

CHARACTERIZING THE ECONOMIC VALUE OF AN EPITHERMAL AU-AG ORE WITH LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS): POSSIBILITIES AND LIMITATIONS

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Abstract

LIBS was applied to 19 Au-Ag ore samples to investigate if this technique can be used to distinguish between economic and sub-economic ore either by direct detection of these elements or by using other elements as indicators. However, the Au and Ag grades of the samples are below the detection limit of the LIBS setup that was used. Furthermore, sample heterogeneity imposed difficulties for extracting quantitative compositional information from LIBS spectra due to signal intensity variations and chemical matrix effects. By applying a principle component analysis to the LIBS dataset it was discovered that LIBS can be used to distinguish waste samples by using the spectra as chemical fingerprints of alteration mineralogy. This means that there is potential that an on-line LIBS system can be used to monitor of the economic value of epithermal Au-Ag ores by using the alteration mineralogy as indirect indicators.

Introduction

Laser induced breakdown spectroscopy (LIBS) is a sensor technique that utilizes a pulsed laser beam to determine the chemical composition of a material. The laser ablates a small amount of material on the surface of a sample and breaks it down into excited atoms and ions to form a plasma. A spectrometer is used to record the emission spectrum of this plasma. Analysis of the atomic emission lines in this spectrum can provide both qualitative and quantitative information on the chemical composition of the ablated material (Cremers & Radziemski, 2006; Hark & Harmon, 2014).

LIBS requires little to no sample preparation, is practically non-destructive and the data acquisition time of a single LIBS spectrum is only a few ms. It is therefore technically feasible to use LIBS for on-line ore quality control in mineral processing facilities.

Examples of LIBS sensor systems that can be installed on a conveyor belt are the MAYA Analyser of Laser Distance Spectrometry (LDS, 2015), the FiberLIBS of SECOPTA

(SECOPTA, 2015) and the LIBS ore sorter that is currently being developed by SonicSampDrill (SonicSampDrill, 2013).

LIBS already showed promising results for characterizing the quality of a variety of ore types including; iron ore, copper ore, uranium ore, phosphate ore, nickel laterite and coal (Death, et al., 2009; Porizka, et al., 2014; Kim, et al., 2012; Rosenwasser, et al., 2001; Gaft, et al., 2007). However, in most of these results a sample preparation was performed to create a homogenous sample in the form of a powder or pellet. This means that the heterogeneity that naturally occurs in most rock types is not accounted for. This heterogeneity may have serious complications for characterizing the composition of an ore sample from LIBS surface measurements. For many ore types it is therefore still uncertain if an on-line LIBS sensor system can detect the elements that define ore quality with the required precision. Only for phosphate ore and coal it was shown by Gaft et al. (2007) that a LIBS sensor can be used for on-line evaluation of ore quality parameters.

In the presented study, LIBS was applied to 19 ore samples originating from a South-American mine that exploits an epithermal Au-Ag deposit. The samples are individual particles of splitted drill core that are approximately 5-10 cm long. They represent different rock types with variable Au and Ag grades. LIBS spectra were measured on the surface of each sample to investigate if LIBS can be used to distinguish between economic and sub-economic ore either by direct detection of the Au and Ag contents or by using other elements as indicators. The aim of this was to assess the potential of using an on-line LIBS sensor system to continuously monitor the economic value of the ore that is being mined.

Limitations of LIBS

One of the limitations of the LIBS technique is that it is subject to significant fluctuations in signal intensity. This is caused by variations in plasma generation as a result of an uneven energy distribution between laser pulses and differences in sample composition, crystallinity, density, grain size, hardness and surface roughness (Yaroshchyk, et al., 2010; Hark & Harmon, 2014; Harmon, et al., 2013). This means that some kind of data correction is required to be able to compare different LIBS spectra with each other.

Another limitation of LIBS is that it is influenced by chemical matrix effects (Hark & Harmon, 2014; Harmon, et al., 2013). The electron density of the laser generated plasma depends on the ionization energies of all chemical species that form it. If the occurrence of a certain element in a sample would be replaced by a more easily ionisable element, the electron density of the plasma will be increased which decreases the plasma concentration of elements with higher ionization energies (Harmon, et al., 2013). Furthermore, the atomic emission line intensity is influenced by the atomic transition probability of the excited atom (Martin & Wiese, 2006). The intensity of the atomic emission line of an element is therefore

not solely related to the concentration of that element in the sample. Because of this, a calibration of the LIBS data is required before quantitative compositional information can be extracted.

