocks, Minerals

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Tiivistelmä

Nyky-yhteiskunnassa useiden raaka-aineiden kysyntä on kasvanut, mutta samalla niiden rajoitettu saatavuus luo haasteita. Euroopan unioni (EU) on identifioinut kriittisten materiaalien joukon, johon kuuluvat raaka-aineet ovat keskeisiä talouden, teknologian ja ympäristön kannalta. Nämä raaka-aineet muodostavat modernin yhteiskunnan perustan, ja niiden loppuminen voisi johtaa monenlaisiin huolestuttaviin seurauksiin. Siksi näiden materiaalien saatavuuden varmistaminen on erityisen tärkeää, ja tutkimus niiden havaitsemisen parantamiseksi on merkityksellistä.

Valtaosa EU:n kriittisistä raaka-aineista on metalleja, joita saadaan maaperästä louhituista malmeista. Metalleja tarvitaan jatkuvasti useilla eri teollisuuden aloilla. Samalla kun perinteiset teollisuudenalat, kuten ruostumattoman teräksen valmistus, kuluttaa runsaasti erilaisia metalleja, niin myös uudet vihreän siirtymän myötä nousseet teknologiat, kuten sähköautojen akut sekä uusiutuva energia, tarvitsevat kasvavia määriä useita eri raaka-aineita.

Kiristyneen raaka-ainetilanteen malminetsintöjen sekä kaivoshankkeiden määrä on noussut viime vuosina uusien malmiesiintymien löytymisen toivossa. Malminetsinnöissä saatujen kivinäytteiden analysointiin on olemassa lukuisia erilaisia menetelmiä, joista erityisesti Laser-indusoidun plasmaspektroskopian (Laser-induced breakdown spectroscopy, LIBS) käyttö on ollut viime aikoina keskiössä. LIBS on analyyttinen menetelmä, jossa hyödynnetään pulssilaseria näytteiden analysoimisessa. Laserpulssi irrottaa pienen osan materiaalia näytteen pinnasta muodostaen plasmaa. Plasmassa olevat atomit siirtyvät hetkeksi korkeammille energiatasoille ja palatessaan perustilaansa ne emittoivat kullekin alkuaineelle ominaista valoa. Emittoituva valo muodostaa LIBS-spektrin, joka antaa informaatiota näytteen koostumuksesta. Geologian tutkimuksessa LIBS on herättänyt erityistä kiinnostusta myös siksi, koska tekniikan avulla voidaan suorittaa mittauksia paikan päällä ja tulosten saaminen on nopeaa.

Opinnäytetyö koostuu kirjallisuuskatsauksesta ja kokeellisesta osuudesta. Työssä tutustutaan yleisellä tasolla kiviin ja mineraaleihin sekä EU:n kriittisiin raaka-aineisiin lukeutuviin harvinaisiin maametalleihin ja nikkeliin. Lisäksi perehdytään siihen, miten LIBS-analyysi toimii, ja käydään läpi sen etuja ja haasteita niin yleisellä kuin geologisella tasolla. Kokeellisessa osuudessa tutkitaan Talvivaaran kaivokselta kairattua kivinäytettä LIBS-menetelmällä, ja tavoitteena on selvittää, sisältääkö kivinäyte nikkelimetallia.

Kokeen keskeisin tulos oli, että LIBS-menetelmällä pystyttiin havaitsemaan nikkelin esiintyminen kivinäytteessä. Työstä selviää, että LIBS toimii jo hyvin yleisellä tasolla eri alkuaineiden tunnistamisessa, mutta se kohtaa haasteita analyysin luotettavuuden sekä tarkkuuden kanssa. Ymmärtämällä näitä haasteita paremmin ja keskittymällä niiden kehittämiseen LIBS-menetelmällä voi olla potentiaalia toimia tulevaisuudessa entistä laajemmin osana malminetsintöjä sekä geologista tutkimusta.

Avainsanat Laser-indusoitu plasmaspektroskopia, LIBS, Harvinaiset maametallit, Nikkeli, Kivet, Mineraalit

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1 INTRODUCTION

During the 21st century, our society has become increasingly dependent on certain materials. The rapidly growing electricity and battery industries consistently require more critical metals, such as gallium, and germanium. Additionally, climate change and the green transition have increased pressure on raw material production. While the production of metals should be made more sustainable, new green environmentally friendly technologies require larger quantities of critical metals.[1]

All metals are obtained by mining ores from the bedrock. Even metals like gallium or rare earth elements, which belong to the rarest high-tech metals, are not created from scratch. For modern society, mining and obtaining metals are essential, and their depletion could lead to concerning consequences. Despite the importance of the mining industry, it is overshadowed by its negative societal and environmental impacts. Additionally, establishing a mine is a time-consuming process. From the initial ore exploration to the actual establishment of the mine, it can take over a decade[2]. [3],[1]

The utilization of Laser-Induced Breakdown Spectroscopy (LIBS) is one way to drive mining industry and ore exploration in a more sustainable direction. LIBS is an atomic emission spectroscopic technique that can be used for determining the elemental composition of substances [4]. The technique is fast and capable of analysing samples in different states (solid, liquid, gas). In geological research and mineral exploration, LIBS has given promising results. By utilizing LIBS, the elemental and mineral composition of rocks can be quickly determined on-site, which helps geologists and researchers make quick decisions in real-time. Additionally, LIBS can directly measure samples from rocks, even several meters away. In this way, it is possible to make the planning of mining operations more cost-effective, time-saving and environmentally friendly. [5]

In this bachelor's thesis, the focus is on exploring, how LIBS works and how it can be used to detect critical metals in rocks and minerals. This work consists of both a literature review and an experimental section. The theory section is divided into three subsections. The first part covers general theory related to rocks and minerals. In the second part nickel and rare earth elements, which EU has classified as critical raw materials, are presented. The third subsection focuses on the LIBS process, its benefits, and challenges both at a general level and within a geological framework.

In the third section, the focus is on the experimental part. The purpose of the experiment was to determine how LIBS works when measuring nickel from a rock sample. First, the sample under investigation and its characteristics are presented. In the next section, the execution of the experiment is introduced. In the third subsection, the collected data is processed using MATLAB. The results are examined in the fourth section. The last part presents the conclusions.

2 THEORY

2.1 Minerals and rocks

As previously mentioned, LIBS can be used to analyse substances in solid, liquid, and gaseous states [5]. Nonetheless, this thesis narrows down to the first category, specifically to minerals and rocks.

The foundation of the Earth's solid surface lies in the arrangements of ions, atoms, or ionic groups, which are upheld by different chemical bonds. In other words, minerals are constructed through the precise ratios of anions and cations. Rocks are made of minerals, and rocks form the solid bedrock. The layer of soil is found above the bedrock. [6]

2.1.1 Minerals

Minerals are the basic building blocks of rocks and each of them has a characteristic chemical composition and crystal structure. structure. Rocks typically consist of 3-5 different minerals, ranging in size from 0.1 to 5 mm. For example, granite (a rock type) consists of quartz (a mineral), feldspar (a mineral), and mica (a mineral). The most common elements that occur in minerals are Si (silicon), O (oxygen), Al (aluminium), Fe (iron), Ca (calcium), Na (sodium), K (potassium), and Mg (magnesium) [7].

