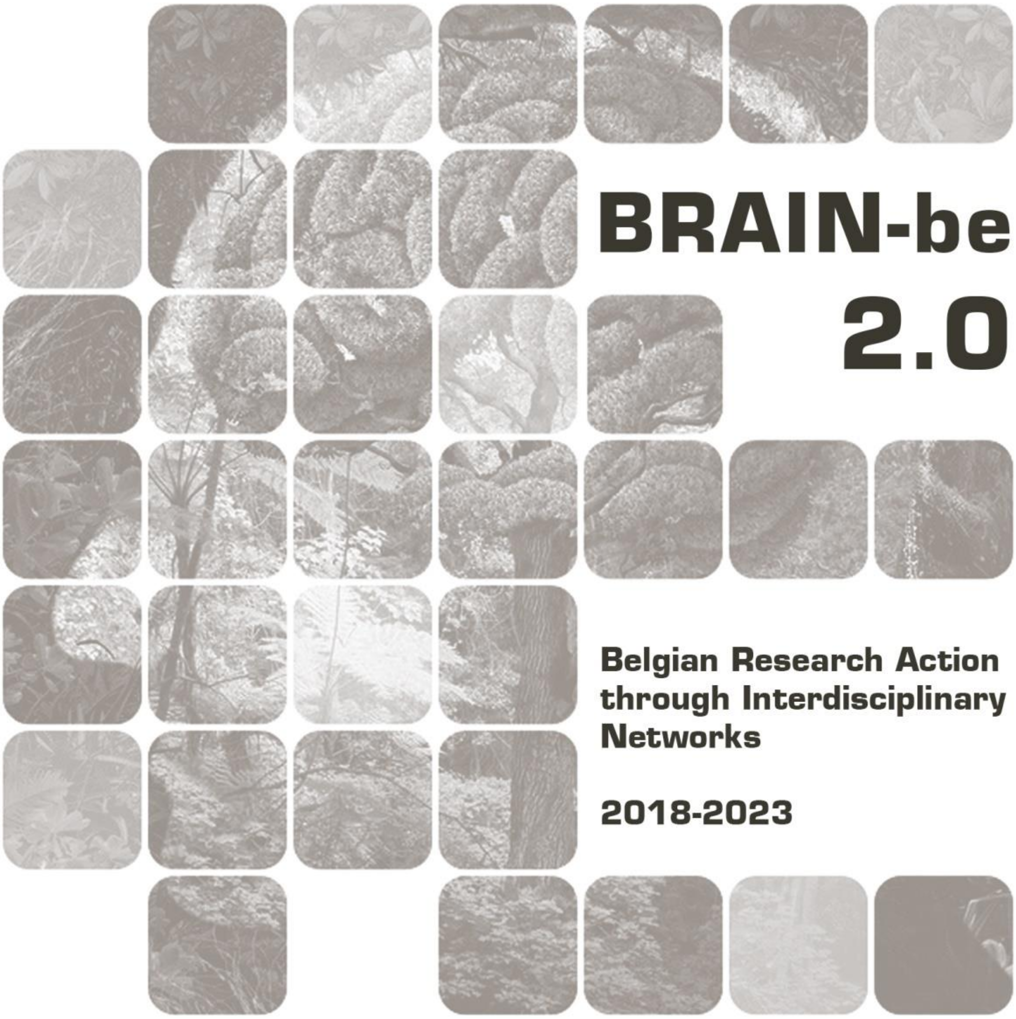

LIBS-SCReeN

Screening Critical Raw materials from exploration to (post)beneficiation using LIBS techniques

Christian BURLET (RBINS-GSB) - Renata BARROS (RBINS-GSB) - Sophie VERHEYDEN (RBINS-GSB) - Jean-Marc BAELE (UMONS) - Séverine PAPIER (UMONS) - Anca CROITOR (KULeuven) - Eric PIRARD (ULiège) - Hassan BOUZAHZAH (ULiège) - Simon NACHTERGAELE (ULiège)

Pillar 1: Challenges and knowledge of the living and non-living world

NETWORK PROJECT

LIBS-SCReeN

Screening Critical Raw materials from exploration to (post)beneficiation using LIBS techniques

Contract - B2/191/ P1/LIBS-SCReeN

FINAL REPORT

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ABSTRACT

Context

Critical Raw Materials (CRM) are economically and strategically important for key industry sectors and future applications but have a high-risk associated with their supply. Meeting the growing demand for CRM is one of the greatest global challenges in the next decades, and (re)exploitation of domestic resources, including recycling, will become increasingly significant. In Belgium, zinc-lead deposits have been known since Prehistoric times and were mainly exploited in the 19th century, but the economic potential of what remains is largely undetermined. It is known these deposits host CRMs such as germanium (Ge) and gallium (Ga). Of equal importance in the case of new mining and beneficiation activities is the presence of elements that can turn into contaminants for the environment, e.g., arsenic (As) and cadmium (Cd).

Flexible, rapid and reliable techniques are needed to enhance our capacity of CRM exploration, exploitation, recycling and environmental impact monitoring. Traditional geochemical characterisation techniques are typically time-consuming, expensive, and require sample preparation, which limits the size and representativity of datasets. In this context, Laser-Induced Breakdown Spectroscopy (LIBS) emerges as an advantageous alternative for characterisation of geological material. The technique is based on emission spectroscopy using high-energy laser pulses as the excitation source. Besides allowing rapid data acquisition with no to little sample preparation, one significant advantage of LIBS is the possibility of simultaneous analyses of major, minor, and trace constituents, including lighter elements (e.g., C, B, Be, and Li) which are notably difficult to detect with many other techniques.

One of the challenges to upscale the application of LIBS techniques for large screening efforts is the generation of large amounts of complex spectral data. This requires adapted technologies of data processing and analyses and can greatly benefit from the evolving landscape of Machine Learning (ML) and Artificial Intelligence (AI) tools. Especially in potential future automated LIBS analyses, data extraction and processing pipelines that are also automated are strongly needed. Protocols for screening, element identification and mineral classification using LIBS represent important steps towards standardisation, which can provide a valuable contribution to the international LIBS community.

Objectives

The project LIBS-SCReeN aimed at improving already existing LIBS technology in Belgian laboratories and developing and implementing further LIBS analytical capacity to test the application of the technique to the whole life cycle of CRM, from exploration of resources to post-beneficiation scenarios of recycling and/or environmental issues. The specific objectives of the project were to 1) develop and implement scientifically sound workflows to exploit LIBS for elemental screening at multiple scales, 2) to optimise element identification workflows from data acquisition to treatment to ensure the applicability of LIBS to different deposits and environmental needs, and 3) to disseminate and cluster local activities with the global scientific LIBS community and EU projects to establish a Belgian LIBS expertise hub.

Methodology

The project utilized two primary LIBS setups: one at UMONS and another at RBINS-GSB, with a third setup being developed at ULiège. Methodological approaches included :

- **Reference Sample Analysis**: Comparing LIBS elemental analyses with SEM-EDS, µXRF, and LA-ICP-MS on 13 reference rock samples.
- **Sample and Core Inventory**: Cataloguing historical Zn-Pb ore samples from geological collections at project partner institutions and collaborating with UGent for drill core samples.
- **Screening Approaches**: Implementing targeted and randomized screening methodologies on hand samples and drill cores to evaluate user-bias and automation suitability.
- **Soil Contamination Screening**: Conducting semi-portable LIBS analyses on soil samples from Belgian and French sites to assess heavy metal contamination.

Key Achievements

1. **Development of LIBS Workflows:** The project successfully developed and tested screening protocols from data acquisition to LIBS spectral processing. Hundreds of rock and soil samples were analyzed, demonstrating LIBS's capabilities in detecting CRM and potential environmental contaminants. Two methodological approaches were compared: targeted analyses with fewer, more controlled measurements, and randomized, automated analyses with less user bias.
2. **Optimization of Element Identification:** LIBS techniques were optimized for various scales, from hand-sized samples to entire core samples. The project enhanced setups at UMONS, RBINS-GSB, and ULiège. Advanced machine learning models were developed to manage large spectral data volumes, enabling differentiation between mineral phases and rapid detection of critical elements such as germanium (Ge) and gallium (Ga), as well as pollutants like cadmium (Cd) and arsenic (As).
3. **Screening Pilots:** A total of 408 samples were screened, encompassing a wide variety of mineralogical compositions associated with Zn-Pb occurrences in Belgium. The screening pilots highlighted LIBS's ability to provide detailed multiscale distribution maps of chemical elements, showcasing its potential for both CRM exploration and environmental monitoring. Soil analyses from contaminated sites, such as the Sclaigneaux brownfield, validated LIBS's effectiveness in environmental applications.
4. **Dissemination and Valorization:** The project engaged in extensive communication and dissemination activities, including workshops, conference presentations, and collaborations with international research institutions. The establishment of the Belgian LIBS Research Cluster (BELIBS) was a significant outcome, aiming to continue LIBS research and offer expertise and services through the infrastructure developed during the project.
5. **Digital Presence and Publications:** The project maintained a robust digital presence with a dedicated LinkedIn page and Twitter profile, attracting followers and generating significant engagement. A series of educational videos on YouTube explained the main tasks and innovations of the LIBS-SCReeN project. Additionally, several peer-reviewed publications and conference abstracts were produced, further disseminating the project's findings.

Conclusions

The LIBS-SCReeN project demonstrated that LIBS is a powerful tool for CRM exploration and environmental monitoring. The development of optimized workflows and advanced data processing techniques, combined with the establishment of BELIBS, positions Belgium as a leader in LIBS research and application. Future research could focus on further refining these techniques and exploring new applications in various industrial and environmental contexts. The project's findings enhance the capacity to use LIBS in for pollutant-free CRM exploration and exploitation in diverse environments, including the recycling industry.

1. INTRODUCTION

Critical Raw Materials (CRM) are economically and strategically important for key industry sectors and future applications, with no viable substitutes with current technologies, and for which the supply is dominated by one or few producers therefore having a high-risk associated with their supply. Meeting the growing demand for CRM is one of the greatest global challenges for the next decades. In Europe, the importance of CRM for the EU economy incentivised the CRM Act, launched by the European Commission in 2023. The Act aims to ensure EU's access to a secure and sustainable supply of CRM for reaching 2030 climate and digital objectives. In this context, (re)exploitation of domestic resources, including recycling, will become increasingly significant. Research and development are more required than ever regarding resource availability, multi-scale CRM identification and characterisation, and environmental impact of mining and processing CRM. Flexible, efficient and reliable measurement techniques are needed to enhance our capacity of CRM exploration, exploitation, recycling and environmental impact monitoring.

The LIBS-SCReeN project was devoted to the optimisation and application of innovative Laser-Induced Breakdown Spectroscopy (LIBS) techniques for multiscale detection and characterisation of CRM. The choice of LIBS is due to the emergence of this technique as a promising technology within the geosciences, offering a rapid, quasi non-destructive and versatile method to analyse geological samples including rocks, soils, and even remote planetary surfaces. It utilises a focused laser pulse on a sample in gas, liquid or solid state to create plasma, which upon cool down has characteristic light emission that can be analysed to determine the elemental composition of the material. Its ability to provide real-time elemental information across a wide range of materials has proven invaluable in many geoscientific fields, including those related to mineral deposit life cycles.

To frame CRM screening in the Belgian context, the project focused on Belgian zinc-lead (Zn-Pb) deposits. This type of mineralisation is known worldwide to potentially host CRM such as germanium (Ge) and gallium (Ga), increasingly demanded for the development of green energy technologies and therefore with high criticality in the EU economy. Zn-Pb deposits have been known in Belgium since Prehistoric times and were mainly exploited in the 19th century, but the economic potential of what remains is largely undetermined. Of equal importance is the fact that many elements in these deposits, and remaining material such as tailings, can turn into contaminants for the environment as a result of their extraction and beneficiation, including Zn and Pb and others such as cadmium (Cd), arsenic (As), copper (Cu) and thallium (Tl).

Elemental distribution in Zn-Pb deposits is highly dependent on mineralogical and textural features and can present complex heterogeneities. To (re)characterise resources in view of current and future needs, it is therefore crucial to understand the occurrence and distribution of both CRMs and elements that may lead to environmental issues in different minerals and/or zones. LIBS has a lot of potential to fulfil both these tasks because it can simultaneously analyse major, minor, and trace constituents, with flexible setups and little to no sample preparation needed. However, it is important to note that these efforts generate large amounts of data which are challenging to handle manually. There is therefore a large potential for developing automation protocols in the treatment of LIBS data streams.

The LIBS-SCReeN project aimed at demonstrating that coupling LIBS and advanced machine learning pipelines is a way to overcome the challenges mentioned above. In this Final Report we contextualise the project, detail the methodological approaches for LIBS screening, and present the results obtained. By offering a highly flexible, rapid and reliable measurement technique along with integrated data analysis methods, the findings of LIBS-SCReeN can enhance our capacity of pollutant-free CRM exploration and exploitation in various environments, including the recycling industry.