Hydrothermal alteration at epithermal ore deposits

Epithermal Au-Ag deposits are formed by hydrothermal activity that is driven by a magmatic intrusion occurring at several kilometres below the Earth's surface.

Hydrothermal activity is the movement of hot aqueous (hydrothermal) fluids through the Earth's crust and interaction between these fluids and the rocks through which they pass. The hydrothermal fluids responsible for epithermal deposit formation originate from the magma and are released due to cooling of the magmatic intrusion (Pirajno, 1992). Au, Ag and other elements are dissolved within these fluids as ions or complex ions. After release from the magma, the hydrothermal fluids flow towards the surface due to the relatively high pressure and temperature. The ascending magmatic fluids may subsequently mix with meteoric fluids which changes the fluid chemistry and temperature.

Epithermal Au-Ag deposits form at depths up to 1500 m below the surface and temperatures < 300 °C. Sharp pressure and temperature gradients in this environment result in boiling of the hydrothermal fluids, which changes fluid composition and forces Au and Ag to precipitate (Simmons, et al., 2005; Pirajno, 1992). The hydrothermal fluids that introduce Au and Ag in epithermal deposits also introduce, remove and/or redistribute other pre-existing components of the host rock. This is referred to as hydrothermal alteration (Pirajno, 1992). Hydrothermal alteration results in the formation of alteration minerals. The type of alteration minerals that are formed depends on the pressure and temperature of the hydrothermal fluids and on the composition of both the hydrothermal fluids and the host rock (Pirajno, 1992). Because precipitation of Au and Ag also depends on hydrothermal fluid properties, it is related to the formation of specific alteration minerals (Simmons, et al., 2005; Sillitoe, 1993; White & Hedenquist, 1995).

Experimental

Testwork approach

The setup that was used for acquiring LIBS spectra consisted of a pulsed Nd:YAG laser (Litron Nano LG), operated at 1064 nm and at 2 mJ per pulse. 10 pulses were used in each LIBS measurement. The light emitted by the generated plasma was recorded with a CCD spectrometer of Spectral Industries using a 210 – 840 nm spectral range. The spectral resolution of the LIBS spectra varied from 0.04 nm (@ 210 nm) to 0.12 nm (@ 840 nm). The gate delay was set at 1.2 µs.

41 LIBS spectra were acquired along a 4 cm long line (1 mm spacing) on the surface of each sample. Subsequently, the samples were pulverized and used for geochemical analyses. These analyses involved fire assay followed by atomic absorption spectroscopy (AAS) for determination of Au and Ag contents and inductive coupled plasma atomic emission spectrometry (ICP-AES) with aqua regia digestion for determining whole rock composition. Additionally, X-ray diffraction (XRD) was performed to get information on the mineralogy of the samples.

Spectral pre-processing

The acquired LIBS spectra were corrected for instrumental noise by subtracting the dark current from the measured spectra. The dark current is a measurement of the spectrometer response when there is no radiation entering it. Subsequently, a continuum background correction was performed on the LIBS spectra. The continuum background is radiation that occurs due to bremsstrahlung and recombination radiation (Yaroshchyk & Eberhardt, 2014). Correcting the continuum background was required because significant differences in the baseline intensity of the LIBS spectra were observed. The correction was performed by following the approach presented by Yaroshchyk & Eberhardt (2014). This approach estimates the continuum by using a moving minimum together with a smoothing function. The correction is made by subtracting the estimated continuum background from the original spectrum.

Data analysis

The LIBS spectra were corrected for signal intensity fluctuations by converting them to standard normal variates (SNV). This operation sets the mean and standard deviation of each spectrum to 0 and 1 respectively. The result is that the total signal intensity of all spectra becomes equal. The 10 purest LIBS spectra were calculated from the SNV corrected dataset by using the SIMPLISMA method of Windig & Guilment (1991). The elements responsible for the 30 most intense peaks in each of the purest spectra were identified by comparing the wavelength position of these peaks with the NIST atomic spectra database (NIST, 2015). This analysis was aided by calculating correlation coefficients from the LIBS data to find peaks that strongly correlate to each other. This was used to identify peaks that are produced by the same element.