The latest evaluation by The Commission of New Minerals and Mineral Names (CNMMN) has revised the number of known minerals to 5955 in July 2023 [8]. To simplify the handling, the extensive range of minerals must be divided into groups [9]. Minerals can be sorted into different groups using various criteria, including their elemental composition, crystal arrangement, connections with other minerals, natural occurrences, or history. One of the oldest and still extensively used mineral classifications is the Dana Classification System, published by James Dana in 1837. It divides minerals into nine classes based on their chemical composition and crystal structure. The classes are Native Elements, Sulphides, Sulphates, Halides, Oxides, Carbonates, Phosphates, Silicates, and Organic Minerals. [6]

Silicates constitute the majority of various rock types, comprising approximately 90-95% of the Earth's crust. This mineral group can be further divided into subgroups, including Nesosilicates, Sorosilicates, Cyclosilicates, Inosilicates, Phyllosilicates, and Tectosilicates. Silicates have a crystalline structure composed of silicon and oxygen, forming a four-sided silicon-oxygen tetrahedron (SiO_4 tetrahedron) as presented in figure 1. At the center of the tetrahedron, there is a silicon atom surrounded by four oxygen atoms. [10], [7]
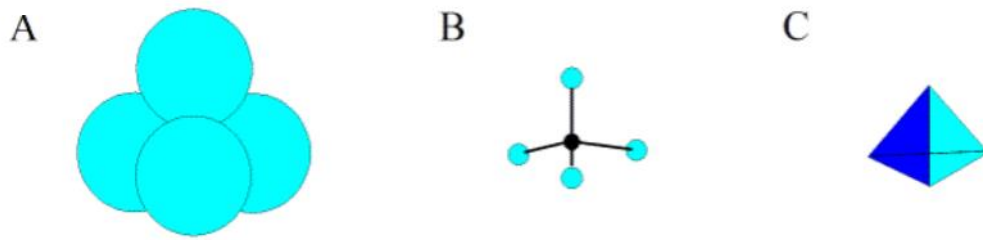
FIGURE 1.   Three different illustrative images of the tetrahedral (SiO$_4$) structure [10].

Accurate mineral identification usually requires the examination of their chemical composition and crystal structure, which necessitates the use of analytical instrumentation. However, minerals also have several visually observable characteristics that help differentiate the species from each other. These characteristics include, for example, color, hardness, cleavage, luster, specific gravity, and crystal form. [7]

Ore refers to a natural mineral deposit from which the extraction of metals is economically viable. Examples of such minerals include chalcopyrite, which yields copper, and bauxite, which yields aluminium. Before ores can yield usable metals, they undergo various enrichment and refining processes. Metals form the foundation of modern industrial societies, and ensuring their availability is particularly important. [3]

2.1.2 Rocks

The Earth's crust can be divided into the oceanic crust and the continental crust. The oceanic crust is mainly composed of basalt (rock) and is relatively thin, with an average thickness of about 7 kilometers. The continental crust is thicker, with an average thickness of about 40 kilometres, and it consists of various rock types. [6]

Rocks are formed from interconnected minerals. Although there are thousands of different minerals, only about 30 of them are significant in terms of rock formation [9]. The compositional and structural characteristics of rock types depend on their origin, which classifies them into igneous rocks, sedimentary rocks, and metamorphic rocks. [7]

Igneous rocks are formed from cooled magma in volcanic eruptions or in the Earth's crust or mantle. Sedimentary rocks are formed through the accumulation and lithification of weathered products from all three rock groups. These rocks are typically relatively lightweight and porous. Metamorphic rocks are any type of rocks that have undergone changes in temperature, pressure, or chemical environment, resulting in chemical or physical transformations. [7], [6]

2.2 Critical raw materials

The European Union has identified a group of critical raw materials (CRMs) that are significant for modern technology, the economy, and the environment. The criticality of these materials is based on their economic importance and supply risk from the EU's perspective. The evaluation has done every 3rd year since 2008. In the latest review in 2023, the European Union identified 34 materials as critical raw materials. CRMs are listed in table 1.[6], [11]

TABLE 1.   Critical Raw materials in 2023 [11].

Main results of the 2023 criticality assessment

The following 34 raw materials are proposed for the CRM list 2023:

2023 Critical Raw Materials (*new CRMs in italics*)			
aluminium/bauxite	coking coal	lithium	phosphorus
antimony	*feldspar*	LREE	scandium
arsenic	fluorspar	magnesium	silicon metal
baryte	gallium	*manganese*	strontium
beryllium	germanium	natural graphite	tantalum
bismuth	hafnium	niobium	titanium metal
boron/borate	*helium*	PGM	tungsten
cobalt	HREE	phosphate rock	vanadium
		*copper**	*nickel**

In the following subsections, rare earth elements and nickel are presented. Both elements belong to the EU's critical raw materials, as indicated in Table 1. The selection of these elements was based on my personal interest and the fact that in the experimental section, the aim was to detect nickel using LIBS.

2.2.1 Rare earth elements

The rare earth elements (REEs) are a group of 17 elements including scandium (atomic number 21), yttrium (atomic number 39), and the lanthanides (atomic numbers 57-71). The lanthanides consist of lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium [12]. Metals are further divided according to their weight into light rare earth elements (LREE: La-Sm) and heavy rare earth elements (HREE: Eu-Lu) [1]. Rare earth elements are quite abundant in the Earth's crust, despite of their misleading name. The challenge lies in their low concentrations in the soil. Rare earth elements occur in small amounts in several different minerals, which makes their economic extraction difficult. [13]

The demand for Rare Earth Elements REEs has increased due to the adoption of new, more sustainable technologies. For example, Neodymium and praseodymium are strongly magnetic materials and due this property their most significant application area is in permanent magnets. Permanent

magnets are needed, for example, in wind turbine generators in windmills and in electric vehicle motors. Another significant use of rare earth elements REEs is in NiMH batteries, where materials such as lanthanum, cerium, and small amounts of neodymium are used. [1]

The availability of rare earth elements is further complicated by the fact that their mining is concentrated in specific geographical areas. The largest deposits of REEs are in China, which accounts for about 86 percent of the world's annual production. This has led to the dependency of many Western countries on China for these metals. To improve the situation, the mining of REEs has been reinitiated in recent years in some Western countries. Additionally, numerous mineral exploration projects have been initiated worldwide, including in Finland. Additionally, in some projects, Laser-Induced Breakdown Spectroscopy LIBS has been utilized for elemental identification. [14]. Despite the efforts, obtaining these metals is still quite challenging and expensive. [15]

2.2.2 Nickel

Nickel (Ni) is an element of the iron group with the atomic number 28. It is a silver-gray metal that is tough and corrosion-resistant [16]. Metal usually occurs in nature as sulphide minerals, and it is one of the most used metals in the industry due to its many useful properties. [17]

Pentlandite is the most common nickel-containing sulphide mineral on Earth and a significant source of nickel metal. The chemical formula of pentlandite is $(Fe,Ni)_9S_8$ and it is part of the pentlandite mineral group. This mineral group also includes argentopentlandite $Ag(Fe,Ni)_8S_8$, cobalt pentlandite $(Co,Ni,Fe)_9S_8$ and sugakite $Cu(Fe,Ni)_8S_8$. Pentalandite is a small-grained, soft, brittle and bronze-yellow mineral. The crystal system of pentlandite is cubic, but it occurs mostly as precipitates or grains in other minerals. Nickel metal is obtained in a process where ore containing pentlandite is crushed and foamed. [17], [9]

Currently, the nickel market can be observed to have two main segments. Firstly, the usage of nickel in rechargeable batteries has significantly increased due to the growing popularity of electric cars and the higher demand for renewable energy. Simultaneously, the traditional use of nickel in stainless steel manufacturing maintains a strong position. Nickel's versatility makes it a significant metal in diverse markets, as it serves both new innovations and traditional sectors.[18]

