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Data Descriptor

Portable Analyses of Strategic Metal-Rich Minerals Using pXRF and pLIBS: Methodology and Database Development

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Abstract: Strategic metals are indispensable for meeting the needs of modern society. It is then necessary to reassess the potential of such metals in Europe. For the exploration of strategic metals, portable XRF (X-Ray Fluorescence) and LIBS (Laser Induced Breakdown Spectroscopy) are powerful techniques allowing their multi-elementary analysis. This paper presents a database providing more than 2000 pXRF data and more than 4000 pLIBS spectra acquired on minerals from the Mineralogy and Petrology Museum of National and Kapodistrian University of Athens (NKUA), selected based on their potential in bearing strategic metals. The combination of these two portable techniques, along with expanding dataset on strategic metal-rich minerals, provides valuable insights into strategic metal affinities and demonstrates the effectiveness of portable tools for exploring strategic raw materials. Indeed, such database allows to strengthen the knowledge on strategic metals by producing statistic and chemometric analyses (e.g., boxplot, PCA, PLS) on their distribution.

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Keywords: strategic raw materials; XRF; LIBS; handheld tool; exploration; geology

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1. Summary

Strategic metals are raw materials indispensable to the economy, defense, and energy policy of a country (e.g., energetic transition and digital technologies). The list of such metals is specific to each country and is regularly updated depending on the needs of the society (e.g., In, Re, Mo for United States) [1]. Among strategic metals, Critical Raw Materials (CRMs) are particularly important. The criticality of a raw material is a relatively new concept depending on its economic importance and the supply risk for a country. For example, in 2023, 34 raw materials were considered critical (e.g., Bi, Ge, Ga, Sb) in Europe [2]. Reassessing the potential of strategic and critical metals would decrease the supply risk and reduce the price rises linked to increasing demand. To better evaluate resources, an understanding of the distribution and deposition modes of such metals is required. However, some of the strategic metals mainly constitute rare and small mineral phases present as inclusions in other minerals (e.g., bismuthinite (Bi_2S_3) in pyrite (FeS_2)) or as substitution elements in other mineral phases (e.g., Re in molybdenite (MoS_2)) [3–8]. It is thus very challenging to identify those metals directly in the field.

Elemental recognition by the use of spectroscopic portable tools such as XRF (X-Ray Fluorescence) or LIBS (Laser-Induced Breakdown Spectroscopy) can provide quick feedback during the exploration of strategic metals [9–13]. Hence, the use of portable tools permits optimizing decisions such as rock sampling in order to reduce the amount of rocks to collect and select the best pieces for the time-consuming and costly analytical steps. Furthermore, they allow the acquisition of a large number of data directly in the field and permit a discussion on their relative and absolute distribution at different scales of investigation.

To improve the use of portable tools in the exploration of strategic metals, it is useful to create a database obtained on minerals potentially rich in such metals. Such a database has several advantages. Firstly, it provides a variety of signal information on minerals of the same species, which has the potential to enable spectral matching. This approach permits mineral identification without requiring the quantitative steps of analytical work, which is especially challenging with minimal sample preparation in field settings [9,14,15]. Secondly, multiplying measurements of strategic metal-bearing minerals helps to identify all phases in which these elements are likely present. That can be done in the field with cost-effective methods such as portable tools. Thirdly, a database allows the comparison between pXRF and pLIBS analyses and their efficiency in detecting particular strategic metals depending on the scientific or economic question. Finally, by providing large datasets, it makes it possible to perform statistical analysis on multi-elementary information such as elemental composition, mineralogical assemblage, and ore deposits [16,17]. It gives a general idea of strategic metal affinities with petrological, geochemical, and geological settings and can be used as a tool to predict mineralization.

Since 2021, the program Erasmus + ARTeMIS (Action for Research and Teaching Mineral Exploration Inclusive School), gathering international partners (Université de Lorraine (France), Friedrich-Alexander Universität Erlangen-Nürnberg (Germany), Aristotle University of Thessaloniki (Greece), and National and Kapodistrian University of Athens (Greece)), aims to teach, study and understand the distribution and formation of strategic metals in the Western Thrace region (NE Greece) by using portable spectroscopic tools [18].

In the frame of this partnership, during the period of May and July 2023, the Mineralogy and Petrology Museum of the National and Kapodistrian University of Athens (NKUA) opened its collections to build a database of chemical data through pXRF and pLIBS analyses on minerals potentially rich in strategic metals. The present paper introduces the mineralogical and elemental database that was recorded during that period.