Thirteen different elements were found from the purest LIBS spectra. Unfortunately, these did not include Au and Ag. It was therefore investigated if any of the measured LIBS spectra contained a peak at the wavelength position at which the NIST database reports the most intense Au and Ag peaks. For both the Au and the Ag, two peaks were identified that could represent these elements. However, the maximum intensity that was observed for all these peaks is only just above the noise level. Because of this, it is unsure if the

peaks are really produced by Au or Ag, or that they are noise peaks. Correlation coefficients showed that the two Au peaks as well as the two Ag peaks didn't correlate with each other. This indicates that at least one of the two peaks that were identified for each element is not representative.

The intensities of all the Au and Ag peaks were calculated from every SNV corrected LIBS spectrum. Furthermore, the intensity of the most diagnostic peak of each of the other thirteen elements was calculated. In these calculations peaks had to follow the condition of being a local maximum that matches the wavelength position of the element peak within a 0.3 nm range. Using a wavelength range for matching peaks was required because small shifts in the element peak locations were sometimes observed. These shifts can be attributed to differences in the Stark effect that are caused by variable electron densities resulting from the chemical matrix effect (Martin & Wiese, 2006). In case an element peak was not found for a certain LIBS spectrum a peak intensity of 0 was assigned. An average peak intensity was calculated for each sample from all the LIBS spectra that were measured on it. These average peak intensities were compared with the results of the geochemical analyses.

Apart from the SNV correction, also an internal standard was used to correct the LIBS spectra for signal intensity fluctuations. This involved calculating peak intensity ratios between the peak of an element of interest and the peak of a common matrix element. The disadvantage of using peak intensity ratios however is that these only provide information on the relative abundance between elements. This therefore requires a relationship between the occurrence of an element of interest and the relative abundance between this element and some other element. The peak intensities for calculating peak ratios were extracted by using the same approach as with the SNV corrected data.

Principle component analysis

The final step in the LIBS data analysis was to apply a principle component analysis (PCA) to the SNV corrected LIBS spectra. PCA is a procedure in which the data is projected onto a k-dimensional space by a linear orthogonal transformation (Wold, et al., 1987; Jolliffe, 2002; Eriksson, et al., 2006). These k-dimensions are commonly referred to as the k number of principle components. The first principle component (PC) represents the direction that describes the largest amount of variance in the variable space of the original data. Each subsequent PC represents the direction of the largest remaining variance that is orthogonal to those of the previous PCs. The result is that the projection of LIBS spectra on the first few PCs can be used to easily distinguish between spectra that are relatively similar and spectra that are more different. This projection of spectra is also known as the PCA scores. One of the advantages of PCA is that the contributions of the original variables to each PC can be used to identify the wavelength regions for which the spectra

are most different (Eriksson, et al., 2006). These contributions are referred to as the PCA loadings.

Prior to the PCA, the data was mean centered. Mean centering is a standard procedure with PCA that is performed by calculating the average spectrum of the dataset and subtracting that average from each spectrum. The result is that the average of the data is set at the origin of the variable space. This is needed to ensure that the principle components will describe maximum variance (Jolliffe, 2002).

Data analysis results

None of the SNV corrected LIBS element peak intensities correlated with the element concentrations determined by geochemistry. Furthermore, most of the peak intensity ratios also did not correlate with the geochemical data. It resulted that it was not possible to characterize the Au and Ag contents of the samples by detecting these elements with a LIBS sensor. Although peaks were found in the LIBS spectra that could possibly represent Au or Ag, no difference in peak intensity was observed between samples with low and high Au and Ag concentrations. This concerns both the individual LIBS spectra and the sample averages.