Compared to rare earth elements, the production of nickel is distributed more evenly across different regions, and it does not face the same kind of supply issues. There are also few operating nickel mines in Finland. The largest of them is the Boliden Kevitsa mine in Sodankylä, which started its operations in 2012. Another operating nickel mine in Finland is in Sotkamo's Talvivaara, which started its mining operations in 2008. Additionally, the Hitura copper and nickel mine in Nivala operated for over half a century before its closure in 2017. However, in recent years, ore exploration has been resumed in the area in the hope of discovering new deposits. LIBS technology has also been used in some mineral exploration projects in Nivala, and the results have been promising. [19]. [20]

2.3 LIBS-theory

Laser-inducted breakdown spectroscopy is a fast and straightforward technique that can be used to analyse different materials. LIBS uses a short duration laser beam to create plasma on the sample's surface. When the plasma cools down, a characteristic spectrum of light is emitted. By studying the emitted spectrum patterns, the composition of the sample can be determined. [21]

The idea of using lasers for spectrochemical analysis began shortly after the invention of lasers in the 1960s. Just couple years later, researchers observed laser-induced plasma, leading to the development of LIBS. Over the decades, LIBS has undergone significant progress, and numerous papers have been published on the topic. Especially, the publications where LIBS has been used on the Curiosity rover on Mars have significantly increased its popularity within the scientific community. [22],[21]

LIBS has been applied in various fields, such as biology, archeology, industry, plasma research, soil analysis, and environmental pollution assessment. In addition to this, LIBS plays a significant role in geosciences. Geologists are particularly interested in LIBS because of its ability to analyse various samples fast, with minimal preparation. In relation to this topic, there are several publications available. Some studies have concentrated on the quantitative analysis of both minor and major elements present in the ore. Others have aimed to identify and categorize the ore, distinguishing precious minerals from non-precious ones. Additionally, certain research has focused on elemental imaging of the ore. [22], [23]

2.3.1 Process

In this chapter, the LIBS process and its physical background are examined in more detail. Special equipment is required for LIBS analysis, and the key components needed include items such as a laser, mirrors, lenses, optical fiber, a detector, and a computer, as you can see in Figure 2. Various physical and chemical phenomena occur during the analysis, which will be explained below.
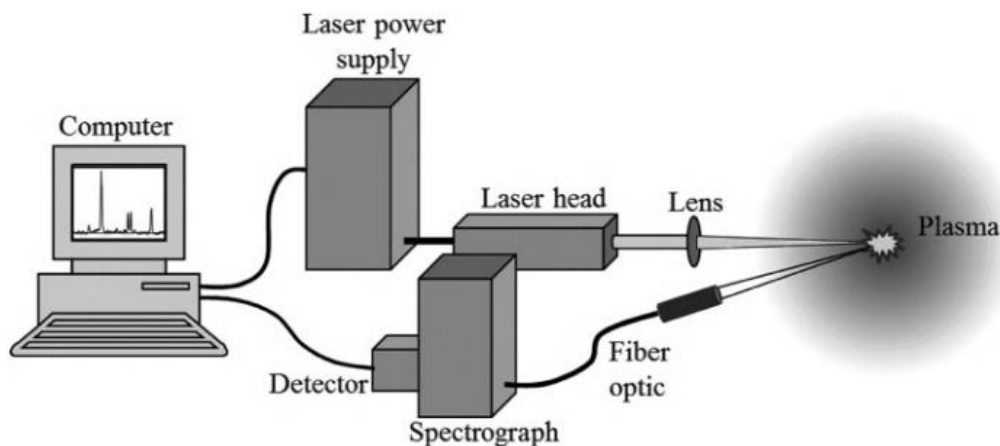
FIGURE 2. LIBS apparatus [22].

The LIBS process can be considered to start when the laser beam hits the surface of the sample [21]. A laser is a device that produces coherent light, meaning that all light waves have the same wavelength. A laser beam is generated through stimulated emission. In stimulated emission, light interacts with the electrons of atoms in a material, causing them to move to higher energy levels. When the electrons return to their normal states, they emit photons, thus strengthening the light. [24]

For successful and accurate LIBS analysis, the laser must meet specific criteria. The laser should have a particular wavelength and intensity. It should also be capable of focusing the beam onto a small area. These properties are crucial for the formation of plasma, which in turn enables obtaining results. Different wavelengths play a significant role in how materials interact during LIBS analysis. Some wavelengths are more suitable for specific materials than others. For example, the CO2 laser with a wavelength of 10.6 μm is strongly reflected by copper and certain metals. However, CO2 laser is well absorbed by glass and aqueous solutions with high infrared absorption. The laser's intensity is also crucial for successful LIBS analysis. The laser's irradiance should be approximately in the range of GW/cm² to ensure that the material undergoes ablation and produces a strong emission signal. If the pulse energy is too low, the plasma may not generate clear emission signals. For this reason, using very short-duration laser pulses is advisable, as it allows for higher pulse energy. The pulse duration varies between 5 and 20 ns depending on the laser. Furthermore, the laser needs to have very good precision and focus the pulse on a small area, which ensures better accuracy and sensitivity in the analysis. [22]

Various different laser types can be used in LIBS analysis, such as N2, CO2, ArF, KrF, XeCl, Nd:YAG, and Ti-sapphire. The Nd:YAG laser is commonly used in LIBS applications, operating at fundamental wavelength of 1064 nm. The Nd:YAG laser also meets the previously mentioned requirements well. It enables good beam quality, can produce high pulse energies, and its fundamental wavelength can be easily adjusted to generate different harmonics. Additionally, this laser is available in compact form, making it suitable for small-sized instruments. [22]

Lenses or curved mirrors are used to direct the laser beams onto the surface of the sample to a specific point. With the help of lenses, the laser beams energy can be concentrated, which contributes to plasma formation. In most cases, lenses are also employed to collect the emission light, which is then directed to a optic cable. [22], [25]

When the laser pulse hits the surface of the sample, the intense heat causes the particles in the material to vaporize and transform into plasma. At this moment, the plasma's temperature is very high and it can exceed 50000 K [4]. The high energy in the plasma excites the ions and atoms present in the material, causing them to move to higher energy states. Initially, the plasma emits a broad spectrum of white light. This white light does not yet provide specific spectroscopic information about the elements, but after a few hundredths of a nanosecond, the plasma starts to cool down, and the excited particles return to their ground states. When this happens, they emit light with characteristic wavelengths for each element. This emitted light carries information about the sample's chemical composition. These light signals are directed through an optical fiber to the detector and spectrometer. Then the detection system analyses the light, and it creates an unique LIBS spectral signature. One important aspect to consider in light beam measurements is time delay. As mentioned earlier, during the early stage of plasma formation, the emitted light from the plasma does not provide information about the elements present. Therefore, a time delay between the laser pulse hitting the

sample and measuring the emitted light's wavelengths from the plasma is commonly used in LIBS measurements. [26]

2.3.2 Advantages

From the perspective of mineral exploration, one of the most significant benefits of LIBS is its portability. LIBS-technology brings laboratory capabilities to the field, enabling on-site analysis and eliminating the need to transport rock samples to distant laboratories. In contrast, many other common techniques like electron microprobe, instrumental neutron activation analysis and atomic absorption spectrometry are laboratory-based and it can take several weeks before the analysis is done. Furthermore, the rapid operation time of LIBS and the minimal sample preparation required enhance work efficiency. Geologists and researchers using LIBS can access real-time data, aiding in decision-making while saving time, costs, and environmental resources. [25]