2. Data Description

The database is divided into two sections: pXRF and pLIBS archives. For each portable instrument, the tree structure is as follows:

1. "Photos" folder >> date ("Year_Month_Day") folders >> PNG files. The "Photos" folder includes photos of the analyzed samples and photos of the spots where the analyses were performed on the sample. For the pXRF, the red circles have the diameter size of the analyses;
2. "Spectra" folder >> date (Year_Month_Day) folders >> data of each tool;
3. A CSV file for each tool ("pXRF/pLIBS_database.csv") giving a description of the analyses and samples. The different information is:
    - "Date": date of the acquisition (Year/Month/Day);
    - "Mineral": analyzed mineral;
    - "Chemical formula": mineral's chemical formula;

- "Sample ID": sample's name. The sample ID was retained when the sample had already been named in a previous study. When no name was available, the given ID corresponds to the mineral followed by a number;
- "References": when available, bibliographic references from previous studies conducted on the sample;
- "Type of sample": single crystal mineral or mineral in rock;
- "Surface state": flat, rough, or polished block;
- "Locality": sample's locality;
- "Country": sample's country;
- "Type of deposit": sample's deposit type as described in the literature when available. With question mark: hypothetic (determined as the most probable) due to a data lack;
- "Analysis ID": pXRF/pLIBS analysis name appearing in the database ("Spectra" folder);
- "Number of locations": only for pLIBS. Number of locations of analyses done on the same spot;
- "Cleaning shots": only for pLIBS. Number of cleaning shots per location;
- "Shots": only for pLIBS. Number of laser shots per location;
- "Shots to average": only for pLIBS. Number of shots to average per location;
- "Sample photo ID": sample photo name appearing in the database ("Photos" folder);
- "Spot analysis photo ID": name of the photo showing where the analysis was performed ("Photos" folder);
- "Comment": any comment on the analysis;
- "pXRF/pLIBS on sample": yes/no;
- "pXRF/pLIBS analysis ID on sample": pXRF/pLIBS analysis name on the same sample;
- "pXRF/pLIBS on spot": yes/no;
- "pXRF/pLIBS analysis ID on spot": pXRF/pLIBS analysis name on the same spot of the sample.

2.1. Portable XRF Database

For pXRF data, there are 2 types of files given by the instrument:

- Firstly, 2070 MCA files corresponding to the raw XRF spectra with no processing treatment. They relate to the intensity (counts) for each channel. Each analysis leads to two spectra (0 and 1), one at high voltage (0) in the tube and one at lower voltage (1), optimized for high- and low-Z elements, respectively. The header of MCA files contains 21 lines of general information on analytical conditions with the pXRF (e.g., live time, real time, filter position). The format of the MCA file name is "Analysis ID_Filter position_Date_Hour", with "Analysis ID" corresponding to the number of the analysis given by the instrument (cf. "pXRF_database.csv" file). "Filter position" relates to the tube voltage (0 or 1). "Date" is the date of acquisition ("Year.Month.Day" format) and "Hour" is the hour and minutes. The hour is noted on a 24-h clock, hence numbers ranging from 13 to 23 are for pm times.
- Secondly, there are 13 CSV files corresponding to interpreted data in weight% for elements included in the quantification program of the pXRF. There is one CSV file for each day of pXRF measurements. In the CSV file, there is the date ("Date") corresponding to the acquisition date and time (Day/Month/Year and Hour:Minutes in 24-h clock), the analysis number ("Analysis ID") referring to MCA file name, the real time of the acquisition in seconds («Real time»), and the reference of the pXRF tool

("Serial number"). Then, there are all the elements with their relative error which the pXRF can quantify in weight%. For the element hydrogen ("H"), the value corresponds to all light elements ($Z < 12$) undetectable with this pXRF.

2.2. Portable LIBS Database

Data from the pLIBS correspond to 4394 CSV files providing the signal intensity (arbitrary unit a.u.) at each wavelength (nm). For each sample, there is a spectrum averaging a number of individual spectra also given in the database. All spectra are calibrated in wavelength by Profile Builder (manufacturer software). The name of each file has the following format "Analysis ID_Date_Hour_Spectrum number". "Analysis ID" refers to the "pLIBS_database.csv" file. For pLIBS, the analysis ID is given by the name of the sample followed by the analyzed mineral and a number. "Date" and "Hour" are the date and time of the acquisition ("YearMonthDay_HourMinutesSeconds" format). "Spectrum number" corresponds to the average spectrum on the spot or the number of the location in the spot.

3. Sample Selection

Minerals are selected based on their potential to bear strategic metals according to literature references [3,4,6–8,16,19–21]. In total, 138 samples of 4 native element minerals, 8 sulfides, 5 sulfosalts and 2 arsenides (Table 1) from 13 different countries and different ore deposits were analyzed, with a strong focus on the Western Thrace region (NE Greece) (Figure 1), where porphyry–epithermal deposits are abnormally enriched in strategic metals (Bi, Sn, Re, Te, Se, In, Ga, Ge) [6–8,19–21]. Indeed, the porphyry–epithermal deposits of NE Greece are among the richest in the world in accessory (strategic and critical) metals, together with Capillitas in Argentina [22,23], Mt Carlton in Australia [24], and Toyoha in Japan [25].

Table 1. List of selected minerals with the number of analyzed samples by pXRF and pLIBS and the number of analyses with each tool on each mineral. For minerals within rock samples, endmembers of the tetrahedrite–tennantite group are difficult to distinguish then to avoid misinterpreted data, all minerals of this group are named "tetrahedrite–tennantite". For a more comprehensive classification of tetrahedrite–tennantite group minerals see Biagioni et al., 2020 [26]. ND = No Data.