2. STATE OF THE ART AND OBJECTIVES

2.1 Belgian Zn-Pb deposits

Ore deposits of Zn and Pb in Belgium are classified as Mississippi Valley type (MVT), which are typically characterised by epigenetic, strata-bound Zn-Pb sulphides occurring within carbonaceous host rock. The primary mineralogy mainly consists of sphalerite (ZnS), galena (PbS) and pyrite/marcasite (FeS_2). Deposits are hosted in Palaeozoic rocks and subdivided in three districts: the district of the Brabant Parautochton, a 120 km belt of 10-25 km width stretching across Belgium from Saint-Amand (France) to west of Aachen (Germany); the district of the Dinant Synclinorium, a 125km belt of 10-15 km width stretching from Beaumont to Bomal via Givet, where a subdistrict of fluorite and barite deposits are found in the central part; and the southeasternmost Ardenne district with scarce ore deposits (Dejonghe, 1998). Primary Zn-Pb sulphide ore bodies in Belgium are overlaid by nonsulphide deposits, often referred to as “calamine”, which are mixtures of minerals such as smithsonite ($ZnCO_3$), hemimorphite ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$), hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and willemite ($Zn_2SiO_4$), locally associated with Fe-oxyhydroxides, clays and Pb and Fe secondary minerals (Coppola et al., 2008).

The production of Zn and Pb was historically important in Belgium. The exploitation of Zn-Pb deposits dates to Prehistoric times, with mining activity peaking between 1850 and 1870. Since the beginning of the 20th century, Zn-Pb mining has steadily declined, with the last mines being closed between 1936 and 1945 due to exhaustion of reserves, dewatering problems, and refractory ores (Dejonghe, 1998).

Some CRMs are typically linked to MVT Zn-Pb mineralisation’s, attracting extra interest in these well-known and well-developed resources. For example, MVT deposits are notably one of the most important hosts of Ge-rich sphalerite (Frenzel et al., 2014). Globally, Ge and Cd are common byproducts of zinc ore processing, while small amounts of Ga are produced from zinc-processing residue (USGS, 2023). This considered, and within the context of the recent EU’s 5th list of CRMs, in Belgium the economic interest is particularly on Ge, which is used in optical fibres, infrared optics and satellite solar cells, and Ga, which is used in semiconductors and photovoltaic cells (EC, 2023).

But in light of possible future (re)exploitation of domestic resources, including recycling, it is important to consider the elements in MVT deposits that are of environmental concern. In Belgium, Zn-Pb mining and smelting in different districts such as Plombières (a.k.a. Bleiberg), La Calamine and Sclaigneaux caused significant Zn, Pb and Cd contamination of surrounding soils, sediments and waters, mostly due to chemical remobilisation of heavy metals in accumulated mine waste and atmospheric fallout of dusts enriched in contaminants from smelter chimneys (Cappuyns et al., 2006; Liénard and Colinet, 2016). Other heavy metals such as Cu are also significant contaminants in sites of former Zn-Pb-related industrial activity (Liénard et al., 2014). Consistent monitoring of soil health is key in the Belgian context.

2.2 The LIBS technique

The chemical composition of rocks and soils is of fundamental importance in the geosciences, especially in the context of mineral deposits and their life cycles. Traditional geochemical characterisation techniques such as XRF, ICP-AES, ICP-MS, among others, are typically time-consuming and expensive, which limits dataset sizes and therefore their representativity. In addition to their inherent longer analytical time, these techniques require sample preparation such as pelletization, melting or digestion, adding to total time and costs of analyses.

The LIBS technique (Figure 1) is based on emission spectroscopy which uses high-energy laser pulses as the excitation source. The laser is focused on a sample (solid, liquid or gas) that needs no special preparation, inducing a plasma with excited atoms and ions of the chemical elements present, which means that their electrons temporarily jump to greater energy states. When cooling, the electrons in excited states return to their lowest energy states. This process emits light which has specific wavelengths for each chemical element. The light emitted is collected and analysed by a spectrometer, and wavelength peaks identified by the spectrometer can be plotted by software in LIBS spectra. One of the significant advantages of LIBS includes the possibility of simultaneous analyses of major, minor, and trace constituents, including lighter elements (e.g., C, B, Be, and Li) which are notably difficult to detect with many other techniques.

Due to its simplicity in terms of instrumentation and operation, LIBS is extremely flexible and can be derived in many configurations, with point-and-shoot, line or area scanning capabilities, being able to cover from microscopic to field scales. These instruments typically achieve fast and sensitive analysis, with micro to milliseconds analytical time per single laser shot and detection limits in the parts per million (ppm) range (Fabre, 2020), varying depending on the element. For these reasons, application of LIBS across the broad spectrum of the geosciences continues to grow, especially for the geochemical characterisation of geological material (Harmon and Senesi, 2021).

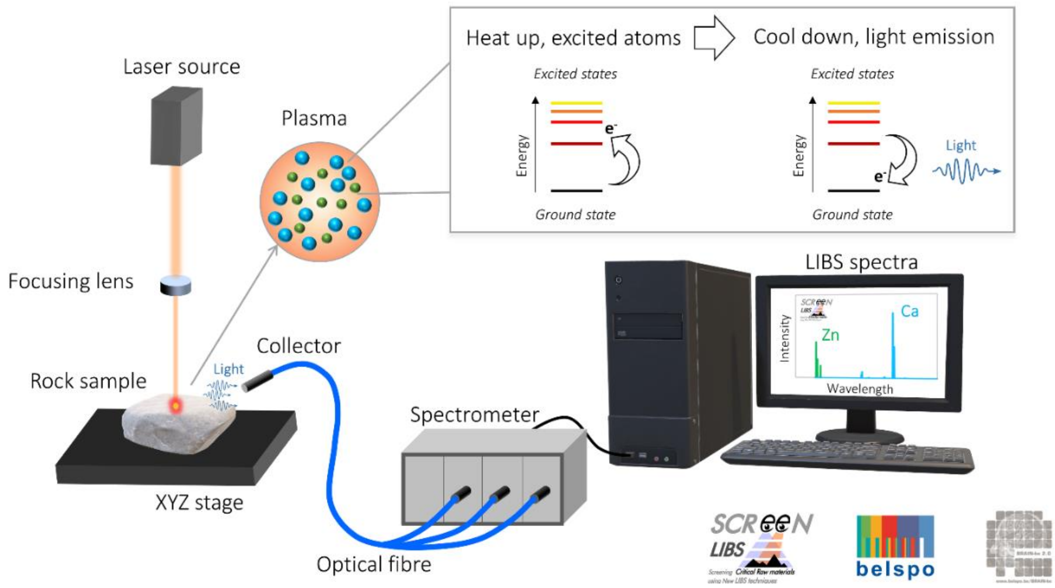


Figure 1: Scheme illustrating the principles of the LIBS technique.

With the capability of acquiring very large amount of data, typically in the range of tens of shots per second, on un- or minimally prepared samples, detailed multiscale distribution maps of almost all chemical elements can be obtained with LIBS. These chemical maps can be obtained by rastering the surface of the sample, which allows studying the distribution of the different elements in the sample. LIBS imaging has been pioneered in the early 2000s (Menut et al., 2003) and is now a powerful tool allowing acquisition of high resolution, multi-elemental chemical maps from a variety of materials including geomaterials (e.g., Caceres et al., 2017).

2.2 Current challenges and venues for innovation

The presence of elements of economic interest and environmental hazard in the same geological formations is common and can become an issue when exploiting resources Sound environmental monitoring for minimisation of environmental impacts is essential in new ventures of mineral deposit development. LIBS is a suitable all-round tool for geochemical characterisation and monitoring in the laboratory and on the field. However, analysing LIBS data is a complex and intense process. The successful design of a LIBS application is highly dependent on the optimisation of the data analysis methodology. Therefore, the translation of LIBS into a powerful technique is constrained by the high level of expertise required for mastering the processing and analysis of LIBS data.

To date there are no standardised design, settings or operation for the LIBS technology, which are needed to demonstrate the suitability of this method for widespread and larger scale applications to the whole recovery line of CRM. Protocols for screening, element identification and mineral classification using LIBS, as those that were developed by LIBS-SCReeN, represent important steps towards standardisation, providing a valuable contribution to the international LIBS community.

The generation of large amounts of spectral data, as it was the case during the project, requires adapted technologies of data processing and analyses and can greatly benefit from the evolving landscape of Machine Learning (ML) and Artificial Intelligence (AI) tools. Especially in potential future automated LIBS analyses, data extraction and processing that is also automated is strongly needed. This includes first several spectra pre-processing steps, such as background subtraction, peak alignment correction, normalisation, feature engineering, which aim at removing the possible artefacts present in the data and enhance the information of interest. Additionally, each chemical element has a specific LIBS spectral profile with several peaks appearing at specific wavelength. Therefore, when screening a sample, the obtained LIBS spectrum is a linear combination of the spectral profile of all the elements contained. Processes for identifying and quantifying peaks at element specific wavelength position also need automatization in such large data streams.

2.3 Objectives of the project

LIBS-SCReeN aimed at improving already existing LIBS infrastructure in Belgium (at UMONS) and developing and implementing further national LIBS analytical capacity (at RBINS-GSB and ULiège) in order to test the application of the technique to the whole life cycle of CRM, from exploration of resources to post-beneficiation scenarios of recycling and/or environmental issues. The specific objectives of the project can be summarised as follows:

1. Develop and implement scientifically sound workflows to exploit LIBS for elemental screening at multiple scales, demonstrating the ability of LIBS to perform fast and accurate screening of Zn-Pb deposits and associated processing sites in Belgium, including soils.
2. Optimise CRM identification workflows to ensure its applicability to different deposits and environmental needs.
3. Disseminate and cluster project’s activities with the global scientific LIBS community and EU projects to establish a Belgian LIBS expertise hub.

3. METHODOLOGY

3.1 LIBS setups

Two different setups were used for LIBS analyses during the project, one at the Geology and Applied Geology Department of UMONS, which was already operational before the project started, and one at RBINS-GSB, which was built during the project. These setups are currently operational for single shot and multi shot acquisition and include high precision XYZ stages for LIBS mapping.

At UMONS, the LIBS instrument is composed of a flashlamp-pumped Nd: YAG Q-switched laser (Lumibird-Quantel QSmart 450) with 5 ns pulse duration and maximum 20 Hz repetition rate used at 266 nm wavelength (quadrupled-frequency), with energy set to 15 mJ resulting in a spot size of ~200 µm when focused with a f=100 mm uncoated planoconvex lens. Light is injected into a multifurcated optical fibre connected to a high-resolution (0.05 to 0.10 nm from UV to NIR) multichannel spectrometer (Avantes ULS2048) with 11379 wavelength datapoints and 10 µm entrance slit.

At RBINS-GSB, the instrument includes a compact pulsed diode-pumped Nd:YAG laser (Lumibird-Quantel Viron) with pulse energy of 50 mJ at 1064 nm, pulse duration below 9 ns, maximum repetition rate of 20 Hz; focusing is done using a single 25mm diameter plano-convex lens (Edmund Optics YAG-BARR coated) with f=50 mm. the LIBS emissions are collected with multifurcated optical fibers connected to 5 spectrometers: a 4-channel Avantes Avaspec EVO 4096CL covering wavelength range of 200-572 nm with 0.07-0.09 nm spectral resolution, plus a single channel Avantes Avaspec EVO 2048CL covering wavelength range of 570-686 nm with 0.18 nm spectral resolution. All spectrometers use entrance slits of 10 µm width.

A third LIBS setup is being built at the GeMMe group in ULiège, and will be dedicated to core scanning, with a fast repetition laser (100Hz) and a wide detection range (200-1000nm). While built with other funding sources, the construction of this LIBS started during LIBS-SCReeN and was partly designed during the project in collaboration with RBINS-GSB and UMONS.

3.2 Rock sample analyses

3.2.1 Reference samples and ground truthing

An important step in the demonstration that the LIBS technique is suitable to detect CRM in ore material or soils was to compare the LIBS elemental analyses with the elemental analyses of already more routinely used methods. A total of 13 reference rock samples of Belgian Zn-Pb ores were selected to compare LIBS elemental analyses with SEM-EDS, µXRF and LA-ICP-MS elemental analyses. All reference samples were analysed through the generation of LIBS maps and 3 samples were selected for detailed ground truthing work. Major elements served to reconstruct the framework minerals of the geomaterials (mineralogical composition, grain size and shape/texture) using threshold and colocalization methods. This way, theA a distribution of trace elements could be superimposed on the mineral maps. Such an approach is also desirable for mitigating matrix effects and spectral interference issues (Fabre et al., 2018). Finally, with its capability of detecting light elements, LIBS can quickly discriminate sulphides from oxidized Zn minerals, for which it is expected that the trace elements content are different.

The comparison with SEM-EDS involved both spot analyses and line profiles. EDS spots were located in areas of high LIBS signal for Fe, As, Ge and Tl. There is good overall consistency between elemental concentrations of Fe and As and the respective LIBS intensities, although differences occur at low concentrations. Ge and Tl were not detected by EDS. Line profiles of EDS spots were performed to quantify Pb, Zn, Cd, Cu, Sb and Ag, and compare with a LIBS intensity line profiles measured by image analysis. A direct comparison is not possible due to the difference in resolution of the LIBS images and size of EDS spots (few µm) but comparing the trends of both profiles yields satisfactory results. Discrepancies observed are due to differences in spot sizes, detection limits and matrix effects. The comparative results obtained for a mixed sphalerite/galena sample from UMONS of unknown location (likely from Schmalgraff) have been published in Baele et al. (2021).