The technique is also a micro-destructive, meaning it does not cause significant damage to the sample and it requires only a minimal amount of material for analysis. This characteristic is particularly valuable, when dealing with precious or irreplaceable materials. [27]

Furthermore, LIBS can easily detect lightweight elements (helium, lithium, beryllium, boron, carbon, nitrogen, and oxygen). These elements are often abundant in natural materials but are challenging to determine by many other analytical techniques. There has been particular interest in the ability of LIBS to detect lithium (atomic number 3) effectively. This metal also belongs to the group of critical raw materials and is essential in many traditional and new applications. [5]

2.3.3 Limitations

One of the major drawbacks of LIBS is the matrix effect. This phenomenon occurs when the signal given by LIBS is not only determined by the quantity of a specific element present in a sample. Instead, it is influenced by the physical and chemical properties of the sample itself, such as its composition, how it interacts with light, and its thermal conductivity [4]. To simplify, if the same amount of a specific element is found in different host materials, the emitted light spectra measured by the LIBS can still vary [25]. [28]

Another common challenge in LIBS is self-absorption. In optimal situations, the laser-generated plasma can be considered optically thin, indicating that the emitted light from the plasma spreads evenly and is not absorbed within the plasma itself. However, if the plasma is very dense, it can absorb its own emission light. This can lead to the emission lines not exhibiting a linear relationship with the concentration of the element. [28]

The third major drawback in LIBS is its limited sensitivity. Although LIBS can identify elements present in materials at concentrations as low as parts per million (ppm), it has higher limits of detection (LOD) compared to some other analytical techniques. This means that LIBS may not be as suitable for detecting trace levels of certain elements or compounds that are present at very low concentrations in the sample. In contrast, some other techniques, such as ICP-MS (Inductively Coupled Plasma Mass Spectrometry) or XRF (X-ray fluorescence), can achieve much lower LODs in the part per billion (ppb) range, making them more suitable for ultra-trace analysis.[28], [29]

3 SAMPLES AND METHODS

The aim of this study was to investigate, how LIBS can be used to detect nickel in a rock sample. This chapter introduces the sample under study and outlines the necessary experimental setup. In addition, the measured data and its processing with MATLAB is discussed.

3.1 Samples

In this study, a rock sample obtained from the Talvivaara mine was analysed. The sample was drilled from a depth of 278.9 meters and split in the longitudinal direction into two halves, as shown in Figure 4. The LIBS analysis focused only on the flat surface of the sample, which required supporting the piece with a thin plastic stand (see figure 3 and 4). When viewed from the top, the flat surface of the sample resembled a parallelogram, with approximate dimensions of 182 mm x 38 mm. Upon visual inspection, the sample appeared to be dark gray and relatively smooth. Additionally, there were significant amounts of gleaming streaks visible in the sample. The layered appearance suggests that the sample might be schist.
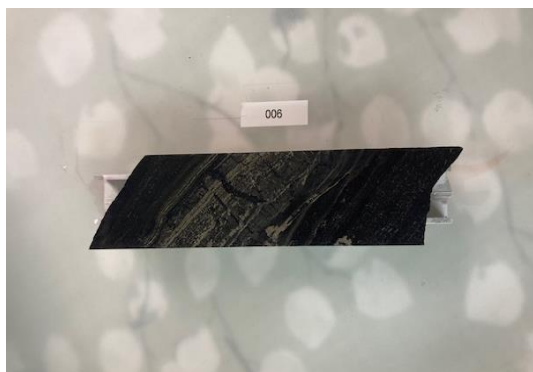
FIGURES 3 & 4. Sample viewed from above and from the front.

3.2 Experimental methods

The aim of this experiment was to investigate how LIBS works and to determine whether or not a rock sample contains nickel. Three specific points on the samples suface were selected for examination to determine, if nickel could be detected in them. The experiment was conducted in collaboration with an academic supervisor, Ph.D. candidate Ilkka Laine, and Lumo Analytics senior Operator Nicolas Barban. The study was conducted using Lumo Analytics' equipment on July 27, 2023.

Before scanning, the surface of the sample was grinded with sandpaper to remove impurities. After that, the sample was cleaned with water in an ultrasonic cleaner for 5 minutes. Following that, the sample was further immersed in denatured ethanol.

The scanning was performed using Lumo Analytics' laser scanner (LASOLIBS). The laser used for scanning was the Cobolt Tor Xe, and it operated at a wavelength of 1064 nm. The scanning process was carried out in two stages. Firstly, the sample's profile was scanned, resulting in a point cloud representation of the sample. From this point cloud, the specific surface was selected for more precisely high-detail LIBS scan. In this way, the elemental composition of the sample was measured.
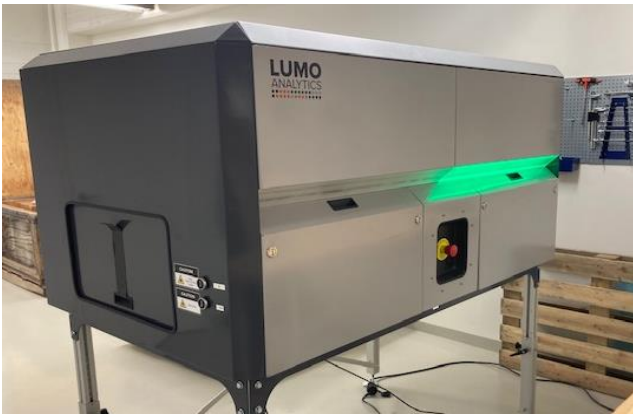
FIGURE 5.   LASOLIBS laser scanner

As a result of the profile scanning, a point cloud (Figure 5) was obtained. This point cloud was examined in more detail using 3D point cloud and mesh processing software. From the point cloud, a specific area was selected for the high-detail scan. The x, y, and z parameters were chosen and the values are presented below.

X: 210 – 248 mm

Y: 300 – 482 mm

Z: 258 mm
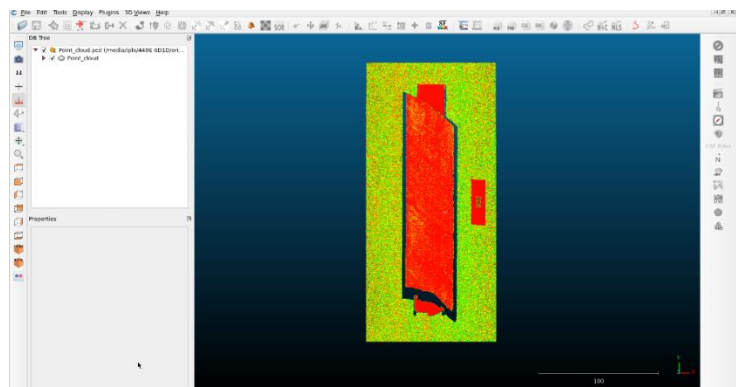
FIGURE 6. Point cloud of the samples profile

After recording the x, y and z parameters, a high detail scan was performed using the same device. Below is a table of high-detail scan properties.

TABLE 2.   Scan details

Laser wavelength (nm)	1064
Laser pulse energy (nJ)	500 ± 50
Laser pulse length (ns)	$1.5 - 3.5$
Resolution (mm)	0.1625
Duration of the scan (min)	15

3.3 Data processing

Approximately 250 000 measurement points were collected from the sample's surface through the high-detail scan. The data was processed using MATLAB, where codes were used to create elemental images and spectral plots.