Mineral	Category	Chemical Formula	pXRF		pLIBS	
			Samples	Analyses	Samples	Analyses
Native antimony	Native element	Sb	1	5	ND	ND
Native arsenic	Native element	As	7	21	1	4
Native bismuth	Native element	Bi	6	26	3	6
Native tellurium	Native element	Te	2	7	1	2
Arsenopyrite	Sulfide	FeAsS	2	15	2	23
Chalcopyrite	Sulfide	$CuFeS_2$	ND	ND	4	16
Covellite	Sulfide	CuS	1	3	ND	ND
Galena	Sulfide	PbS	14	194	13	146
Molybdenite	Sulfide	MoS_2	28	190	14	102
Pyrite	Sulfide	FeS_2	9	53	11	96
Sphalerite	Sulfide	ZnS	12	82	6	51
Stibnite	Sulfide	Sb_2S_3	5	32	5	13
Boulangerite	Sulfosalt	$Pb_5Sb_4S_{11}$	3	23	3	46
Enargite	Sulfosalt	Cu_3AsS_4	2	13	1	5
Nagyagite	Sulfosalt	$Pb_5Au(Te,Sb)_4S_{5\text{-}8}$	ND	ND	4	13

Table 1. *Cont.*

Mineral	Category	Chemical Formula	pXRF		pLIBS	
			Samples	Analyses	Samples	Analyses
Tetrahedrite	Sulfosalt	$(Cu,Ag)_{10}(Fe,Zn)_2Sb_4S_{13}$	3	15	4	9
Tetrahedrite–tennantite	Sulfosalt	$(Cu,Ag)_{10}(Fe,Zn)_2(Sb,As)_4S_{13}$	27	308	11	204
Safflorite	Arsenide	$(Co,Fe,Ni)As_3$	3	19	2	27
Skutterudite	Arsenide	$(Co,Fe,Ni)As_{2\text{-}3}$	3	29	3	43

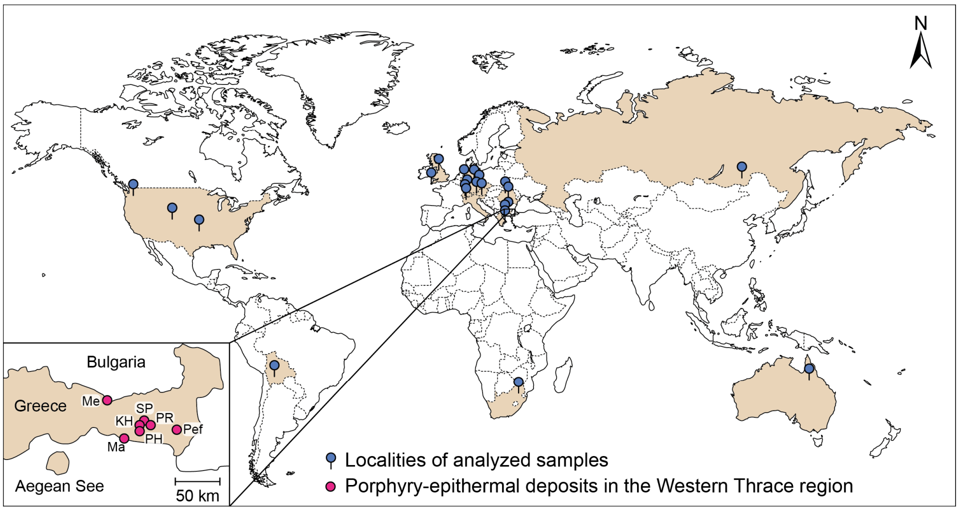

Figure 1. World map with the localities of the analyzed samples. A strong focus was placed on samples from porphyry–epithermal deposits in the Western Thrace region (NE Greece). KH: Konos Hill; Ma: Maronia; Me: Melitena; Pef: Pefka; PH: Perama Hill; PR: Pagoni Rachi; SP: Saint Philippos.

3.1. Minerals as Single Crystal Samples

A part of the analyzed samples are exhibited at the Museum of Petrology and Mineralogy of NKUA collection. It corresponds to 73 single crystal samples representing good reference minerals as they are big enough to undertake several analyses on one mineral (Figure 2a). Single crystal minerals, especially native element minerals, allow the acquisition of good characteristic peaks of strategic metals in order to better identify them with portable tools (black and blue spectra stand respectively for pXRF and pLIBS analyses in the following figures) (Figures 3a and 4a). It is also possible to collect, for each mineral, by spectral extraction, a typical spectral signature useful for the mineralogical recognition for future analyses of unknown mineral phases (Figures 3b and 4b) [27–29].