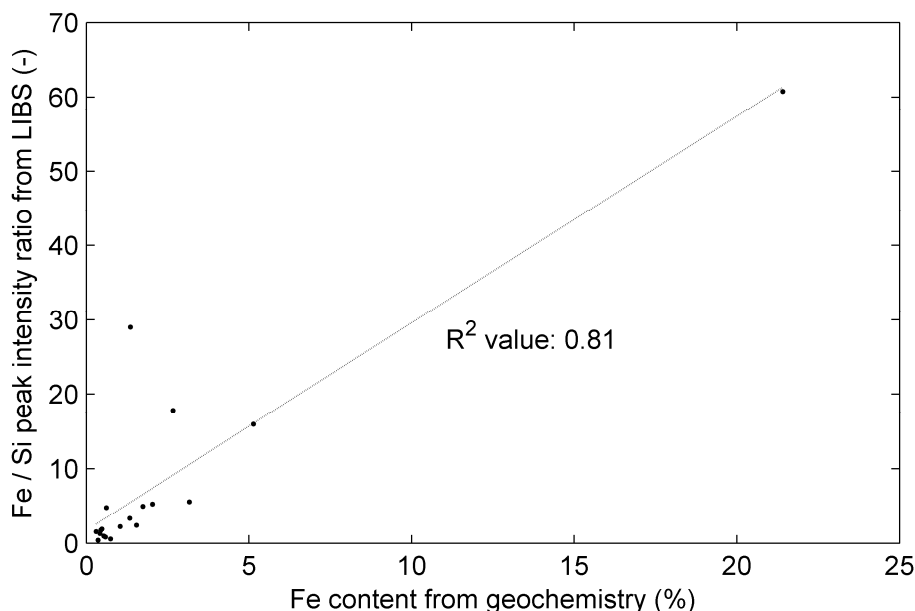


Figure 1: Fe / Si peak intensity ratio from LIBS vs. Fe concentration from geochemistry.

The only correlation that was found is between the Fe / Si peak intensity ratio from LIBS and the Fe content determined by ICP-AES. This correlation has an R^2 value of 0.81 and is presented in figure 1. The reason that the Fe / Si peak ratio from LIBS was compared with the Fe concentration and not the Fe / Si concentration ratio was because

the ICP-AES results for Si were not accurate due to the aqua regia digestion. However, XRD showed that the Fe in the samples does not occur as Fe-bearing silicates, but only as Fe-oxides or Fe-sulphides. This implies that an inverse relationship exists between the Fe and Si content of the samples. For this reason it was assumed that the Fe / Si peak ratio from LIBS is representative for the absolute Fe concentration determined by geochemistry.

There are several possible causes for the fact that no correlation resulted between LIBS and geochemistry for almost all elements. Most of these are related to the heterogeneous composition of the samples. Almost all samples are quartzites or mudstones containing variable amounts of veins and fractures that are infilled with mainly Fe-bearing minerals. Furthermore, the samples originated from different locations within the deposit and were therefore subjected to different types of hydrothermal alteration during deposit formation. This produced different assemblages of alteration minerals in the samples.

The spot size of a single LIBS measurement was around 100 μm in diameter. This means that the total surface area that was measured by the 41 LIBS spectra on each sample is only about 0.32 mm^2 . Given the heterogeneous nature of the samples, the chemical information on such a small surface area does not necessarily correspond to the geochemistry of a sample volume that is in the order of tens of cm^3 . Even if the entire sample surface would have been measured with LIBS, it would still be unsure if the surface information represents the volumetric composition of the sample.

Because of the relatively small spot size of the LIBS measurements and the heterogeneity of the samples, completely different mineral assemblages were measured. Due to the matrix effect, the relationships between LIBS peak intensities and element concentrations will be different for each of these mineral assemblages. The standard approach to deal with matrix effects is to construct calibration curves (Cremers & Radziemski, 2006; Harmon, et al., 2013). However, since the differences between sample matrices are relatively large, different calibration curves are likely required for each type of mineral assemblage (e.g. Porizka, et al., 2014). This could be an explanation for the fact that no correlation was observed between the SNV corrected LIBS spectra and the geochemical data. The only way to deal with this is to investigate the relationships between LIBS and geochemistry for each mineral assemblage separately. However, this requires separate geochemical analyses of all the veins, infilled fractures and host rock minerals. Since some of these veins and fractures are very small (< 1 mm) this may become very difficult to achieve.

The most dominant matrix minerals in the samples are either silicates or Fe-oxides. The matrix effects are therefore largely related to the occurrence of Fe and Si. Ratioing the peak intensities of these two elements corrects for the matrix effect that is produced by them. This could be the reason that a correlation resulted between the Fe / Si peak intensity ratio from LIBS and the Fe content from geochemistry, while no correlation

resulted for any of the other elements. Furthermore, since Fe- and Si-bearing minerals are fairly abundant in the samples it is also possible that the representation of these elements on a small surface reflects the volumetric composition of the sample much better than that of elements that are less abundant.