The code shown in Figure 7 was used to generate elemental images. From these images, it was possible to examine which elements are present in different areas of the sample. The images are in RGB format, and to keep the task simple, only three different color images were used for analysis. Nickel, oxygen, and sulfur were selected for examination.

```matlab
%% pictures

nikkeli_wavelength = 220.5753;%M.wavelengthBoth(359,1);
g_selected = 359; %nikkeli
nikkelikuva = squeeze(M.spectraBoth(g_selected,:,:));
figure;
imagesc(nikkelikuva);
set(gca,'YDir','normal');


r_selected = 7617; %rikki
b_selected = 6478; %happi

R = imadjust(rescale(squeeze(M.spectraBoth(r_selected,:,:))));
G = imadjust(rescale(squeeze(M.spectraBoth(g_selected,:,:))));
B = imadjust(rescale(squeeze(M.spectraBoth(b_selected,:,:))));
Z = zeros(size(R));
figure;image(cat(3, R, Z, Z)); title('Sulfur');set(gca,'YDir','normal');
figure;image(cat(3, Z, G, Z)); title('Nickel');set(gca,'YDir','normal');
figure;image(cat(3, Z, Z, B)); title('Oxygen');set(gca,'YDir','normal');
figure;image(cat(3, R, G, B)); title('Sulfur-Nickel-Oxygen');set(gca,'YDir','normal');
```

FIGURE 7.   MATLAB code for elemental images

In Figure 8, it can be seen where nickel is present in the sample. Figures 9 and 10 depict oxygen and sulfur. Oxygen was selected for examination because it provided clarity to the image. Sulfur was selected because nickel is often found in sulfide minerals, which contain sulfur. In Figure 10, all elemental images are plotted together in a single image.
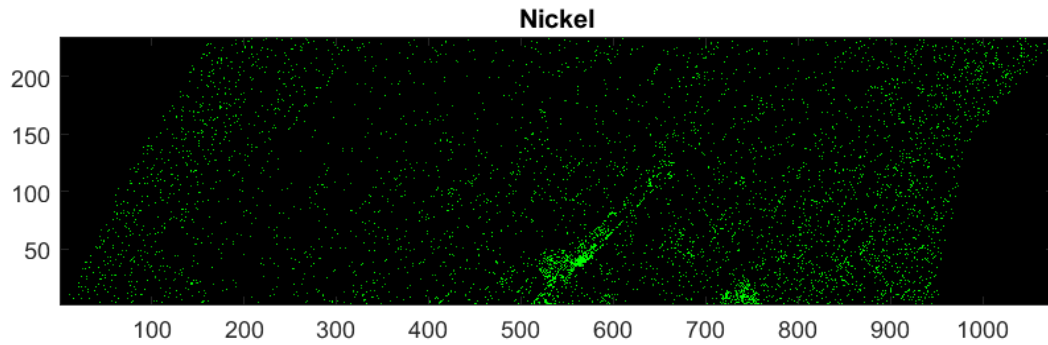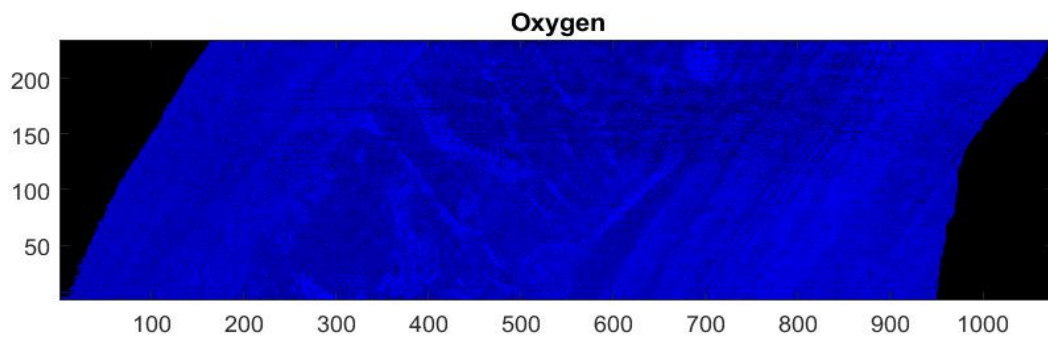

FIGURE 8.   Elemental image of nickel
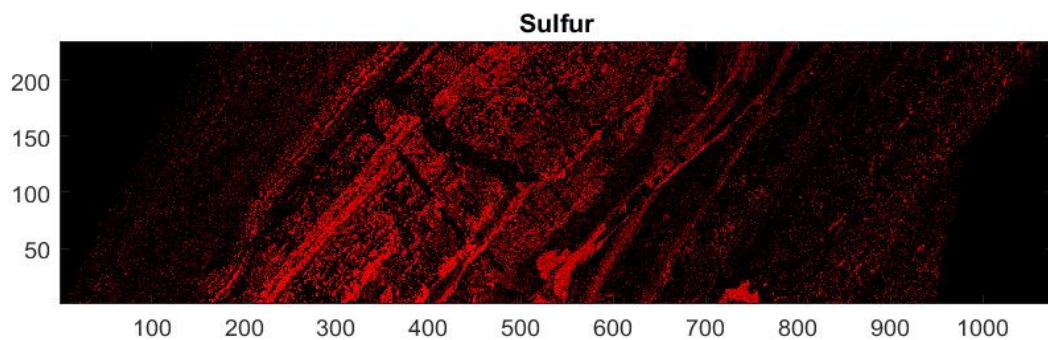

FIGURE 9.   Elemental image of oxygen

FIGURE 10. Elemental image of sulfur
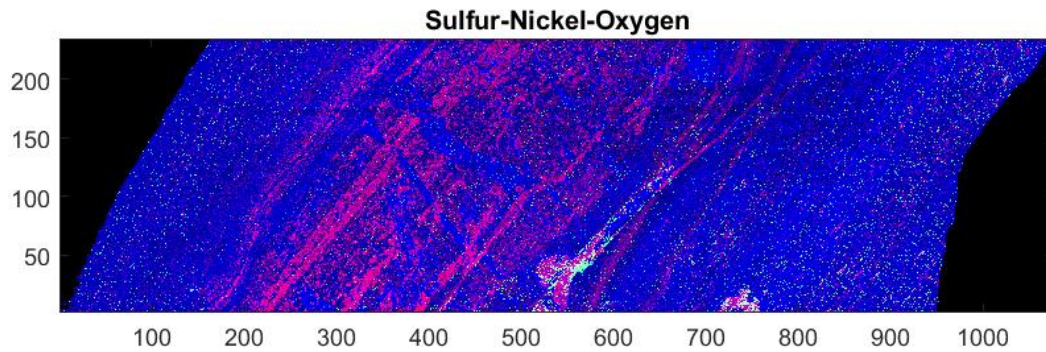
FIGURE 11. All three elements plotted in one image

Three examination points were chosen from figure 12. The examination points were selected in a way that the first point was chosen from an area where nickel is likely to be present based on the image. The other two points were chosen from areas where the presence of nickel cannot be entirely certain.