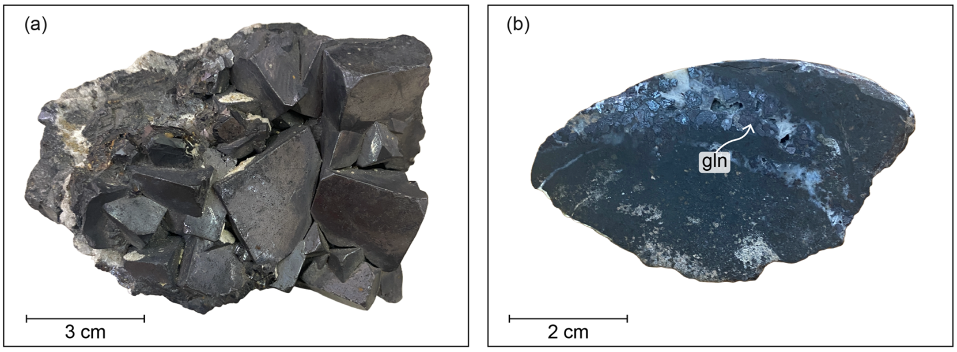

Figure 2. (**a**) Single crystal mineral (galena) exhibited at the Mineralogy and Petrology Museum of Athens (sample Galena-3, Lavrion (Greece)); (**b**) Mineral (galena (gln)) within a rock sample (sample PD68, Perama Hill (Greece)) from the P. Voudouris personal collection.

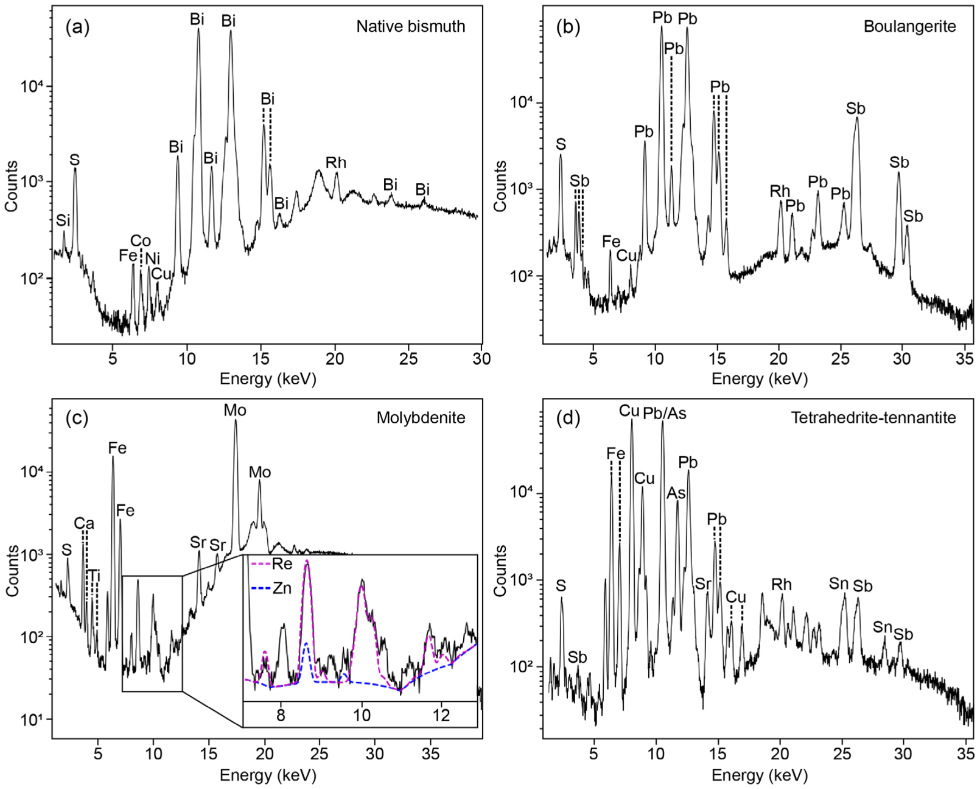

Figure 3. Portable XRF spectra from MCA files. (**a**) Typical native bismuth spectrum showing Bi peaks using pXRF (spectrum 3584); (**b**) Typical boulangerite spectrum (spectrum 4342); (**c**) Molybdenite spectrum showing the detection of a strategic metal (Rhenium (Re)) and overlapping at 8.6 keV between Zn and Re (spectrum 3263); (**d**) Tetrahedrite–tennantite spectrum with Pb detected probably due to inclusion of galena (spectrum 4622). For all spectra, detected Rh is a peak induced by the detector.