As a validation experiment, comparison was also made between LIBS mapping and µXRF (and to a minor extent SEM-EDS) mapping. For many elements, LIBS mapping picks up more detailed heterogeneities than the other two methods (

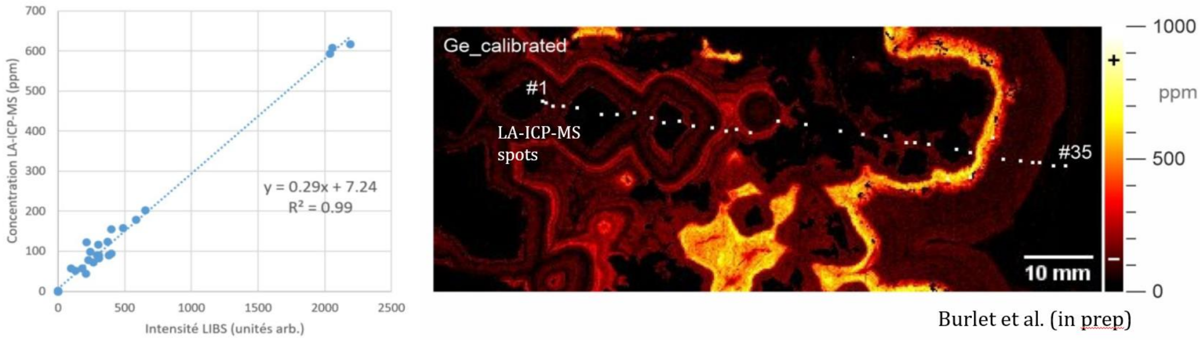


Figure 2A). LIBS is more suited to map elements that are not detectable by µXRF (unless when in high concentration or with very specific setups), including elements of interest such as Ge and Tl. For Fe and Cu, LIBS yields similar, although slightly noisier maps when compared to µXRF. For Ag, Sb and Cd, matrix effects and/or interferences (peak overlap) must be accounted for as LIBS and µXRF maps can be very different. For these elements, LA-ICP-MS analyses (see below) demonstrated that LIBS is closer to actual concentrations.

LA-ICP-MS analyses were done in the University of Lorraine Georesources Department. The comparison of LA-ICP-MS with LIBS images is satisfactory when manually matching analytical spots using Fiji image analysis software (R2>0.8), but it can often be improved with full georeferencing of the LIBS maps, including corrections for e.g., deformation. Therefore, LIBS is able to provide accurate information about the relative concentration (Fig. 2) and may even represent a better alternative for some elements (e.g., Ge, Tl). Finally, the good to excellent linear correlation between LA-ICP-MS concentration and LIBS signal allows using the trend line as a calibration curve and therefore obtaining absolute concentration in each pixel of the LIBS images.

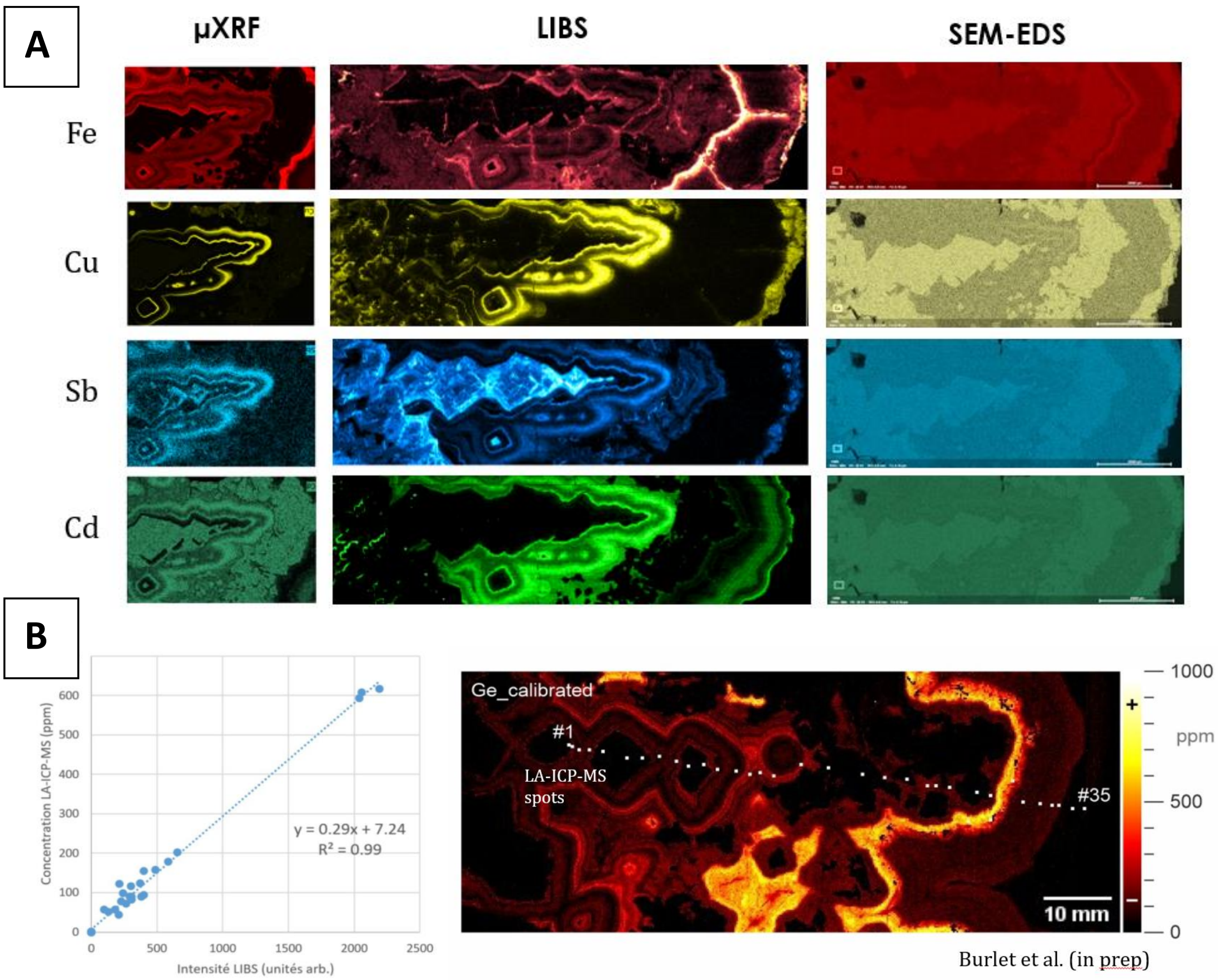


Figure 2: Comparison of selected LIBS maps with different analytical techniques; A) comparison with µXRF and SEM-EDS elemental mapping. B) Comparison with spot analyses of germainium with LA-ICP-MS, where the good correlation allows calibrating the LIBS map based on LA-ICP-MS values.

3.2.2 Sample and core inventory and selection

In order to apply the LIBS technique to suitable Zn-Pb rock samples and considering the limited access to known Belgian deposits in the field, an inventory of historical samples related to Zn-Pb ore deposits in Belgium was carried out targeting the geological collections of the project partners RBINS-GSB, ULiège and UMONS. A total of 1902 samples were identified (Figure 3), from which around 900 are samples of Zn-Pb ore samples (i.e., containing ore minerals such as sphalerite and galena), which include 7 of the reference samples that are catalogued with known locations, and the remainder are samples of other minerals associated to the ore minerals, collected from the ore districts. Information such as location (mostly approximate), sample dimensions and mineralogy, sourced from collections metadata, is recorded for each sample when available. For core samples, given the scarcity of Zn-Pb core samples among project partners' collections, a collaboration was established with Prof. Stijn Dewaele from UGent for an assessment of the historical Zn-Pb drill core boxes from Plombières (Figure 3) that form part of their teaching material.

From the total inventory, 408 hand samples were selected for screening in a way to represent all different Zn-Pb districts in Belgium, and a variety of mineral types (>50 different minerals); from the available core, 8 specimens were selected for LIBS mapping and development of automated mineralogical classification workflows. The distribution of screened samples is displaying in Figure 3.

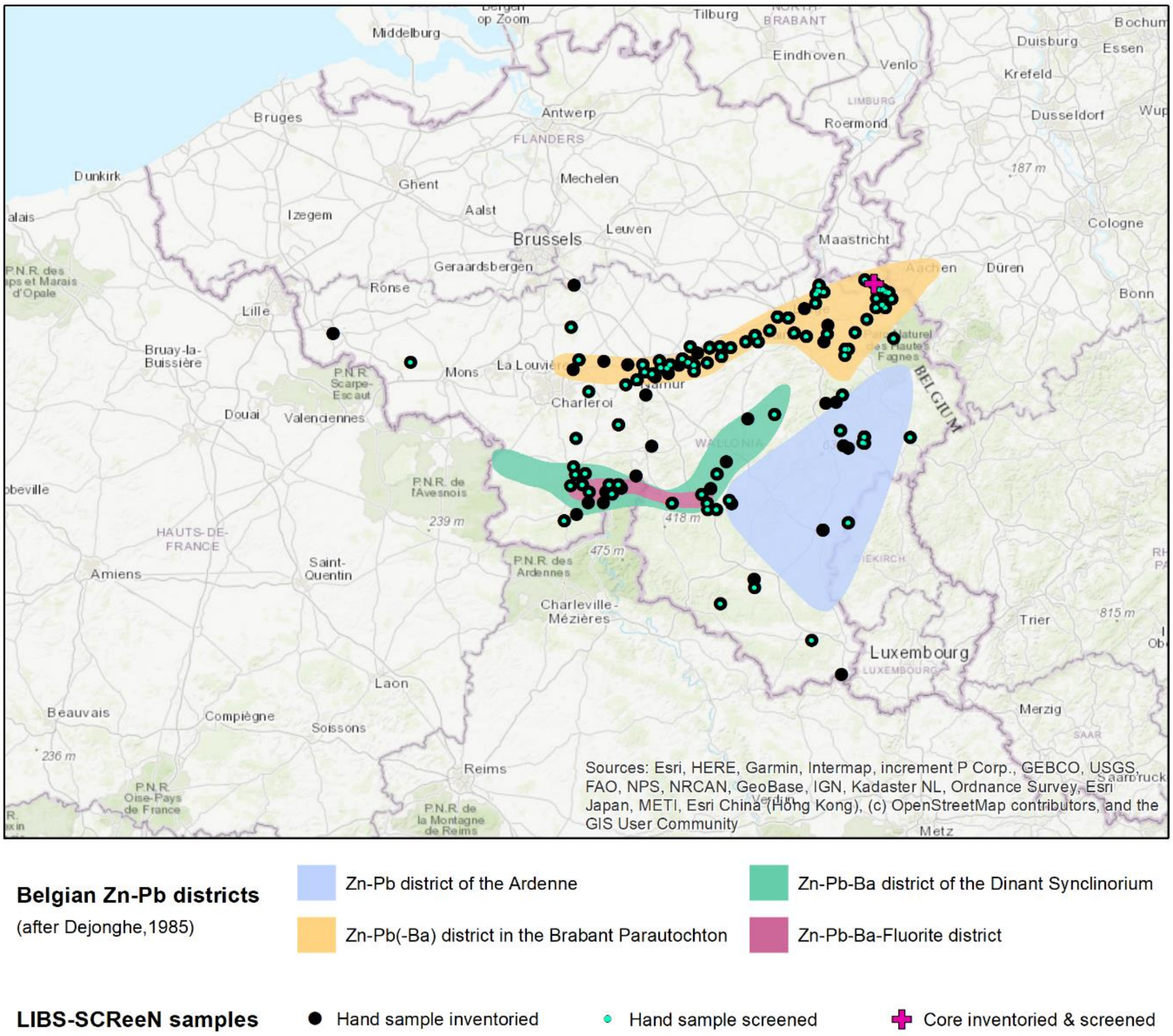


Figure 3: Distribution of hand samples and core inventoried and screened in the different Zn-Pb metallogenic districts in Belgium.