Point 1: [37, 563]

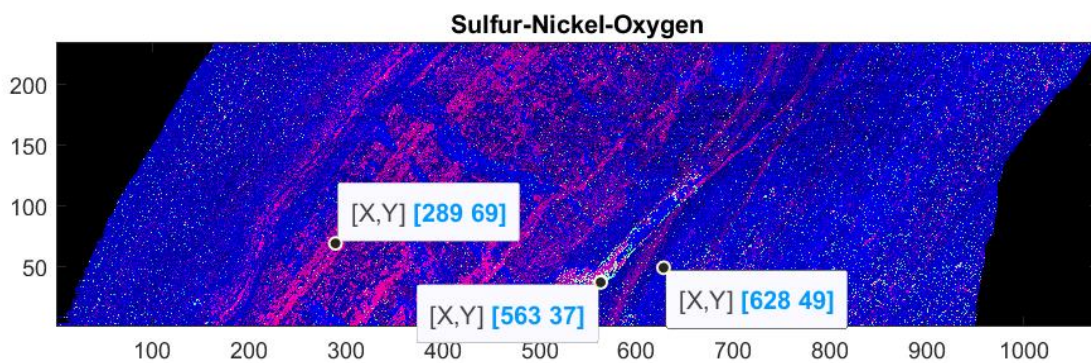Point 2: [69, 289]

Point 3: [49, 628]

FIGURE 12. Three selected points

The spectras were drawn from each of the three measurement points using the code shown in Figure 13.

```
%% Draw emission peaks
ekakiisupiste = [37 563];
tokakiisupiste = [69 289];
eikiisupiste = [49 628];

wavelengthBothLumo = M.wavelengthBoth;
ekakiisuspektri = M.spectraBoth(:,ekakiisupiste(1),ekakiisupiste(2));
tokakiisuspektri = M.spectraBoth(:,tokakiisupiste(1),tokakiisupiste(2));
eikiisuspektri = M.spectraBoth(:,eikiisupiste(1),eikiisupiste(2));

figure;plot(M.wavelengthBoth,ekakiisuspektri)
hold on
plot(M.wavelengthBoth,tokakiisuspektri)
plot(M.wavelengthBoth,eikiisuspektri)
plot(wavelength_Avantes_Aalto_2020,nickel_reference_spectrum)
legend("point 1"," Point 2","point 3","Nickel")
xlabel("Wavelength (nm)")
ylabel("Intensity")

figure;plot(M.wavelengthBoth,ekakiisuspektri)
title("Point 1")
xlabel("Wavelength (nm)")
ylabel("Intensity")
figure;plot(M.wavelengthBoth,tokakiisuspektri)
title("Point 2")
xlabel("Wavelength (nm)")
ylabel("Intensity")
figure;plot(M.wavelengthBoth,eikiisuspektri)
title("Point 3")
xlabel("Wavelength (nm)")
ylabel("Intensity")
```

FIGURE 13. MATLAB code for spectral pikes

The spectral lines from the three observation points were compared to the reference spectrum of nickel measured at Aalto-University. In addition, the NIST Atomic Spectra Database was utilized to acquire information about the wavelengths at which emission peaks occur for nickel [28].
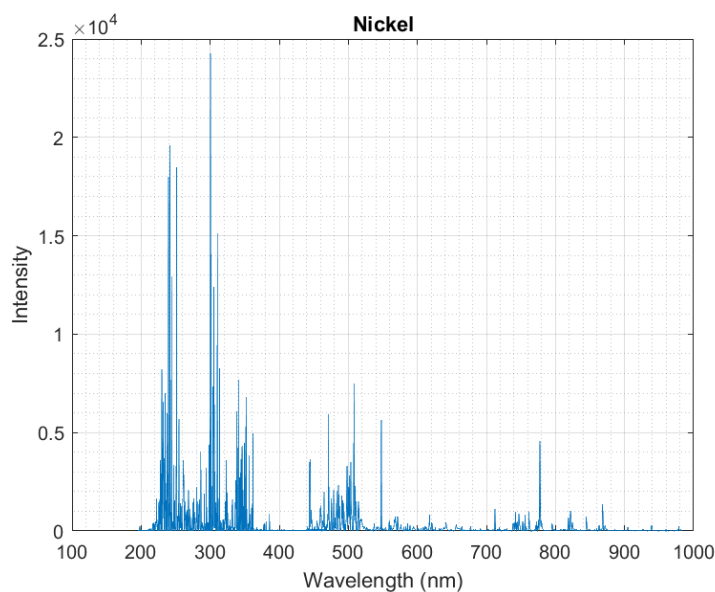
4 RESULTS

The three selected observation points yielded the following spectrographs (figures 13, 14, 15). Also, the spectra of three different measurement points were combined with the spectrum of nickel into a single image (figures 16, 17). With the help of these images, the potential presence of nickel in the points could be assessed. In simple terms, the more the emission peaks of points 1, 2, and 3 resembled the emission peak of nickel, the more likely it is that nickel is present in those points. According to the NIST Atomic Spectral Database, nickel exhibits strong emission peaks in the range of 227 - 236 nanometres. For this reason, this interval was chosen as the range of examination.
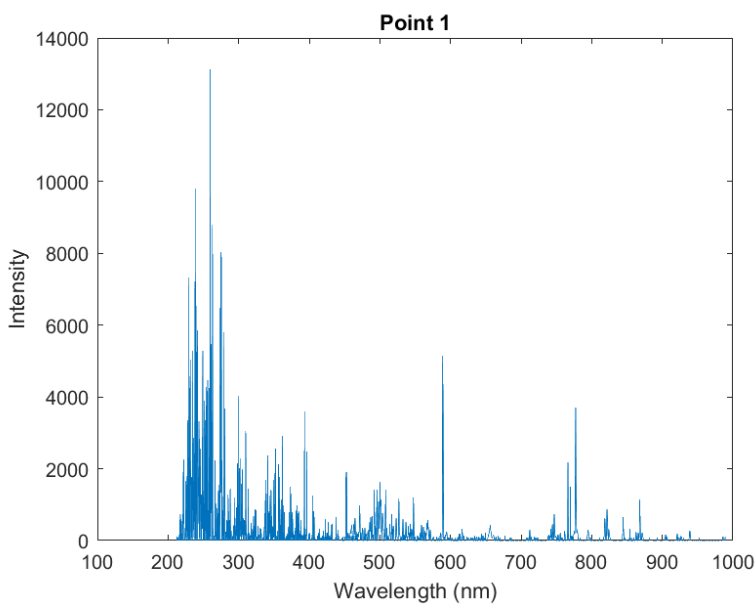

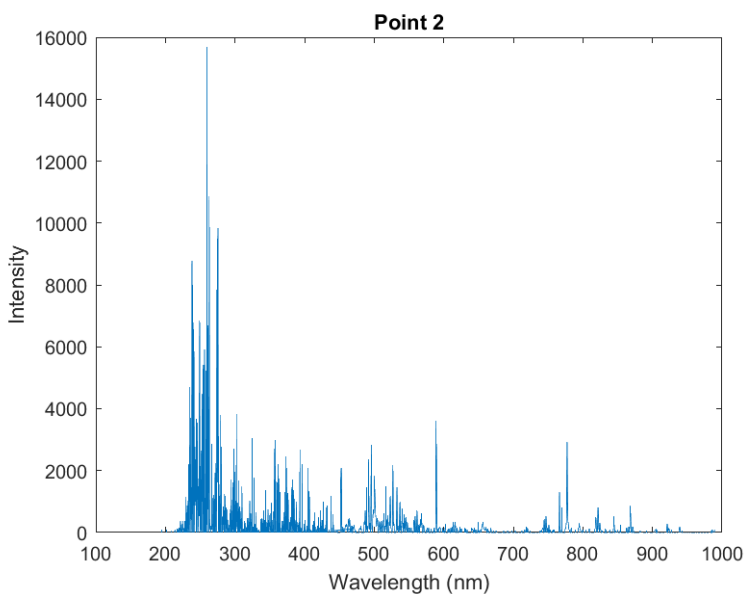FIGURE 13. Emission spectrum in measurement point 1