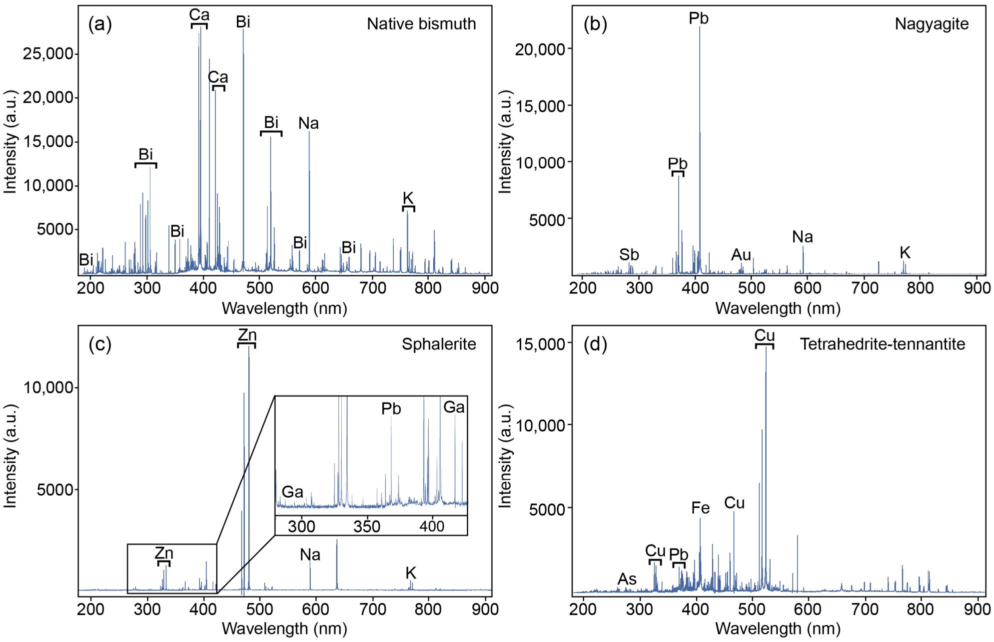

Figure 4. Portable LIBS spectra. (**a**) Native bismuth spectrum showing characteristic peaks of Bi with pLIBS (spectrum bismuth_2_1). Na and Ca can come from the hosting rock and the very good detection limit gives a high peak; (**b**) Typical nagyagite spectrum (spectrum nagyagite_1_1); (**c**) Sphalerite spectrum enriched in Ga (spectrum pd68_sphalerite_3); (**d**) Tetrahedrite–tennantite spectrum with peaks of Pb probably due to inclusion of galena (spectrum ki1_sousl_tetrahedrite_tennantite_1).

3.2. Minerals Within Rock Samples

The other part of the analyzed samples is from the personal collection of P. Voudouris (NKUA, Greece), corresponding to minerals of interest from the Western Thrace region. The interesting minerals are present within a mineralogical assemblage in a rock as opposed to single crystal samples (Figure 2b). In total, 65 different samples, with rough or flat surfaces, were analyzed with portable tools. When available, polished blocks of Western Thrace samples were analyzed. Minerals were first selected by microscopy with reflected light. In total, 40 polished blocks were analyzed only with the pXRF, as pLIBS is micro-destructive and may damage the sample. Some of these rock samples were previously analyzed and these data were published. These references can be found in the CSV files.

The interest of such samples is to multiply data in the same geographic area where the presence of strategic metals was recognized, giving the opportunity to evaluate the mineralogical affinities of such metals (Figures 3c and 4c). It is then possible to compare the relative abundance of these metals in one type of mineral among different ore deposits and have a first idea of the metal distribution over Western Thrace localities.

3.3. Sample Preparation

The result reliability depends on the sample preparation. For quantitative pXRF analyses, dry, homogeneous and flat samples of infinite thickness are required [30–32]. For a qualitative application with both devices, a classical element detection is possible without a strictly flat surface but the sample needs to cover the window limiting the loss of signal. In the present study, when only rough samples were available, analytical points were selected to be as flat as possible. All samples were dry and stored in similar conditions at the Museum avoiding an impact of humidity on the analyses. Single crystal minerals were considered as homogeneous regardless of potential zonations. Altered minerals were discarded and the selected samples did not present noticeable supergene alteration possibly increasing the porosity or influencing the quality of the signal. Available sample photographs in the database allow to estimate the preparation and quality of each sample.

4. Analytical Techniques

The majority of the samples were analyzed with pXRF and pLIBS due to the complementarity of both techniques. Firstly, pXRF provides quantitative results (in ppm or wt%) for a specific range of elements with good detection limits for base metals [9]. Portable XRF is unable to detect elements lighter than Mg and a reliable quantification of Au, Hg and PGEs is generally limited mainly due to nugget effects [9]. Portable LIBS is not quantitative without calibration curves but allows detection of lighter elements than pXRF (i.e., Li, F, Be, B, C and Na). Secondly, pXRF is a non-destructive technique allowing to analyze a 4 mm diameter spot on depths ranging down to a few hundred microns depending on the element measured and the sample composition. That makes possible to gather bulk rock analysis with a limited number of measurements. On the opposite, pLIBS is a micro-destructive method analyzing a 100 µm diameter area to a few microns depth by laser ablation. Prior to analysis, the laser ablation can be used as a cleaning shot to remove an undesirable layer [9]. Hence, pLIBS provides better data on small-sized crystals. Thirdly, pLIBS is faster than pXRF with up to 10 analyses in one second, depending on the number of cleaning shots and number of shots averaged for a single measurement. Portable XRF analysis can take up to several minutes to provide reliable results. Lastly, both techniques require an operator safety training: radiation protection due to its open-beam X-ray source for pXRF [9] and laser operating regulation for pLIBS.

In some cases, only one technique was used due to specific sample characteristics (surface, size, preparation). For example, some minerals were too small to allow pXRF analysis and would lead to mainly analyzing the hosting rock and not the mineral of interest. In other cases, the sample shape would lead to a low signal, which triggers the X-Ray tube interlock compulsory for radioprotection management. Portable LIBS could not be applied on transparent or soft minerals because the device could not detect the sample or the plasma emission was not sufficient enough, which in turn switches on the laser interlock compulsory in user safety management.