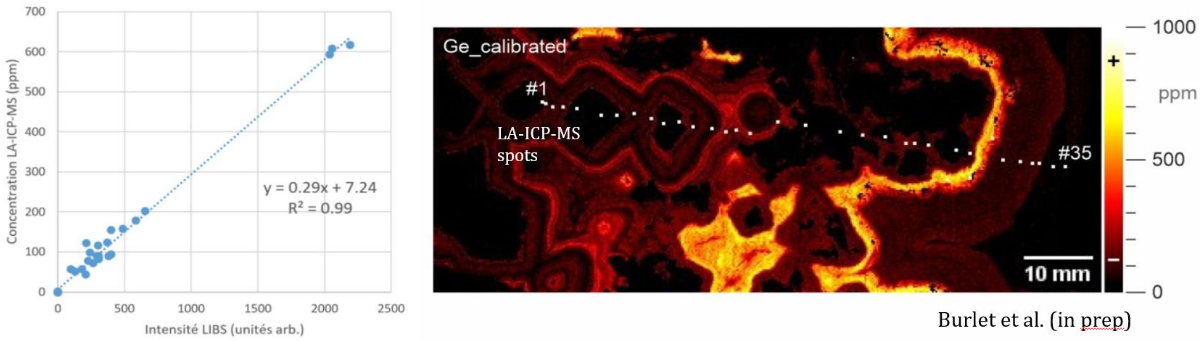
3.2.3 hand samples LIBS screening approach

LIBS is in essence an in-situ probing technology with a spot size ranging from a few to hundreds of microns. However, rocks are, in general, highly heterogeneous materials and a critical issue in LIBS analyses is the representativity of single spot measurements. This issue can be circumvented by taking advantage of the high-speed measurement capability of LIBS, which allows acquiring a large number of spectra by moving the laser beam or the sample in order to probe its whole surface. Therefore, both the average (bulk) composition and the degree of heterogeneity can be measured in seconds or minutes. This was the basic principle guiding the screening methodology.

Based on the geological material studied, we compared two different methodological screening approaches with the goal to compare the detection performance in different scenarios of user-bias and suitability to full automation. These approaches were:

1. *Targeted*: fewer LIBS spots per sample and greater visual textural and mineralogical control. This method consisted of visual selection of relevant mineral phases within a sample and manual navigation through the sample for optimal focus. Depending on the size or complexity of the sample, 6 to 30 spot analyses were performed (10 in average), each spot representing the averaged spectrum of 10 laser shots (with the first shot for dark measurement and the subsequent 3 shots for cleaning the surface removed).
2. *Randomised*: more analysed spots per sample with little textural and mineralogical control. This method used a Python-based software developed in-house to automatise single-spot data acquisition, set up to 30 points regardless of sample size or textural complexity, with time between measurements set up between 5 and 10 seconds depending on the sample to allow for manual navigation to the next spot and optimal placement for refocusing.

The screening strategy was developed with focus on economically or environmentally relevant elements: Ge, Ga, As, Tl & Cd. The distribution of the varied number of LIBS screening spots was based on the mineralogical heterogeneities of each sample, which can be generally separated in patchy or layered styles (Figure 4). When zoning was present, screening points were disposed in a way to cover different layers considering lessons learned from the mapping & ground truthing (cf. Figure 2), in order to minimise the chances of missing target elements during the screening process. Elements such as Ag, Cu and Ge are restricted to certain generations in the host minerals.



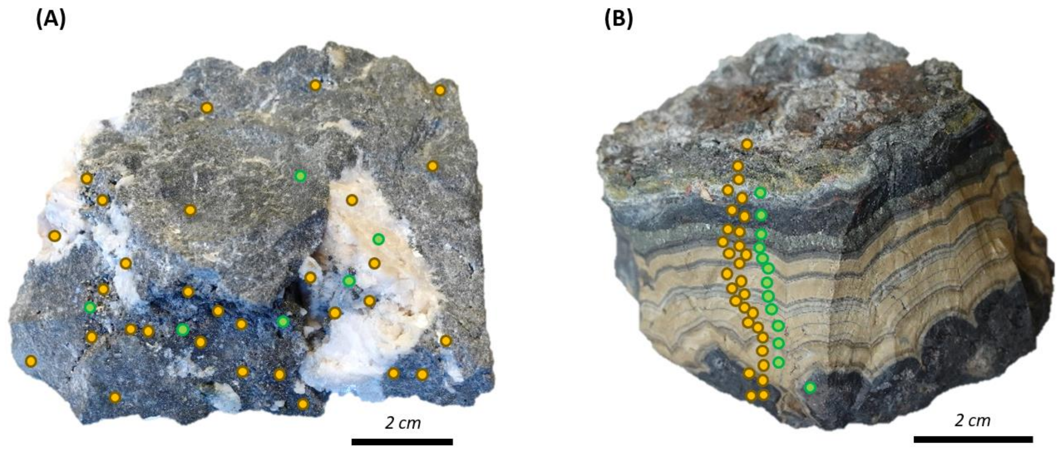


Figure 4: Schematic illustration of the distribution of LIBS screening spots in hand samples. Green dots represent the targeted screening approach and yellow dots randomised screening – spot size not to scale. (A) Spots in a sample with patchy heterogeneity versus (B) spots in a sample with layered heterogeneity.

Analyses were carried out in two batches between July and October 2022. The first batch totalled 168 samples and was first analysed at UMONS and then analysed at RBINS-GSB (except for 3 samples that were too small for a 30-point screening); the second batch totalled 243 samples that were first analysed at RBINS-GSB and then at UMONS.

3.2.4 Drill cores LIBS imaging approach for screening

Core drilling is one of the most useful sample collections in mineral resource exploration projects. The core preserves undisturbed textures of the rock and its mineralizations which allows more precise metallogenic studies and resource/reserve estimations. In parallel to the hand sample scanning, we thus wanted to develop a screening method to analyse these materials based on 2D LIBS imaging and automated mineralogical classification algorithms. During LIBS-SCReeN, and end-to-end procedure was designed for routine acquisition, preprocessing and classification of Pb-Zn drill core, using a spectral reference database associated to the Belgian deposits (galena, sphalerite, pyrite, calcite,…). The classification algorithms are based on state-of-the-art spectra segmentation methods: Spectral Angle Mapping (SAM) and Fully connected Neural Network (Deep Learning).

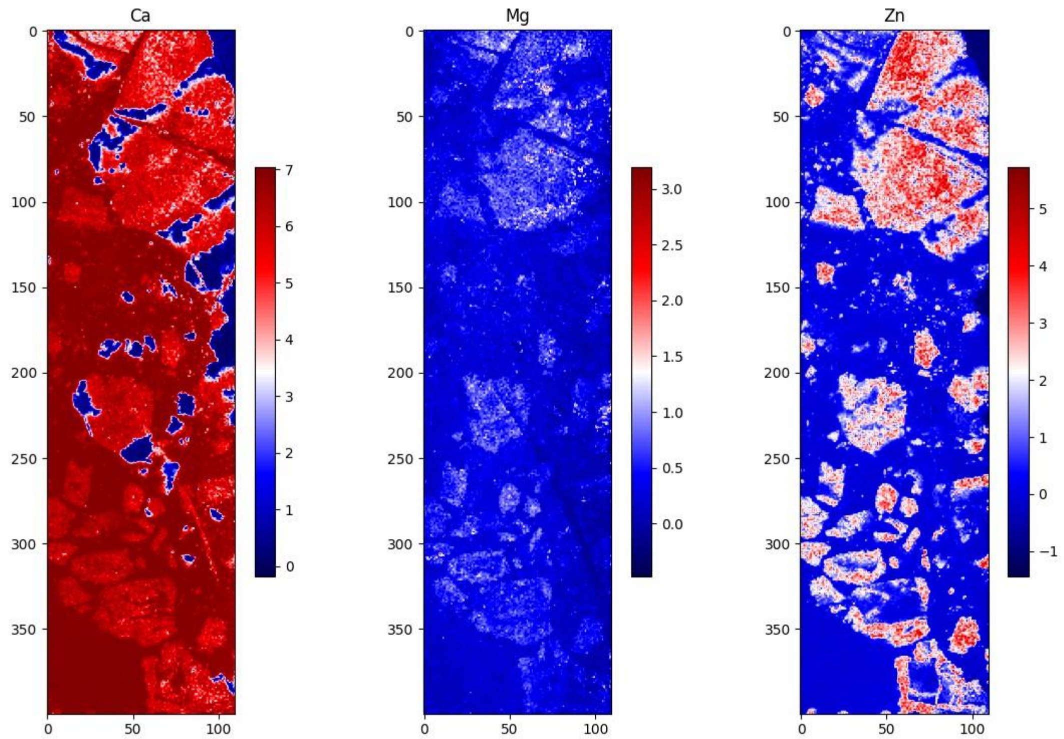


Figure 5: Example of a drill core LIBS image where elemental map have been normalized (SNV method) in preparation for classification

3.3 Contaminated soils screening methodologies

During the project, two approaches were followed and compared to define methodologies for soils contaminations screening using LIBS: a semi-portable and field applicable technique using minimal sample preparation and a more lab-based protocol for refined analysis.

3.3.1. Soils dataset analysis using minimal LIBS setup.

For this approach, we choose to work on a reference soils dataset from the Université Savoie Mont Blanc's (Edytem laboratory). These samples were collected in 2020 from the area around the historical Pb-Zn-Ag mines of Peisey-Nancroix in the French alps. After intensively looking for existing datasets of polluted soils, we choose this case study because the samples were made for a similar purpose than LIBS-SCReeN: rapid screening of soil pollution using XRF technique, with minimal sample preparation (quick grinding, no seaving and manual pelletisation). The dataset is also extensive, and we could perform LIBS analyses of 200 soils samples using the RBINS-GSB LIBS setup in its semi-portable version (see figure 6). For each sample 10 laser shots were made at different locations on the pellet surface. The mean of these 10 shots was used for analysis.

At the same time, XRF measurements were performed on the same samples using a custom XRF calibration model developed at the Edytem laboratory (Guillevic, 2023). The preparation of the 200 samples, plus the XRF and LIBS analysis took only 3 days and 2 people. This experiment represents well how LIBS could be deployed in environmental studies, or in remediation projects for routine soil screening, to reduce the number of samples to be sent to a reference laboratory.

Figure 6: (left) Portable LIBS setup installed at the Edytem laboratory in November 2022 – (right) soil samples dataset.

3.3.2 Soil measurements on a Belgian historic Pb-Zn site.

In order to test a LIBS-based, field-scale scanning method on a Belgian historic Pb-Zn ore treatment site, 17 soil samples were collected at the surface (<10 cm deep) of the Sclaigneaux brownfield, which is an abandoned industrial plant for zinc processing, near Andenne (Figure 7).

Figure 7. Location of the studied Sclaigneaux site, including chimneys (black diamonds), which were connected to the processing plants located to the south, and localities where samples were collected (circles).

For each sampling site, additional samples (labelled 'b' and 'c', with 'a' being the surface sample) were collected 10 to 20 cm deeper when it appeared that there were different layers. The soil samples were photographed and observed, especially for the presence of pebbles, sooth and plant residues. The darker soils indeed exhibit stronger carbon signal under LIBS analysis. The samples were then prepared as follows:

1. 24h drying at 40°C;
2. dry sieving at 2 mm;
3. manual elimination of rootlets and macroscopic plant residues;
4. subsampling with a Jones micro-splitter;
5. milling with a planetary agate miller;
6. pellitisation of 250 mg powder with a pressure of 4 tcm-2 (diameter of the pellets: 10 mm).

For semi-quantitative analysis, standard samples were prepared by artificial contamination of a noncontaminated soil with pure Pb, Zn and Cu compounds in the framework of the master thesis of Maïna FRANC (UMons). The following compounds with lab-grade purity were used: lead nitrate $Pb(NO_3)_2$, hydrated copper nitrate $Cu(NO_3)_2.3H_2O$ and zinc chloride $ZnCl_2$. The compounds were gently milled in different proportions with noncontaminated soil materials in order to achieve a range of heavy metal concentrations (10, 20, 50, 100, 200, 500 and 1000 ppm). All the pellets were prepared as triplicates and analysed at 3 different locations each with 10 successive laser shots.

3.5 LIBS data processing

3.5.1 LIBS data formats

The LIBS acquisition methods used in the project result in point (or multipoint) data, spatially referenced in the case of LIBS maps or with no spatial reference in the case of LIBS screening (Figure 8). Each point analysed, representing a LIBS shot, gives in a LIBS spectrum that represents a linear combination of the spectral profile of all the elements contained in that specific spot.

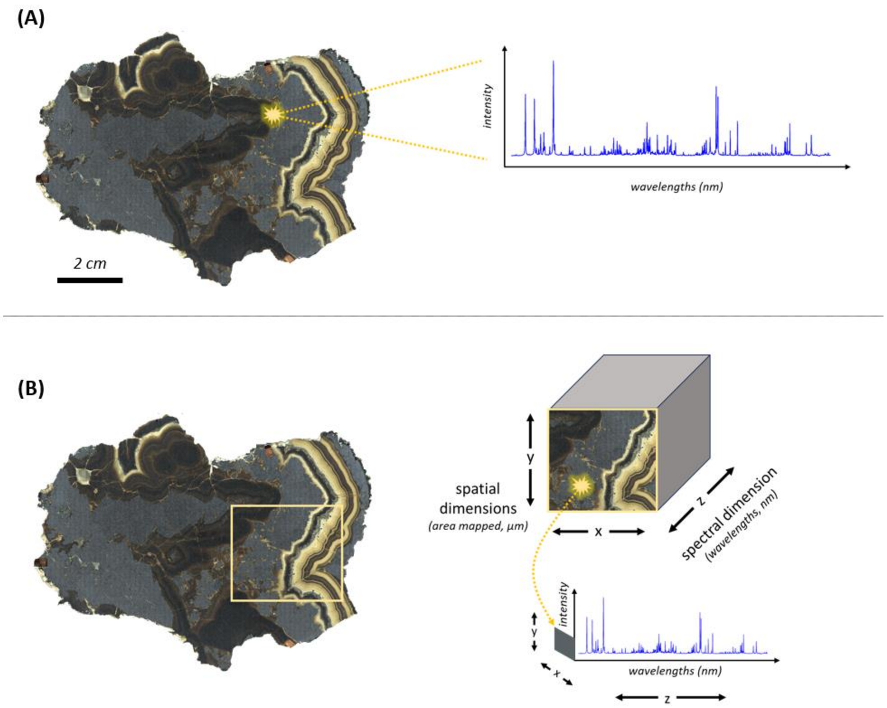


Figure 8. Illustration of LIBS spectra in the difference acquisition methods, A) spot data used in screening and B) data cubes resulting from maps.