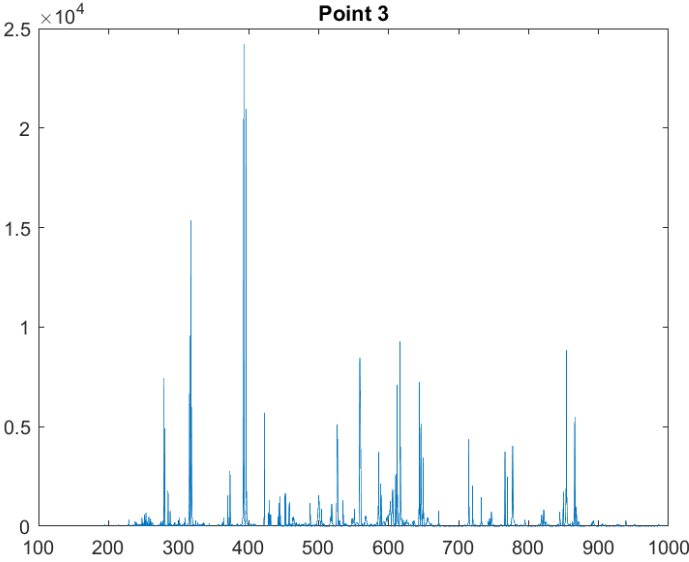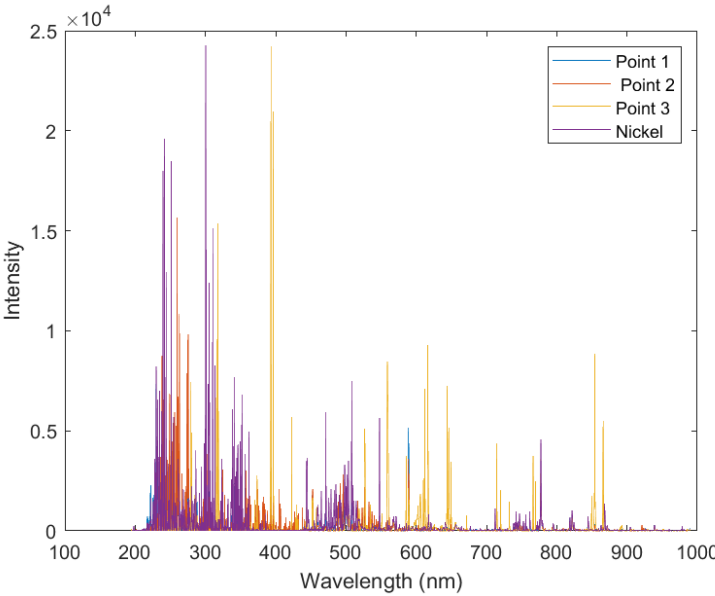FIGURE 14. Emission spectrum in measurement point 2

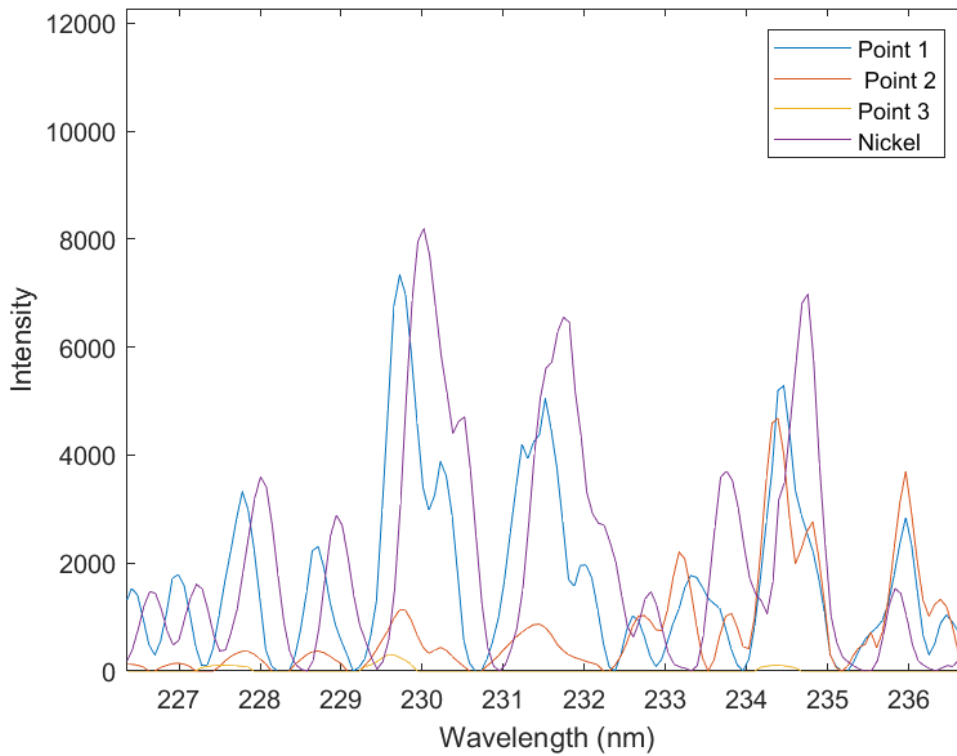FIGURE 15. Emission spectrum in measurement point 3

FIGURE 16 & 17.   All four spectrums plotted in one image.

Unfortunately, the reference curve for nickel couldn't be perfectly placed in the image, but it still allows for some interpretations. Based on the emission peaks, point one strongly indicates the presence of nickel. Point two might contain some traces of nickel, especially when observing the 235 nm range. Point three likely does not contain nickel at all. Due to the limitations of the experiment, it is not possible to be certain in which mineral nickel is present at point 1. However, as mentioned earlier, pentlandite is the most common nickel-containing mineral on Earth, so it is very likely that the discovery at point 1 could be this mineral.

5 DISCUSSION

Nickel was successfully detected in the rock sample using LIBS. It was already known before conducting the experiment that LIBS could measure nickel and other critical metals. The primary purpose of the experiment was to support the understanding of how LIBS functions when measuring rock samples, rather than focusing specifically on measuring nickel or other elements. An important focus for the future should indeed be to further develop LIBS technology to identify elements with even greater accuracy.

This thesis provides indications that LIBS technology has the potential to play a larger role in ore exploration in the future. LIBS performs well on a general level, enabling rapid on-site measurement of rock samples and providing information about their elemental composition. However, the technology faces certain challenges, such as the matrix effect and limitations in accuracy. By understanding these challenges and advancing the technology, LIBS can have promising prospects in ore exploration and geological research.

The demand for critical raw materials is expected to continue growing. Traditional industries consume critical raw materials, and new energy-efficient technologies also contribute to increased material consumption. Regardless of the metal, it is always obtained by mining ores from the Earth's crust. Due to the tightening supply situation, ore exploration has intensified in recent years. Additionally, the global political situation has increased the desire of several countries to enhance self-reliance in raw material production. By considering the perspectives mentioned above and advancing the development of LIBS, the technology is likely to have positive prospects in the future.

6 REFERENCES

[1] Grandell, L. Kriittiset metallit vihreässä energiateknologiassa. Espoo, Finland. VTT, 2014. 86. (electronic) ISBN: 978-951-38-8137-5.

[2] An introduction to minerals, ore and exploration. Geological survey of Sweden. [Online] [24.8.2023]. Available: https://www.sgu.se/en/itp308/knowledge-platform/1-introduction-minerals-ore-exporation/

[3] Taipale, K. Kivet ja mineraalit suomen luonnossa. Helsinki, Finland: Otava, 2010. 182 p. ISBN: 9789511238157 (Printed).