4.1. X-Ray Fluorescence

4.1.1. Portable XRF X-250 Characteristics

Portable XRF spectra were acquired with a SciAps X-250 portable XRF owned by the GeoRessources laboratory (Université de Lorraine, Nancy, France). Its X-ray tube consists of a rhodium anode operating under a maximum voltage of 50 kV. The detector is a standard Silicon Drift Detector (SDD) with an active area of 20 mm^2 and a spectral resolution of 135 eV at the Mn-Kα emission line. It holds an integrated camera to precisely position the analytical spot on the sample. The device window on its nose is covered by a prolene plastic film. The analysis spot diameter is 4 mm (Figure 5). The X-250 detects elements between Mg and U and quantifies 37 elements with the factory calibration (Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Rb, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ba, Ta, W, Hg, Tl, Pb, Ce, Cs, La, Y).

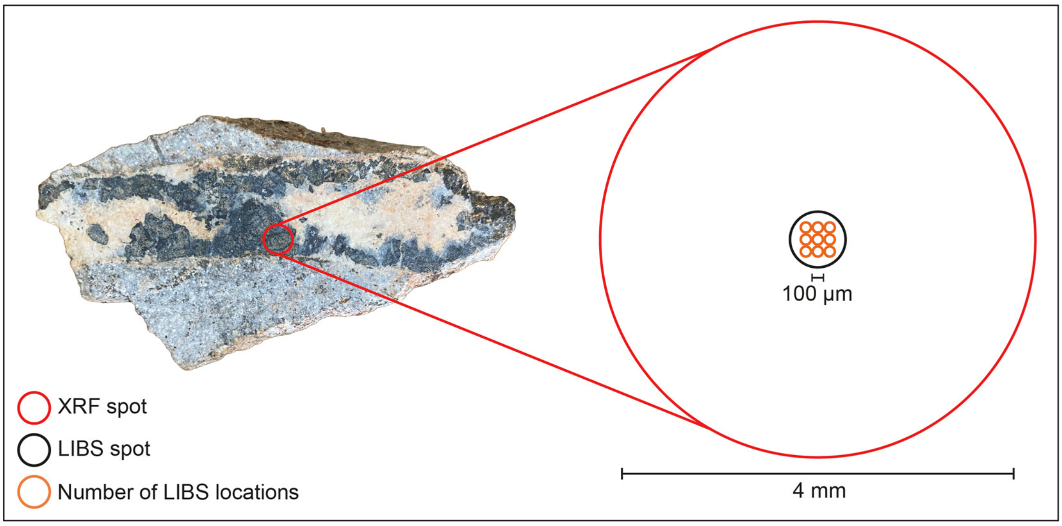

Figure 5. Comparison between sizes of pXRF and pLIBS spots. The pLIBS spot size depends on the number of locations per spot (sample PR17, Pagoni Rachi (Greece)).

4.1.2. Portable XRF Acquisition Settings

Due to the unknown matrix for each sample and the interest in strategic metals, data were acquired using “Mining” mode (Fundamental Parameters calibration) [30] and “Mine” sub-mode with two beams. Beam 1 at 40 kV for 15 s principally measures heavy elements such as transition elements and metals. Beam 2 at 10 kV for 15 s measures light elements in the matrix. When it was possible, at least 3 measurements for each type of mineral in each sample were performed in order to obtain a representative chemical composition of the mineral of interest.

4.1.3. Portable XRF Data

The pXRF provides two types of data: spectra and quantitative data. The raw XRF spectra correspond to MCA files with the intensity (counts) related to channels (can be converted into energy (keV) by the PyMCA software [33]) (Figure 3). Two MCA files per analysis are generated by the pXRF corresponding to each beam for light and heavy elements. The quantitative data are represented in a CSV file with the different proportions (wt%) of the elements included in the quantification program of the pXRF.

4.2. Laser-Induced Breakdown Spectroscopy

4.2.1. Portable LIBS Z-300 Characteristics

Portable LIBS spectra were obtained with a SciAps Z-300 apparatus owned by the GeoRessources laboratory. It detects elements from H to U with variable detection limits. The deposited energy is 5–6 mJ/pulse with a 10 Hz or 50 Hz frequency with an Nd-YAG laser at 1064 nm. Three CCD spectrometers cover a broad spectral range from 190 to 950 nm allowing the detection of one or more emission lines for each element of interest. The emission intensities of the LIBS emission spectra are reported in arbitrary units (a.u.). Analyses were carried out with a constant Ar gas pressure (16 psi), thanks to an Ar canister, allowing an increase in the intensity of the plasma emission. The laser spot diameter is around 100 µm for one analysis at the same location (Figure 5). The camera allows analyses to be made at the required place.

4.2.2. Portable LIBS Acquisition Settings

The acquisition is done with the "Elemental Pro" mode. Each measurement corresponds to an area named location. For each location, one or several laser shots can be performed to remove the dust or pollution on the surface (cleaning shots) and then one or several laser shots are performed for the LIBS analysis (Figure 5). In one studied area (spot), we can proceed to several analyses in different locations depending on the size of the mineral (Figure 5). In this study, the number of locations varies between 1 and 12. The number of cleaning shots varies between 1 and 2, and the number of shots per location varies between 2 and 6, depending on the surface state and the smoothness of the sample. All parameters are reported in the "pLIBS_database.csv" file. As for the pXRF, at least 3 measurements for each type of mineral in each sample were performed when it was possible.