As briefly described in the DMP (deliverable 1.4b), the data format used in LIBS-Screen are linked to these two type of data: point/multipoint analyses are stored is text format (csv or” comma separated values”), easily readable by existing spectral treatment software ex : Spectragryph, Bruker OPUS, as well as python/matlab/R programming languages). The map/imaging data was systematically stored in two equivalent formats: TIF multipages and netCDF as UMONS and RBINS existing instrumentation have been developed to work with these formats respectively. Small python scripts were developed to easily convert one format to the other, and both formats were systematically stored on the LIBS-SCReeN data repository. Almost one terabyte of spectra data has been acquired during the project and is kept on the RBINS partner online storage (Microsoft 365 Teams repository). This data can be made available upon email request. As foreseen in the DMP, the project generated algorithms for data pre-processing and processing are made available in the developed web application (see point 5.3) and in a Github public repository: https://github.com/Nipharqusproject/LIBS-SCReeN.

3.5.2 Data pre-processing pipeline

The developed pipeline for LIBS data cleaning includes several chemometrics specific methodologies for spectral pre-processing, such as background subtraction, baseline correction, peak alignment correction, normalisation, and feature engineering. All these methods aim at removing the possible artefacts present in the data and enhance the information of interest. Their performance was tested and reported on the soil data. Since this pipeline is developed to be LIBS specific, it can be thus applied to any new LIBS data measurements. This pipeline is accessible via the BeLIBS online application, and the source code is published on the project github.

3.5.3 Element identification with focus on CRM

Machine learning models were developed to handle the large volumes of spectral data generated with the screening and mapping approaches. Several advanced machine learning algorithms were implemented, and their performance compared to differentiate between mineral phases such as galena or sphalerite, to map and/or detect critical elements such as germanium, indium or gallium, and to rapidly detect the presence of potential pollutants such as Cd or As in ores and soils. Both unsupervised methodologies for mineral identification and a more supervised and targeted approach for elements identification and classification based on reference atomic spectra database (ex: Kramida et al., 2019).

4. SCREENING PILOTS RESULTS SUMMARY

4.1. Screening of hand-sized and core samples for CRM identification

The 408 samples analysed in both setups represent a large mineralogical variety associated to Zn-Pb occurrences in Belgium (10), with most samples having either sphalerite or galena (from primary sulphide deposits), or smithsonite (from non-sulphide deposits) as the main mineral phase catalogued. Many samples of minerals considered as “blanks” were also analysed, where no CRMs were expected to be identified, such as fluorite and quartz.

The first step in the screening process was to check if we can make the distinction between mineral -phases sphalerite and galena in the ~30 acquired spectra per sample. This was done using the Mons LIBS dataset. Principal component (PC) analyses were performed on the whole dataset and the distribution of the samples using the first 4 PCs could discriminate the 2 mineral phases. We observe that PC1,2 and 4 provide an obvious separation between the sphalerite and Galena, see figure 10. This indicates that it is possible to automatically identify the mineralogical phase behind each spectrum. Also interestingly this data informs us on the heterogeneity of the samples, by determining how many LIBS shots from each sample are labeled galena or sphalerite.

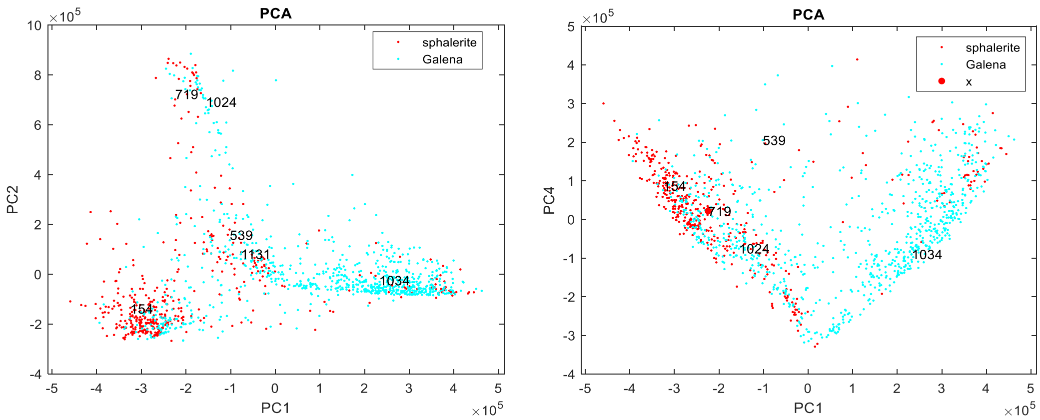


Figure 9. Plot showing the principal components analysis results on the UMONS labelled libs dataset.

Our robust and automatic elemental detection leverages an in-house heuristic approach. This methodology is specifically designed to efficiently identify elements using Laser-Induced Breakdown Spectroscopy (LIBS). We utilize the first 100 LIBS lines from the NIST LIBS database for 17 target elements, including major, minor, and trace elements ('Ag', 'Al', 'As', 'Ba', 'Bi', 'Ca', 'Cd', 'Cu', 'Fe', 'Ga', 'Ge', 'K', 'Mn', 'Ni', 'Pb', 'Si', 'Zn').

The core of our detection method creates a hit table for elemental peaks. This hit table captures the peaks' positions and compares them with theoretical values, identifying any deviations. It also highlights potential overlaps, ensuring accurate peak identification.

wavelengh	presence	distance to elem	flag_1	flag_2	flag_3	flag_4	flag_5	flag_6	flag_7	flag_8	flag_9	flag_10	flag_11
202,22	TRUE	0,007094116	0	0	0	0	0	0	0	0	0	0	0
205,32	TRUE	0,005668335	0	0	0	0	0	0	0	0	0	0	0
217,02	FALSE	0	0	0	0	0	0	0	0	0	0	0	0
220,37	TRUE	0,014927979	0	0	0	0	0	0	0	0	0	0	0
240,18	TRUE	0,001151733	0	0	0	0	0	0	0	0	0	0	0
244,63	TRUE	0,039561157	0	2	0	0	0	0	0	0	0	0	0
247,63	TRUE	0,001368408	0	0	0	0	0	0	0	0	0	0	0
257,73	TRUE	0,027912598	0	0	0	0	0	0	7	0	0	0	0
261,43	FALSE	0	1	0	0	0	0	0	0	0	0	0	0
262,84	TRUE	0,038242187	0	0	0	0	0	0	0	0	0	0	0
266,34	FALSE	0	0	0	0	0	0	0	0	0	0	0	0
280,19	TRUE	0,01715332	0	0	0	0	0	0	0	0	0	0	0
282,34	FALSE	0	0	0	0	0	0	0	0	0	0	0	0
283,29	TRUE	0,00572876	0	0	0	0	0	0	0	0	0	0	0
287,34	TRUE	0,039310303	1	0	0	0	0	0	0	0	0	0	0
357,27	TRUE	0,023579102	0	0	0	0	0	0	0	0	0	0	0
363,97	TRUE	0,001188965	0	0	0	0	0	0	0	0	0	0	0
367,17	TRUE	0,011491699	0	0	0	0	0	0	0	0	0	0	0
368,37	TRUE	0,010228271	0	0	0	0	0	0	0	0	0	0	0
373,97	TRUE	0,02987793	0	0	0	0	0	0	0	0	0	0	0
401,98	TRUE	0,030689697	0	0	0	0	0	0	0	0	0	0	0
405,83	FALSE	0	0	0	0	0	0	0	0	0	0	0	0
500,56	TRUE	0,020235596	0	0	0	0	0	0	0	0	0	0	0
520,12	FALSE	0	0	0	0	0	0	0	0	0	0	0	0

Figure 10 LIBS-SCReeN elemental peak hit table, with peak deviations from theoretical positions and peaks overlaps possibilities

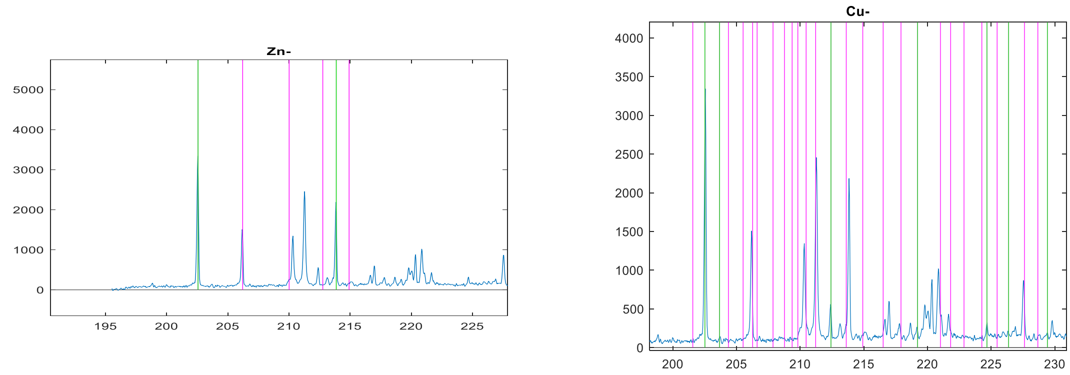


Figure 11 Graphical representation of the hit table, in relation to the LIBS spectra for Zinc (left) and Copper (right).in green, theoretical LIBS peak detected in the spectrum by the algorithm, in pink, peaks not detected.

While not all spectral peaks are identified automatically—some may shift due to spectrometer calibration—the approach is generally satisfactory for analyzing large datasets. The resulting elemental hit tables can be summarized in variance plots, displaying the number of detected peaks per element. This summary allows for rapid identification of outliers in 4 pre-determined geographical locations. By summarizing the elemental hit tables, we can compute the total number of peaks detected per element and conclude on the presence or absence of the specific element. This summary facilitates the rapid identification of outlier samples within the dataset, which indicates the presence of elements of interest such as Ge, Ga, etc….

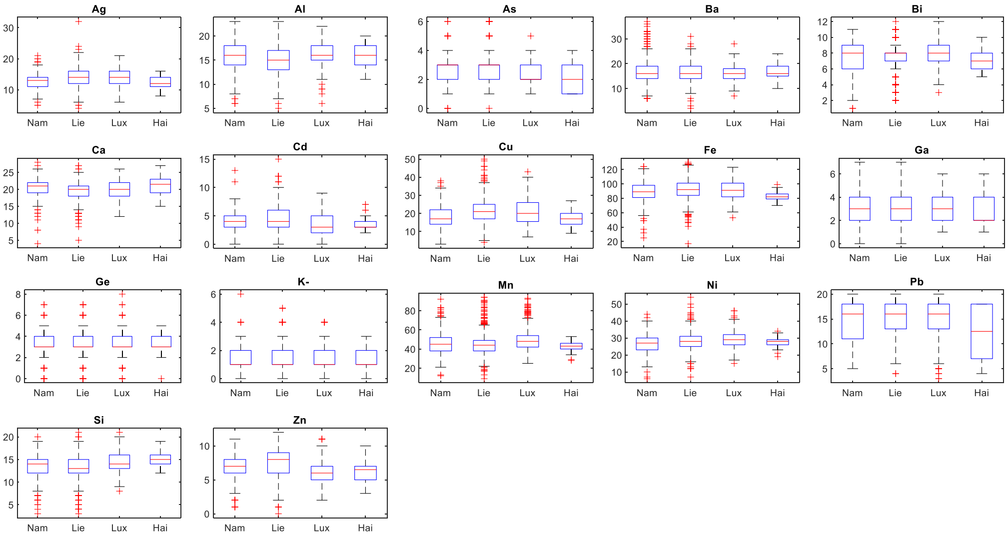
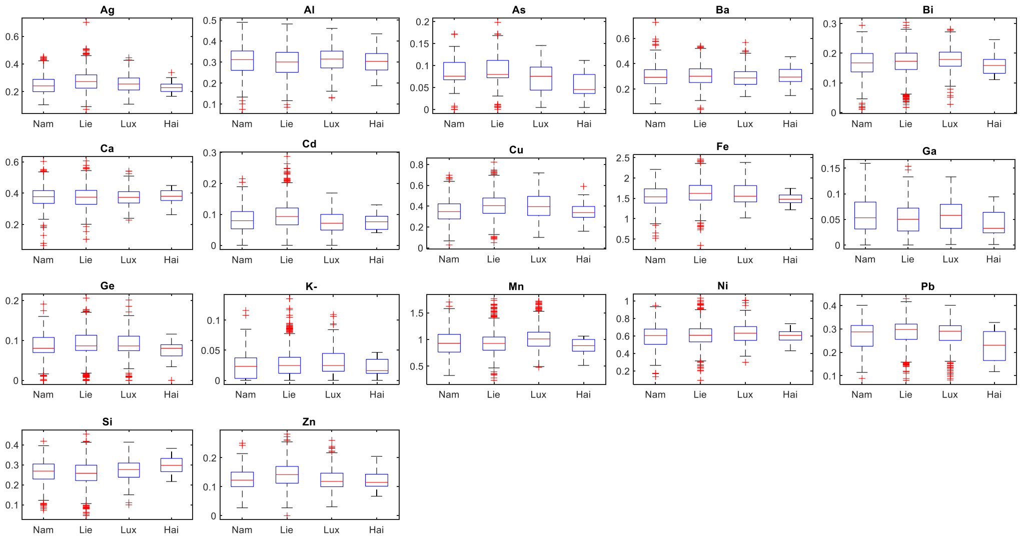
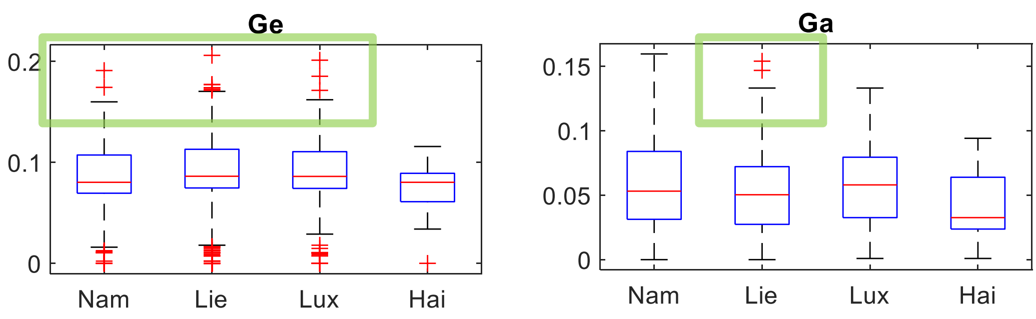