[4] Milori, D. M. B. P. & Martin-Neto, L & Gollany, H. T & de Babos, D. V & Borduchi, L. C. L & Villas-Boas, P. R. Soil analysis using laser-induced breakdown spectroscopy. Earth Systems and Environmental Sciences. Vol. 2. 2023. P. 654-611. Available from: DOI: 10.1016/B978-0-12-822974-3.00211-1.

[5] Harmon, R. S & Lawley, C. J. M. & Watts, J. & Harraden, C. L & Somers, A. M & Hark, R. R. Laser-Induced Breakdown Spectroscopy—An Emerging Analytical Tool for Mineral Exploration. Minerals. Vol. 9. 2019 P. 45. Available from: DOI 10.3390/min9120718.

[6] Romppanen, S. Laser-spectroscopic studies of rare earth element-and lithium-bearing minerals and rocks. Doctoral thesis. University of Jyväskylä, Department of Chemistry. Jyväskylä. 2021. 66 p.

[7] Airo M.-L & Kiuru, R. Petrofysiikan perusteet. University of Helsinki. 2012. 128p. ISSN 0355-8630 (Electronic).

[8] CNMMN. The New IMA List of Minerals. 2023. [Online] [18.8.2023]. Available: http://cnmnc.units.it/

[9] Schuman, W, Kivet ja mineraalit värikuvina. München, Germany: Verlagsgesellschaft mbH, 1972. 222 p. ISBN : 951-1-00445-X (printed).

[10] Lehtinen, M & Nurmi, P & Rämö, T. Suomen kallioperä-3000 vuosimiljoonaa, Luku 2, Geologian peruskäsitteitä. 1998. 23 - 90 P. ISBN: 952-90-9260-1

[11] Milan, G & Constanze, V. Study on the critical raw materials for the EU 2023. 2023. [Online] [1.9.2023] Available: https://op.europa.eu/en/publication-detail/-/publication/57318397-fdd4-11ed-a05c-01aa75ed71a1

[12] Balaram, V .Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. Geosci. Front. vol. 10. 2019. P. 1285–1303. Available from: DOI: 10.1016/j.gsf.2018.12.005.

[13] Keppo, M. Harvinaiset maametallit kiertotalouden kontekstilähtöisessä oppimisessa. Masters's thesis. University of Oulu, Department of Chemistry. Oulu. 2017. 113 p.

[14]   Romppanen, S. & Häkkänen, H. & Kaski, S. Singular value decomposition approach to the yttrium occurrence in mineral maps of rare earth element ores using laser-induced breakdown spectroscopy. Spectrochim. Acta Part B At. Spectrosc. Vol. 134. 2017 P. 69–74. Available from: DOI: 10.1016/j.sab.2017.06.002.

[15]   Wallenius, J. Harvinaiset maametallit pyörittävät maailmaa. Kemia. 2012 p. 15 Availabe from: https://www.kemiamedia.fi/wp-content/uploads/2013/02/kem112_maametalli.pdf

[16]   Habashi, F. Nickel, Physical and Chemical Properties. Encyclopedia of Metalloproteins, R. H. Kretsinger, V. N. Uversky, and E. A. Permyakov, Eds., New York, NY: Springer New York, 2013, pp. 1520–1520. Available From: DOI: 10.1007/978-1-4614-1533-6_338.

[17]   Seitsaari, M. Pentlandiitin online-tunnistusmenetelmät ja niiden soveltaminen Kevitsan kaivoksen malmikiviin. Master's thesis. University of Oulu. 2016. 102 p.

[18]   Campagnol, N & Hoffman K. & Lala, A &Ramsbottom, O. The future of nickel: A classact.Mckinsey.2017.[Online][1.9.2025]Available: https://www.mckinsey.com/~/media/McKinsey/Industries/Metals%20and%20Mining/Our%20Insights/The%20future%20of%20nickel%20A%20class%20act/The%20future%20of%20nickel%20A%20class%20act.pdf

[19]   Laine, I, doctor student. Aalto University, Espoo. Interview 14.8.2023, interviewer, Janna Lappalainen

[20]   Keskipohjanmaa. Rio Tinto etsii nikkeliä ja kobolttia Nivalassa – Geologit aloittavat maastotyöt ensi viikolla. Keskipohjanmaa, 2019. [Online]. Available From: https://www.keskipohjanmaa.fi/artikkeli/rio-tinto-etsii-nikkelia-ja-kobolttia-nivalassa-geologit-aloittavat-maastotyot-ensi-viikolla

[21]   Fabre, C. Advances in Laser-Induced Breakdown Spectroscopy analysis for geology: A critical review. Spectrochim. Acta Part B At. Spectrosc. Vol. 166. 2020. P. 1 - 16. Available from: DOI: 10.1016/j.sab.2020.105799.

[22]   Cremers, D. A. and Radziemski, L. J. Handbook of laser-induced breakdown spectroscopy. New York, USA: John Wiley & Sons, 2013. 432 p. ISBN 9781118567364 (electronic). ISBN 9781119971122 (printed).

[23]   Rifai, K & Özcan, J & Doucet, F & Vidal, F. Quantification of copper, nickel and other elements in copper-nickel ore samples using laser-induced breakdown spectroscopy. Spectrochim. Acta Part B At. Spectrosc. Vol. 165. 2020. P. 105766. Available from: DOI: 10.1016/j.sab.2020.105766.

[24]   Williams, D. Laser basics. Thoracic/physiology. Vol. 9. 2008. P. 550–552. Available From: DOI: 10.1016/j.mpaic.2008.09.008.

[25]   Harmon, R. S & Russo, R. E & Hark, R. R. Applications of laser-induced breakdown spectroscopy for geochemical and environmental analysis: A comprehensive review. Themat.

Issue 7th Int. Conf. Laser Induc. Breakdown Spectrosc. LIBS 2012 Luxor Egypt 29 Sept.-4 Oct. Vol. 87. 2012. P. 11–26. Availble from: DOI: 10.1016/j.sab.2013.05.017.

[26]   Wong, D. M. & Bol'shakov, A. A & Russo, R. E. Laser Induced Breakdown Spectroscopy. Academic Press. 2010, P. 1281–1287. Available from: DOI 10.1016/B978-0-12-374413-5.00062-2.

[27]   Mei, Z & Wang W & Imran, M & Lin, W & Bi, H & Hu, Z. Preliminary study of laser-induced breakdown spectroscopy for non-destructive pressure measurement in confined vacuum interlayers. Vacuum. Vol. 214. 2023. P. 1-3: Available from: 10.1016/j.vacuum.2023.112197.

[28]   Sezer, B & Bilge, G & Boyaci, I. H. Capabilities and limitations of LIBS in food analysis. TrAC Trends Anal. Chem. Vol. 97. 2017. P. 345-353. Available from: DOI: 10.1016/j.trac.2017.10.003.

[29]   Xinglan, F & Li, G & Dong, D. Improving the Detection Sensitivity for Laser-Induced Breakdown Spectroscopy: A Review. Vol. 8. 2020. P. 1-11. Available from: DOI 10.3389/fphy.2020.00068.

[30]

        A., Ralchenko, Yu., Reader, J. and NIST ASD Team (2022). *NIST Atomic Spectra Database* (version 5.10), [Online]. Available: https://physics.nist.gov/asd [Tue Aug 15 2023]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: https://doi.org/10.18434/T4W30F