4.2.3. Portable LIBS Data

The pLIBS provides CSV files corresponding to spectra relating intensities (u.a.) at wavelengths (nm) (Figure 4). The number of spectra for an analysis depends on the number of chosen locations. One spectrum is generated per location, averaging the number of chosen shots per location. A final average spectrum for all locations in a studied spot is always generated.

5. User Note

5.1. Data Quality

The number of pLIBS locations per spot was adapted depending on the analyzed mineral size in order to have a representative spectrum of that given mineral. However, (i) because it is not possible to adapt the pXRF diameter on one side and (ii) because pXRF can detect elements from depths of micrometers to several hundreds of micrometers depending on the element, one cannot fully exclude that the signal from the targeted mineral is mixed with some contribution from the neighboring ones. Moreover, small inclusions of other minerals are not excluded and can explain unexpected chemical composition for some analyses with both devices (e.g., galena (PbS) in tetrahedrite-tennantite (copper arsenic sulfosalt)) (Figures 3d and 4d).

Additionally, for a future quantitative application of pXRF data (wt%), it is necessary to report to the "pXRF_database.csv" file to check the sample preparation and therefore the reliability of quantitative results. It is also important to take in consideration that overlapping between elements not included in the device program can induce under- or overestimated values in weigth%.

5.2. Data Representativeness

The available minerals exhibited at the Museum of Petrology and Mineralogy of NKUA do not aim at providing a representative sampling of each locality. As such, any qualitative or quantitative comparison between each locality (e.g., Washington, Altenberg) for a particular strategic metals must keep in mind that feature. The first-order comparison is mainly done on the absence or presence of strategic metals. Nevertheless, such information remains of importance and will grow in usefulness with an increasing number of analyses available worldwide. However, the compilation of the data can provide a qualitative overview of elemental distribution among each type of ore deposits (e.g., porphyry-epithermal deposits, intrusion-related Mo-W deposits) and feed one's research topic.

The number of data acquired on minerals within rocks from personal collection of P. Voudouris is enough to be considered as representative at different scales of investigation. Firstly, at the sample scale, several measurements were done on a mineral type (e.g., galena, sphalerite) giving representative results for that given mineral. Secondly, that same mineral was analyzed in different samples giving an average composition at the ore deposit scale (e.g., Pagoni Rachi, Pefka). To be more representative, the user can refer to literature to compare samples with similar mineralogical assemblages. Lastly, data were obtained on several ore deposits through potassic alteration (porphyry zone) to argillic alteration (epithermal zone) allowing a compilation of a huge amount of data giving a representative interpretation of the porphyry-epithermal deposits at the Western Thrace region scale. To extend interpretation from the Western Thrace region to other porphyry-epithermal deposits, data can be compared with single crystal minerals in the database. Additionally, the representativeness of the database can be improved by comparing pXRF and pLIBS data on further samples from other studies.

5.3. XRF Data Processing

If required, the MCA files can be processed to look for elements such as strategic metals (Figure 3) and possibly interfering elements with free and open software such as PyMCA [33] (Figure 3c). On the spectrum, the intensity of element peaks is not representative of the quantity of one element compared to the other elements in the sample. However, fitting spectra will provide useful qualitative interference-free data that can be compared for one element between different samples. In order to facilitate comparisons, dead time and X-ray tube intensity corrections should be performed. Quantitative data given by the pXRF can be used without any specific treatment, considering the sample preparation.

5.4. LIBS Data Processing

LIBS spectra can be treated by the internal software Profile Builder or by other programs such as SpectraGryph [34] to recognize the detected elements (Figure 4). With Profile Builder, the recognition is facilitated by using the "LIBZ" or "NIST" databases included in the software. It is also possible to use the "NIST LIBS" database online [35].

It is encouraged to select at least two different emission lines per element to validate the presence of the element. The selection of the best emission lines for each element is based on a non-interference between different emission lines. Then, a qualitative comparison of element content can be performed between different minerals if they present the same matrix.

5.5. Examples of Data Use

Data can be used firstly to highlight the effectiveness of each device on the detection of a particular strategic metal. For example, the Re in a same molybdenite crystal of the PR5 sample is more easily detectable with pXRF than pLIBS (Figure 6a,b). Indeed, Re emission peaks are not detected with pLIBS at 346.5 nm and uncertain at 527.1 nm (theoretical Re peaks of the "LIBZ" database) leaving a doubt on the presence of Re (Figure 6a,b). If this result is recurrent between samples, conclusion can be made on the most appropriate tool for the detection of Re.