Figure 12 variance plots of the number of detected LIBS peak per element, grouped by Belgian provinces.

Additionally, we performed a similar analysis on the sum of peak intensities. By computing the mean and variance of detected peak intensities per element, here we even identify outlier samples more efficiently and detect the high concentrations of certain elements, such as Gallium (Ga) and Germanium (Ge) (see figure 13). Note that these elements are rather difficult to find with currently





used methods. Our LIBS analysis methodology is therefore a real added value in the screening .(ou qqchose du genre)

Figure 13 variance plots of the sum of intensities of detected LIBS peak per element, grouped by Belgian provinces. Bottom : high intensity outliers for Ge and Ga.

Out of this pilot analysis, a tentative map can be drawn with samples of interest for Ge, Ga and the penalty element Cd. (figure 14). This kind of synthetic map can be used as a base for new proception study.

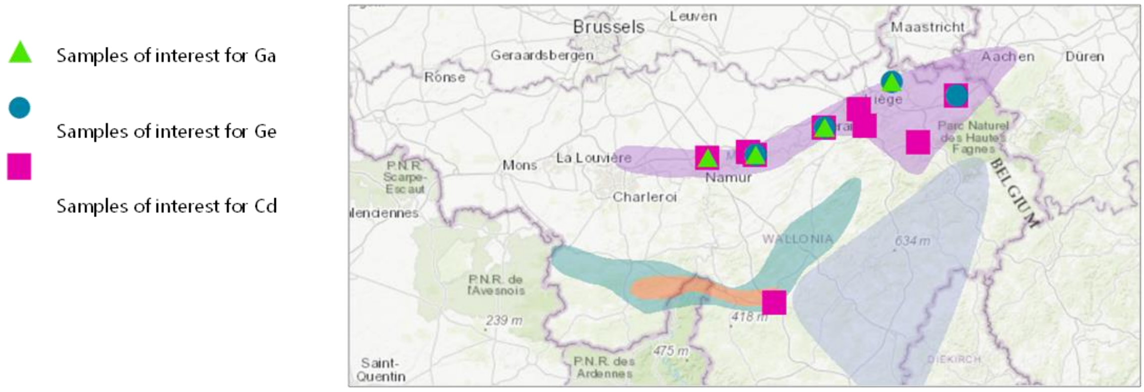


Figure 14 tentative synthetic map of the LIBS screening exercise: locations of interest for Ge Ga and Cd.

4.1.1 Results of imaging and automated mineralogy on drill core LIBS scans

Our neural network approach has also proven highly effective in classifying up to eight phases within core sections, as showed in Figure 14. This technique was applied to the eight available core samples. The outcomes of this work were presented at the Mathematical Geology IAMG conference, and a paper is currently in preparation.

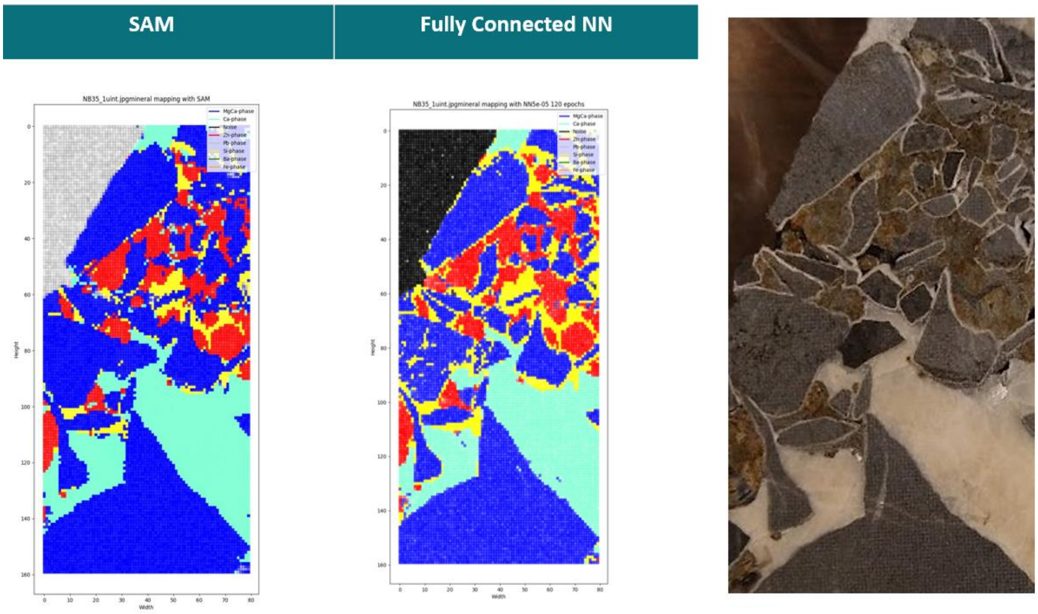


Figure 15: left: example of an automated mineralogical classification made on a Bleiberg Pb-Zn core, comparing the result of the SAM and NN methods, each color represent a specific mineral phase. Right the optical view of the core section, with LIBS ablation points visible.

4.2. Analyses of soils for environmental monitoring

4.2.1 Comparison with soil XRF data using minimal LIBS setup (Peisey-Nancroix dataset)

As a first data exploration step, multivariate statistics were derived from the XRF and LIBS datasets. The Principal Components Analysis for instance (Figure 16) globally show the same correlations/anticorrelations between the soil's groups (groups determined purely from visual inspection of the soils in the previous study).

The Figure 17 shows a plot of LIBS main Pb peak intensity (405.78nm) vs XRF measured PB concentrations on a very large concentrations scale (0->35000ppm), the correlation is imperfect but clearly show how LIBS peak intensities could be used as a quick, screening tool to determine highly contaminated sample from uncontaminated ones, even directly on the field. The non-linearity of the relationship between LIBS and XRF data for samples with high Pb concentrations is likely due to self-absorption of the Pb ion emissions in the plasma. Explain what is self-absorption? This phenomenon is well known and can be compensated either by using a nonlinear regression model or by empirically compensating self-absorption by comparing the Pb peaks full width half maximum (FWHM) instead of height or surface (Palleschi et al.).

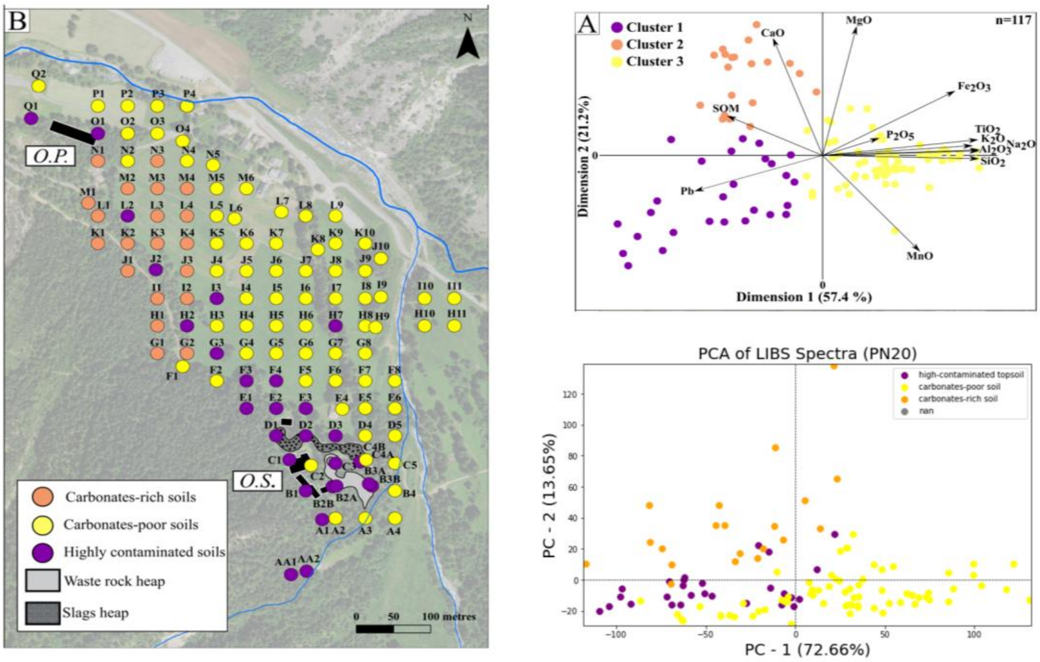


Figure 16 left : soils samples localisation in Peisey-Nancroix mine brownfield with rough soils classification using visual observations; right : XRF and LIBS PCA plots for a first dataset evaluation.

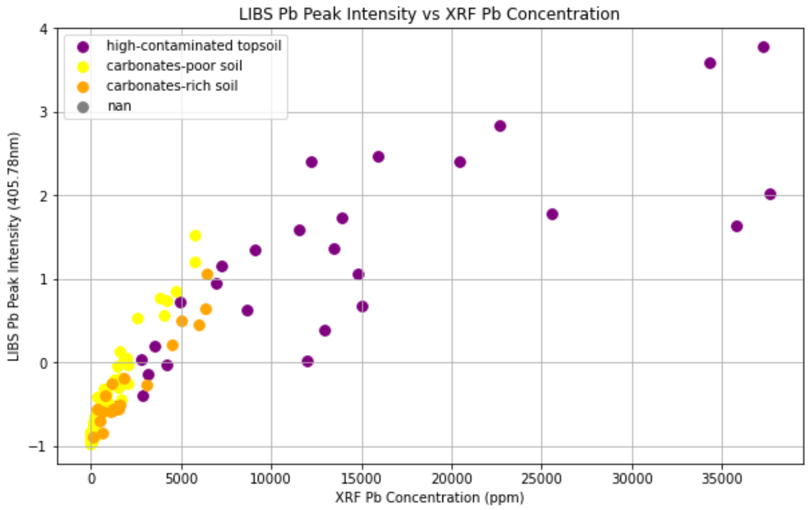


Figure 17 : scatter plot of the LIBS Pb peak height vs XRF measured concentrations for the Peisey-Nancroix soils samples

The figure 18 focuses on soil samples with XRF measured concentration between 0 and 1000ppm, in this range, the relationship between with the LIBS Pb peak heights is much more linear and doesn't seem influenced by variation in carbonate matrix. The dispersion of the measurements can be linked to the limits of the method (no seaving, very limited grinding), but also possibly to the accuracy of the XRF measurements (+-10%). Nevertheless, this demonstrate the feasibility of quick LIBS soils screening as, for example, most samples with more than 100-150ppm of Pb can be quickly identified based on the intensity of the main LIBS pb peak.

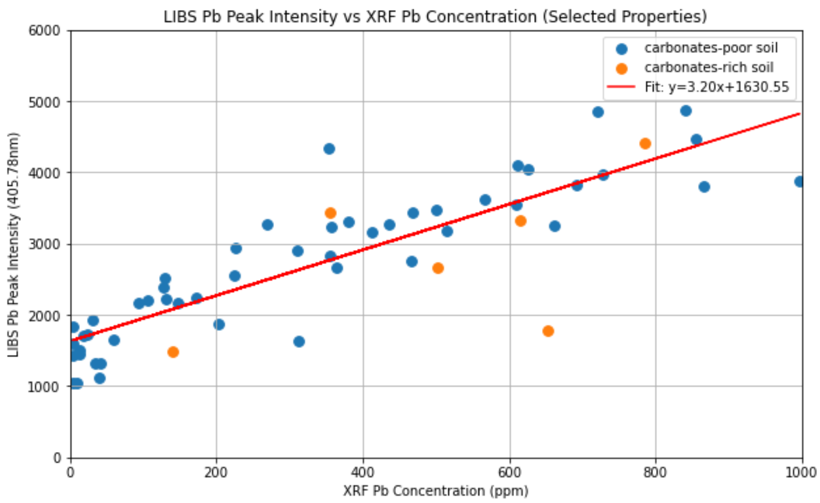


Figure 18 : scatter plot of the LIBS Pb peak height (intensity) vs XRF measured concentrations for the Peisey-Nancroix soils samples between 0 and 1000ppm.

4.2.2 results summary of the Sclaigneaux soils screening pilot

After signal processing and extraction, the LIBS intensities were converted into concentration using the obtained calibration curves (Figure 19) and the spatial distribution of results analysed in QGIS software.

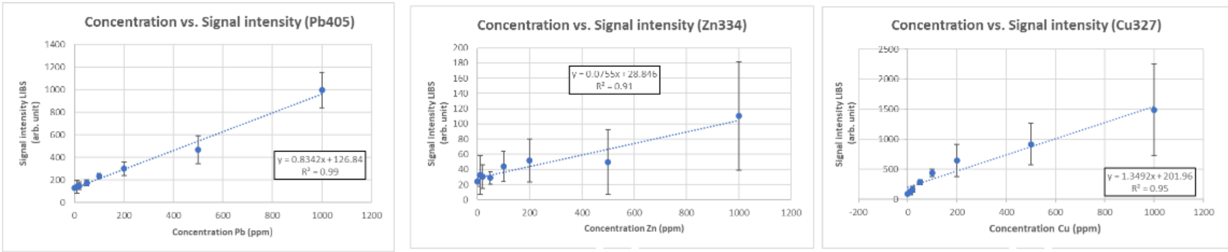


Figure 19. Calibration curves for Pb, Zn and Cu for semi-quantitative LIBS analysis on pressed pellets.

The results of the semi-quantitative LIBS analysis of soil samples in Sclaigneaux are presented in Table 1.

Table 1. Semi-quantitative LIBS analysis of Pb, Cu and Zn in Sclaigneaux samples.
Meaning of the sample label suffix: a=surface, b=10 cm depth, c=20 cm depth.

Sample	[Pb]	[Zn]	[Cu]
5	134.9	451.9	73.8
6	192.2	898.2	128.8
7	12285.7	42713.7	1014.2
8a	3637.8	36454.8	112.2
8b	17176.4	32161.1	1417.1
9a	1327.6	3060.8	149.1
9b	2492.2	6131.8	203.2
10a	2185.1	11250.5	290.4
10b	10200.0	15907.4	914.3
10c	3697.4	5898.0	359.4
11a	1594.7	4318.9	204.0
11b	1246.9	2866.3	163.7
12a	2460.9	9857.7	177.8
12b	1893.5	4569.1	213.5
13	1259.9	4228.4	164.7
14a	4628.5	12603.4	593.7
14b	2357.4	8257.5	279.1
			ppm

Although this analysis tends to overestimate known concentrations of heavy metals in the area (e.g., Lienard et al., 2014), the results are in fair agreement for Pb and Cu. However, for Zn, overestimation is considered excessive as Zn concentrations are overall twice that reported in the literature for this site. The reason for this may be a contamination of the standards used for calibration related to inefficient mixing of the metal compounds with the soil. Indeed , it was noticed that, during making of the standard pellets, the metals tended to stick to the agate pestle and mortar surface, especially the Zn compound, probably because this is a highly hydrophilic chloride compound that becomes soft upon hydration. It is therefore anticipated that the actual concentration in the standards used for calibration are too high compared to real values and therefore Zn content in the measured samples are overestimated. Further investigation of the standards by ICP-AES is necessary.

As with the example of Peisey-Nancroix, relative LIBS intensities, calibrated or not, can be used to map relative heavy metal contamination (fig. 7), where we can see the southernmost sampling sites are most contaminated, which may result from the proximity to the processing plants and/or the presence of several smelter chimneys to the west, which is a frequent prevailing incoming wind direction. Note that other elements such as Ba were found in higher concentration together with Pb, Zn and Cu in these contaminated areas.

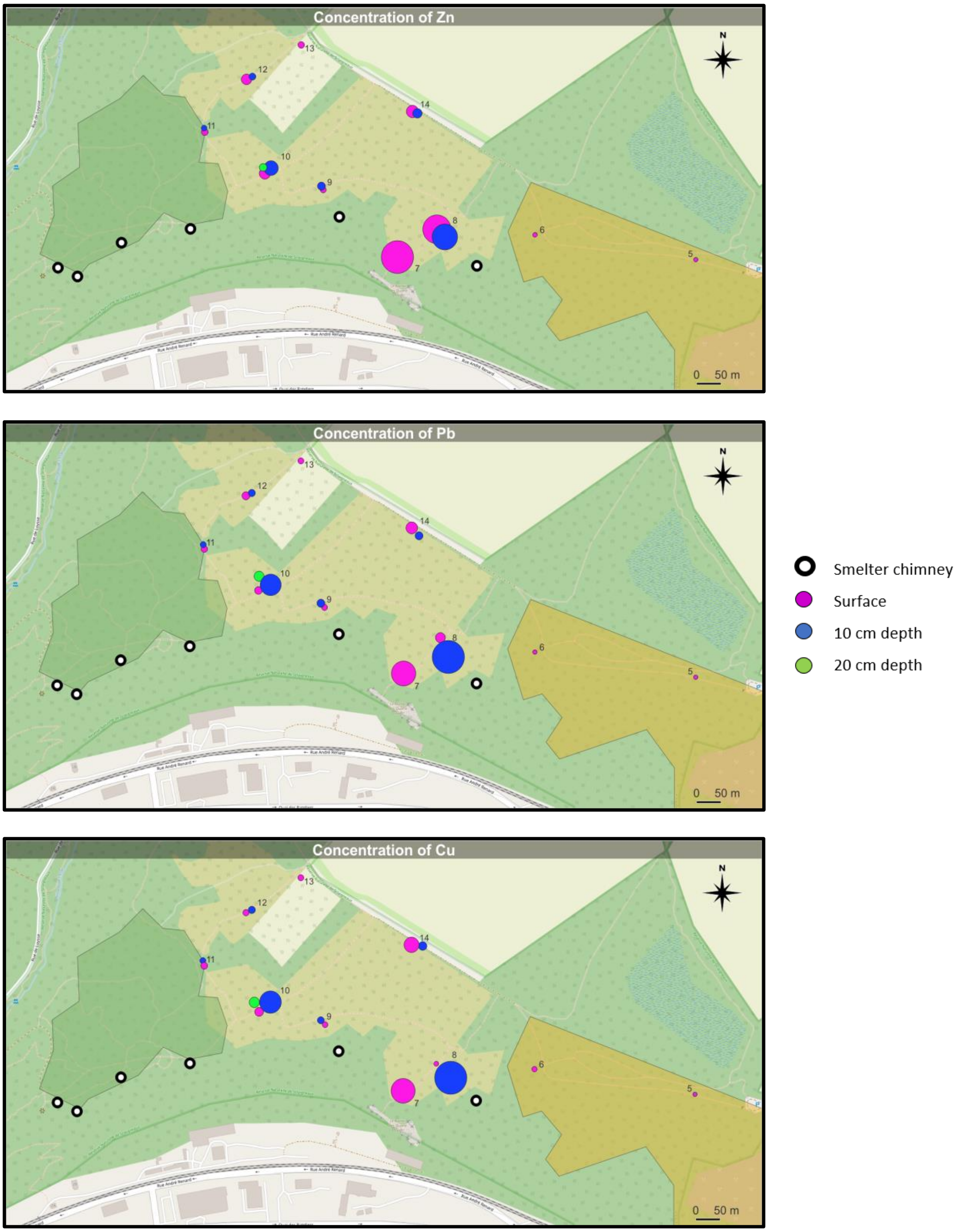


Figure 20. Concentration of Pb, Zn and Cu in samples collected in the Sclaigneaux brownfield (see Table 1 for values).

4.3. Conclusions regarding screening pilots

LIBS-SCReeN screening approach for critical raw materials (CRM) using LIBS has proven to be a robust and efficient method for analyzing both hand-sized and core samples. This first pilot study focused on samples from our institutional collections, with 408 hand samples analyzed, representing a high variety of mineralogical compositions associated with Pb-Zn occurrences in Belgium. Established data exploration techniques such as Principal Component Analysis (PCA) allows to automatically classify mineral phases without the need for manual labelling, enhancing the efficiency of the screening process. The clear separation of samples in the PCA space underscores the method's effectiveness in identifying mineralogical phases and understanding samples heterogeneities.

Our original heuristic approach for elemental detection, utilizing the first 100 LIBS lines from the NIST LIBS database, has allowed us to construct a detailed hit table for elemental peaks. This table not only captures peak positions and deviations but also flags potential overlaps, ensuring high accuracy in automated elemental identification. The graphical representation of these hit tables and variance plots facilitates rapid outlier detection, i.e. those samples with potential target elements such as Ge, Ga and Tl, and enables the visualization of elemental distribution in the defined geographical areas.

By analyzing the sum of peak intensities, we have been able to identify outliers with high concentrations of elements such as Gallium (Ga) and Germanium (Ge). This capability enables the creation of synthetic maps highlighting areas of interest for these specific elements, providing a valuable tool to delineate new exploration targets. Furthermore, our neural network approach for automated mineralogy on drill core LIBS scans has proven highly effective, classifying up to eight phases within core sections. This method showcases the versatility and precision of LIBS for new mineral exploration sampling campaigns.

In environmental monitoring, our semi-quantitative LIBS analysis of soil samples has shown good agreement with known concentrations for elements like Pb and Cu, despite some overestimation for Zn. This highlights the need for further refinement in sample preparation and calibration processes.

Overall, this first plot study of LIBS based screening offers a robust, efficient, and versatile tool for CRM identification in various sample types and proved useful in a first step of reconsidering CRM exploration on Belgian Pb-Zn deposits. The insights gained from this project not only enhance our understanding of mineralogical and chemical variabilities in our historical samples, but already pave the way for future action in the re-exploration of mineralizing processes that concentrated CRM in those areas.

5. DISSEMINATION AND VALORISATION

5.1. Overview of communication and dissemination activities

Within the context to the transition towards a low-carbon future and CRM needed to achieve this, the topics covered by LIBS-SCReeN are of high interest in regional, national, European and global agendas. For this reason, the project had a strategic position to make use of communication and dissemination tools to put the work being developed in Belgium in the spotlight. The communication and dissemination activities detailed below were performed throughout the project's duration and were successful to promote the project and its results, most likely helping to maximise the exploitation of the outcomes of the project.

Clustering events. The consortium made the choice to take part in various clustering activities instead of a single mid-project clustering event to maximise exchange opportunities with external colleagues. These were 1) collaborative field work with the company Impossible Sensing (USA) and the research institute Matís (Iceland) to test LIBS instrumentation in harsh environments, within the European EUROPLANET research infrastructure; 2) cooperative organisation of the European Horizon 2020 ROBOMINERS project's workshop "Innovation in Selective Mining: new trends and technological advances to reduce the environmental footprint of mineral extraction", and 3) Cooperative organisation of the stand "Development of innovative geochemical instrumentation" as part of the international event celebrating the 125th anniversary of the Geological Survey of Belgium. Moreover, some steps have been made to strengthen the collaborative network around LIBS research beyond the consortium. Contact was established with researchers from INESCTEC (Portugal), Université Savoie Mont Blanc (France) and iCRAG (Ireland) opening pathways for future collaboration.

Workshops. The consortium organised 2 workshops as part of the clustering events with ROBOMINERS (Horizon-EU project) and the Geological Survey of Belgium: 1) LIBS discovery workshop on 08 June 2022, and 2) LIBS demonstration workshop on 09 June 2022, both events at the Museum of Natural Sciences, Brussels.