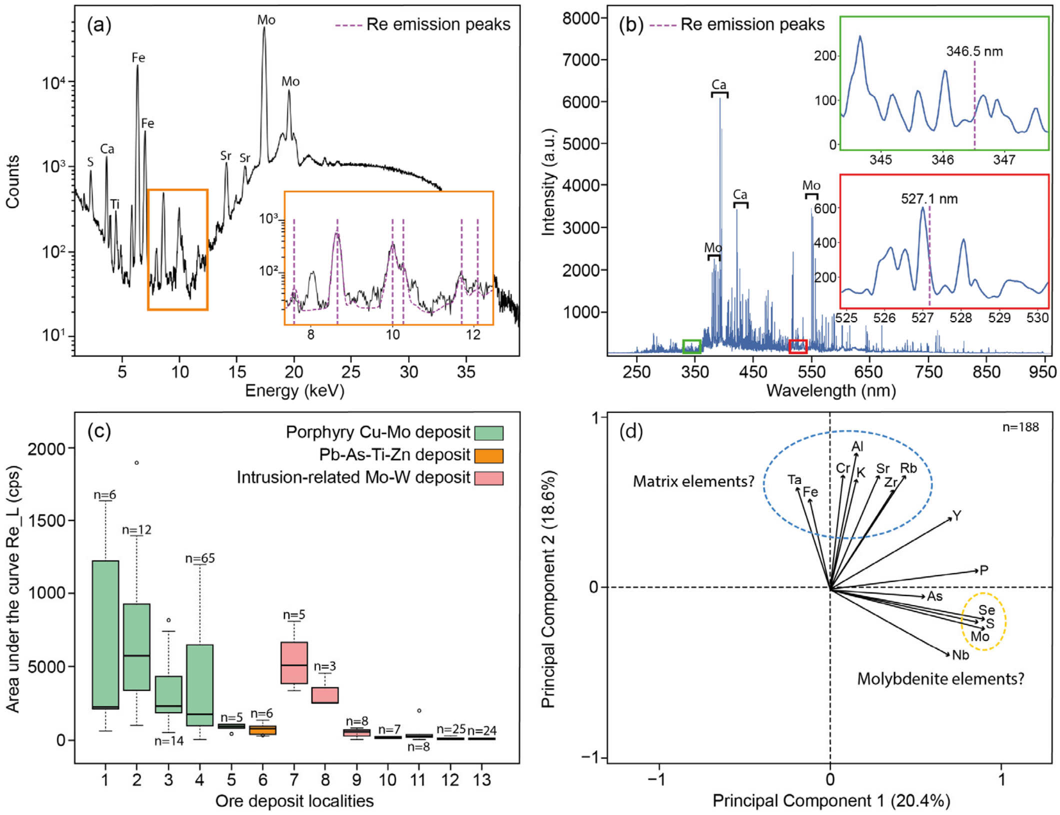

Figure 6. Examples of molybdenite data use. (**a**) Portable XRF spectrum acquired on a molybdenite crystal (spectrum 3263). (**b**) Portable LIBS spectrum of the same molybdenite as pXRF (spectrum pr5_molybdenite_6). (**c**) Boxplot of the area under the curve for Re_L emission lines of pXRF depending on the different ore deposit localities (1: Maronia; 2: Melitena; 3: Lesvos; 4: Pagoni Rachi; 5: Konos Hill; 6: Binn Valley; 7: Altenberg; 8: Horni Slakov; 9: North Queensland; 10: Middleburg; 11: Washington; 12: Kimmeria; 13: Laurion). (**d**) Principal Component Analysis (PCA) performed on pXRF data (wt%) for all molybdenite crystals in the database (see text for details).

Secondly, it is possible to use extracted signal (pXRF or pLIBS) of one strategic metal in order to simply compare its presence or absence depending on an interesting characteristic for the user (e.g., mineralogical assemblage, alteration type, ore deposit type). For example, by extracting the area under the curve of Re_L emission lines (pXRF) of all molybdenite crystals of the database, it is possible to observe two distinct trends (Figure 6c). Indeed, the majority of porphyry Cu-Mo deposits seems to be enriched in Re compared to intrusion-related Mo-W deposits (Figure 6c).

Lastly, chemometric analyses (e.g., PCA, PLS) allow for further insights by combining several parameters to enhance knowledge of strategic metals distribution. For example, a PCA realized on pXRF data (wt%) of all molybdenite analyses of the database shows two groups of elements (Figure 6d). The first component corresponds to major elements (Mo and S) and the second one refers to matrix elements (Al, Fe, K, Sr). Selenium is close to

Mo and S suggesting an affinity with these elements, and then diluted as trace element on the major phase (molybdenite) (Figure 6d). It paves the way to further questions about the presence of Se in molybdenite (depending on the localities, ore deposit type, and mineralogical assemblage affinities).

This is a simple example with molybdenite, but there are numerous options for the user to experiment with the database's results.

To conclude, this database represents a unique opportunity to process data from portable XRF and LIBS analyses of strategic metal-bearing minerals. The dataset highlights the potential of portable tools to extract elemental data from museum collections at a limited cost. The more collections will be measured, the more modern data processing methods based on the existence of labelled datasets will become applicable to portable spectroscopies. It paves the way to an international database which can be supplemented gradually by different authors facilitating the exploration of strategic metals by portable tools without going through costly laboratory analyses. On the other hand, this database also shows that the collection held at the Museum of Petrology and Mineralogy of NKUA hold samples of importance. These are available for further analyses (additional portable tools, laboratory analyses) in the frame of studies focused on strategic metals. Additionally, the strong focus on the Western Thrace region contributes to strengthening knowledge on strategic metal distribution in porphyry-epithermal deposits of that specific area.

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