Oral presentations in conferences. Various presentations were delivered, as listed below:

- Baele, JM.: "Terres pas si rares, mais alors… ? Les rechercher, les exploiter, est-on prêts ? », Conférence Printemps des Sciences, Haute Ecole Condorcet, Ath, 19 mars 2024.
- Nachtergaele, S.: "Automated mineral mapping using LIBS and deep learning". 22nd Annual Conference of the International Association for Mathematical Geosciences IAMG 2023, August 05-12, Trondheim, Norway.
- Baele, JM.: "Two decades of cooperation with the GSB", oral presentation with some emphasis on the LIBS-SCReeN project, GSB125 Meeting, 09 June 2022.
- Verheyden, S.: "Screening Critical Raw materials from exploration to (post)beneficiation using LIBS techniques" - RBINS SaLT Seminar at Lunch Time series, 10 June 2021.
- Verheyden, S.: "LIBS-screening of Lead-Zinc mineralisations for their potential in critical elements - gaining new insights in the Belgian Mississippi Valley Type deposits and their relationship with karst". CCOP 2020 Thematic Session: "Geoscience towards New Normal and Future Earth", December 15-16.

- Verheyden, S.: “Screening Critical Raw materials from exploration to (post)beneficiation using LIBS: first glance at project LIBS-SCReeN”. EAGE - Mineral Exploration Symposium 2020, September 17-18.

Poster presentations in conferences. 2 posters were presented, as listed below:

- Burlet C.: “Testing a screening methodology to identify Critical Raw Materials with Laser-Induced Breakdown Spectroscopy”. 12th Euro-Mediterranean Symposium on Laser-induced Breakdown Spectroscopy EMSLIBS 2023, September 4-7, Porto, Portugal
- Barros, R.: “LIBS-SCReeN project: Screening Critical Raw Materials from Exploration to (post)Beneficiation using New LIBS techniques”. GSB125 Meeting, 09 June 2022, Museum of Natural Sciences - Brussels.
- Barros, R.: “LIBS-SCReeN project: preliminary results”. GSB125 Meeting, 09 June 2022, Museum of Natural Sciences - Brussels.

Blog. An invited blog post for the Mineral Development Network Platform of the EU-Latin America Partnership on Raw Materials entitled “A fresh look at a well-known resource: screening for Critical Raw Materials in zinc-lead deposits in Belgium” was published on the platform (accessible only by members) on 14 June 2022.

A summary of communication and dissemination activities organised, and public reached is presented in Table 2.

Table 2: LIBS-SCReeN communication and disseminations activities summary.

Type of activity	**Number of activities organised**	**Estimated audience reached**
Workshops	2	>60 people
Oral presentations	6	>100 people
Poster presentations	2	>50 people
Clustering events	3	>60 people
Blog	1	>100 people

Besides the activities listed, the consortium also organised various periodic internal progress meetings and 3 dedicated meetings with the external experts of the Follow-up Committee to present and discuss results during the project.

5.2. Digital presence

During the second half of the project, our progress was documented on a dedicated LinkedIn page and Twitter/X profile. The social media and shared content about the project attracted a total of 190 followers and over 15,000 post impressions.

One of the main project dissemination efforts was the video series explaining the main tasks and innovation proposed by LIBS-SCReeN. The videos are available on YouTube and were shared in the project's social media. The information about the video series is summarised in Table 1.

Table 3: LIBS-SCReeN video series information, including view statistics.

Title	Link	Total views (YouTube)	Total views (LinkedIn + Twitter/X)
Finding critical elements using Laser-Induced Breakdown Spectroscopy | LIBS-SCReeN Episode 1	https://youtu.be/FVUAGKxCggg?si=T0QmEGLDE3E_t903	174	2,873
Laser-Induced Breakdown Spectroscopy as a tool for soil monitoring | LIBS-SCReeN Episode 2	https://youtu.be/3OckJoacrZw?si=pUVy4Su3EL4hWGkV	102	1,017
Laser-Induced Breakdown Spectroscopy data processing | LIBS-SCReeN Episode 3	https://youtu.be/Ljnh3yal3h0?si=V_NTjGXu-pTq1K-J	51	173

Barros, R.: Instagram stories in collaboration with the RBINS Communication team about the LIBS field test in Iceland, 25 May 2022. https://www.instagram.com/stories/highlights/17895464000542153/.

Barros, R.: Invited blog post on the Mineral Development Network Platform of the EU-Latin America Partnership on Raw Materials "A fresh look at a well-known resource: screening for Critical Raw Materials in zinc-lead deposits in Belgium", 14 June 2022.https://www.mineralplatform.eu/blog/fresh-look-well-known-resource-screening-critical-raw-materials-zinc-lead-deposits-belgium (MDNP users only)

5.3. Belgian LIBS Research Cluster

To valorise the LIBS analytical facilities that were partly built during the project, the consortium has agreed to establish the Belgian LIBS Research Cluster (BELIBS) to continue engaging in LIBS research beyond the duration of LIBS-SCReeN. BELIBS will act as the LIBS research hub in Belgium, offering expertise and services through the infrastructure now present in 3 institutions, UMONS, RBINS-GSB and ULiège. A dedicated website is now online to showcase the LIBS analytical capacity in Belgium and to attract further external collaborations. This is an important step to consolidate the LIBS expertise developed in Belgium, largely through the LIBS-SCReeN project, and increase the exploitation of the project's results. To sustain this initiative, a small website has been created (http://belibs.naturalsciences.be) which describe the LIBS laboratories and instrumentations available in Belgium for geosciences and showcase a few case studies from LIBS-SCReeN. This website will be maintained beyond LIBS-SCReeN and will incorporate LIBS advances results from other projects (ex: H2020 Robominers, HEU Persephone).

One of the first new collaborations initiated thanks to LIBS-SCReeN and this Belgian LIBS cluster is the use of LIBS mapping in lithium bearing pegmatites, with the KULeuven geology department:

- Acke, J., Borst, A., Dewaele, S., Barros, R., Nachtergaele, S., & Burlet, C. (2024). High-resolution mapping and quantification of lithium minerals in LCT-type pegmatites with LIBS and LA-ICP-MS. Event GAC-MAC-PEG 2024, Brandon University, Canada
- Acke, J., Kwizera, D., Goodship, A., Dewaele, S., Barros, R., Burlet, C., … Borst, A. (2023). Spodumene textural variations in a deformed LCT-type pegmatite. A case study from the Musha-Ntunga area, Rwanda. Mineral Resources in a Changing World, 17th SGA Biennial Meeting, Proceedings. Presented at the Mineral Resources in a Changing World: 17th SGA Biennial Meeting, ETH Zürichv

5.3.1 LIBS web application

This website is also the entry point to an element identification algorithm for spectral lines/peaks assignment in a measured LIBS signal, which was developed during the project. This algorithm is now available for the LIBS community in an open access LIBS web application. The application allows an intuitive user experience via a User Interface module (figure 10), uses a Python engine that processes the input LIBS signals and performs the specific LIBS signal analysis steps in the cloud, since all processes run online. The main innovations with this application are a new and robust peak/baseline detection routine and a contextual elemental peak search (takes into account possible interferences and flags these for the user. These two innovations allow a more efficient elemental detection in spectra from relatively unknown samples.

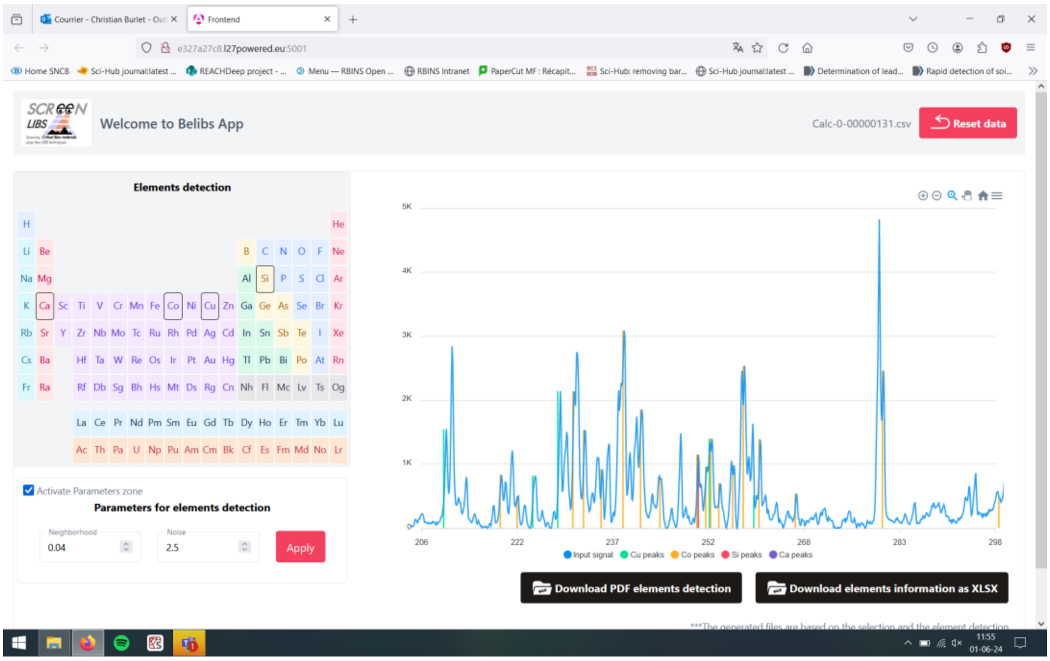


Figure 21 : example of interactive libs spectrum peak identification in the online application

Increase of the federal expertise in the FSIs

The LIBS-SCReeN project increased substantially the federal expertise in raw materials and their geochemical characterization. This expertise was used to investigate and valorize numerous pieces of the collections during the project. It increases our capacity to respond to societal issues as the currently implemented CRAM Act in which RBINS is active through the GSB.

6. PUBLICATIONS

6.1 Peer-reviewed publications

Baele J-M., Bouzahzah H., Papier S., Decrée, S., Verheyden S., Burlet C., Pirard E., Franceschi, G., Dejonghe, L. (2021). Trace-element imaging at macroscopic scale in a Belgian sphalerite-galena ore using Laser-Induced Breakdown Spectroscopy (LIBS). Geologica Belgica 24/3-4, 125-137. https://doi.org/10.20341/gb.2021.003

6.2 Conference abstracts

Barros, R., Burlet C., Croitor, A., Baele J-M., Papier S., Verheyden S., Nachtergaele, S., Bouzahzah H., Pirard E. (2023). Testing a screening methodology to identify Critical Raw Materials with Laser-Induced Breakdown Spectroscopy. 12th Euro-Mediterranean Symposium on Laser-induced Breakdown Spectroscopy EMSLIBS 2023, September 4-7, Porto, Portugal. Abstract Book 135. Link to Abstract Book

Acke, J., Kwizera, D., Goodship, A., Dewaele, S., Barros, R., Burlet, C., Nachtergaele, S., Borst, A. (2023). Spodumene textural variations in a deformed LCT-type pegmatite. A case study from the Musha-Ntunga area, Rwanda. 17th Biennial Meeting of the Society for Geology Applied to Mineral Deposits SGA 2023, August 28-September 01, Zürich, Switzerland. Abstract Book 1-4. Link to Abstract Book

Nachtergaele, S., Barros, R., Burlet C., Verheyden S., Baele J-M., Papier S., Bouzahzah H., Pirard E., Croitor, A. (2023). Automated mineral mapping using LIBS and deep learning. 22nd Annual Conference of the International Association for Mathematical Geosciences IAMG 2023, August 05-12, Trondheim, Norway. Abstract Book 239. Link to Abstract Book

Simon, K., Sobron, P., Barros, R., Stasi, G., Daussin, A. (2022). In-Situ Multispectral Investigation of the Biogeochemistry of the Geldingadalir Lava Field. SciX Conference, October 02-07, Kentucky, USA. Link to Abstract Book

Papier, S., Baele, J-M., Bouzahzah, H., Verheyden, S., Burlet, C., Pirard, E., Croitor, A., Decrée, S., Franceschi, G., Dejonghe, L. (2021). Geochemical imaging at hand-sample scale of Belgian Zn-Pb ores using Laser-Induced Breakdown Spectroscopy (LIBS). Geologica Belgica Meeting 2021, September 15-18, Tervuren, Belgium. Abstract Book 249-250. Link to Abstract Book

Verheyden, S., Burlet, C., Croitor, A., Baele, J-M., Papier, S., Pirard, E., Bouzahzah, H., Pusovnik, M. (2021). Development of a Laser-Induced Breakdown spectrometry (LIBS) instrumentation and protocols for rapid screening of soils. Geologica Belgica Meeting 2021, September 15-18, Tervuren, Belgium. Abstract Book 253-254. Link to Abstract Book

Verheyden, S., Burlet, C. Baele, J-M., Papier, S., Pirard, E., Bouzahzah, H., Croitor, A. (2020). LIBS-screening of Lead-Zinc mineralisations for their potential in critical elements – gaining new insights in the Belgian Mississippi Valley Type deposits and their relationship with karst. CCOP 2020 Thematic Session: "Geoscience towards New Normal and Future Earth", December 15-16, Virtual Event. Abstract Volume 42. Link to Abstract Book

Verheyden, S., Burlet, C., Baele, J-M., Papier, S., Bouzahzah, H., Dislaire, G., Giaro, P., Koch, P., Pirard, E., Croitor, A. (2020). Screening Critical Raw materials from exploration to (post)beneficiation using

LIBS: first glance at project LIBS-SCReeN. EAGE - Mineral Exploration Symposium 2020, September 17-18, Virtual Event. Link to Abstract Book

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