Finally, it should be noted that the aqua regia digestion that was performed in the geochemical analysis is a fairly weak digestion method that is not very well suited for dissolving silicates. It is therefore possible that the geochemical results of some of the elements that occur in silicates (e.g. Al, K, Na, etc.) are not accurate. The aqua regia digestion was selected however to get more accurate results on the As concentration. Characterizing As contents with LIBS was also of interest for the testwork, but is left out of scope in this paper.

Principle component analysis results

Figure 2 presents the scores of the LIBS spectra on the 1st and 2nd principle component (PC) of the PCA model. The dots and plus signs in this figure refer to LIBS spectra that were measured on waste and ore samples respectively. Ore and waste samples were defined on the basis of an economic cut-off grade of 0.20 ppm Au. This cut-off grade is realistic for the mine where the samples originate from. Ag is only a by-product of ore processing and is therefore not included in the definition of ore and waste. For this reason, Ag was also left out of scope during the PCA analysis. Ore material with a low Au grade generally also has a low Ag grade.

The black rectangle in figure 2 indicates a region on the score plot where predominantly LIBS spectra of waste samples occur. It can be observed that by using only the 1st PC waste samples can already be distinguished. The loadings of the 1st PC are presented in figure 3. It should be noted that the peaks of H, O and N in this figure are partly produced by the air that surrounds the sample during the LIBS measurements. These elements are therefore not representative for the composition of the samples.

Since waste samples have relatively high score values on the 1st PC, it can be inferred from the loadings in figure 3 that the LIBS spectra of waste samples are associated with relatively intense Al and Ti peaks compared to the intensity of the Na, Ca, Si and Fe peaks. According to the XRD results, elevated Al and Ti concentrations are produced by a higher abundance of clay minerals and rutile in the samples. These minerals are products of hydrothermal alteration. It therefore results that waste samples can be identified from LIBS spectra that are characteristic for Al- and Ti-bearing alteration minerals.

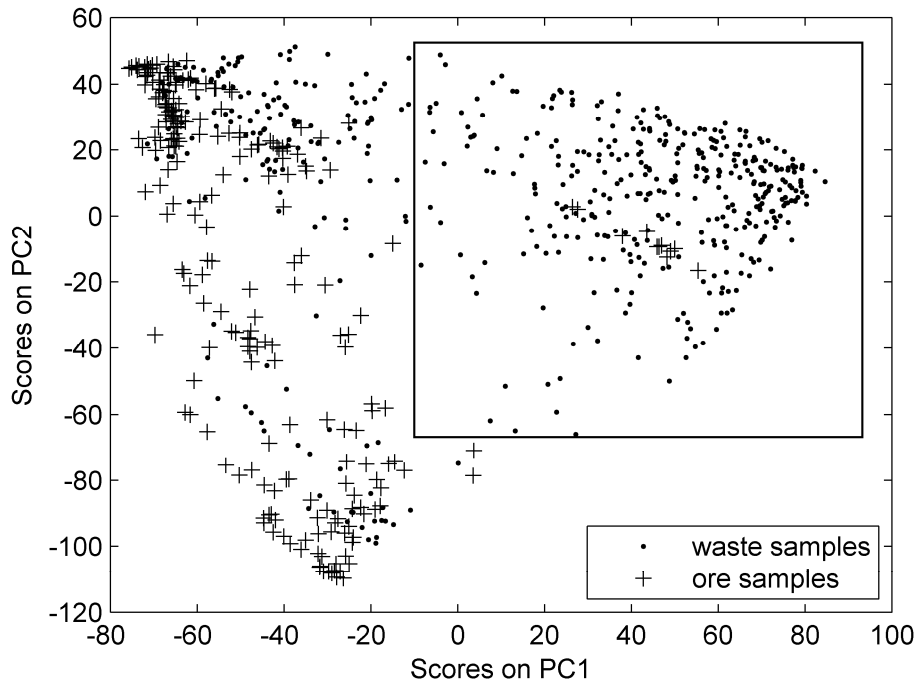


Figure 2: PCA scores on PC1 vs. PC2. The black rectangle indicates a region where predominantly LIBS spectra of waste samples occur.

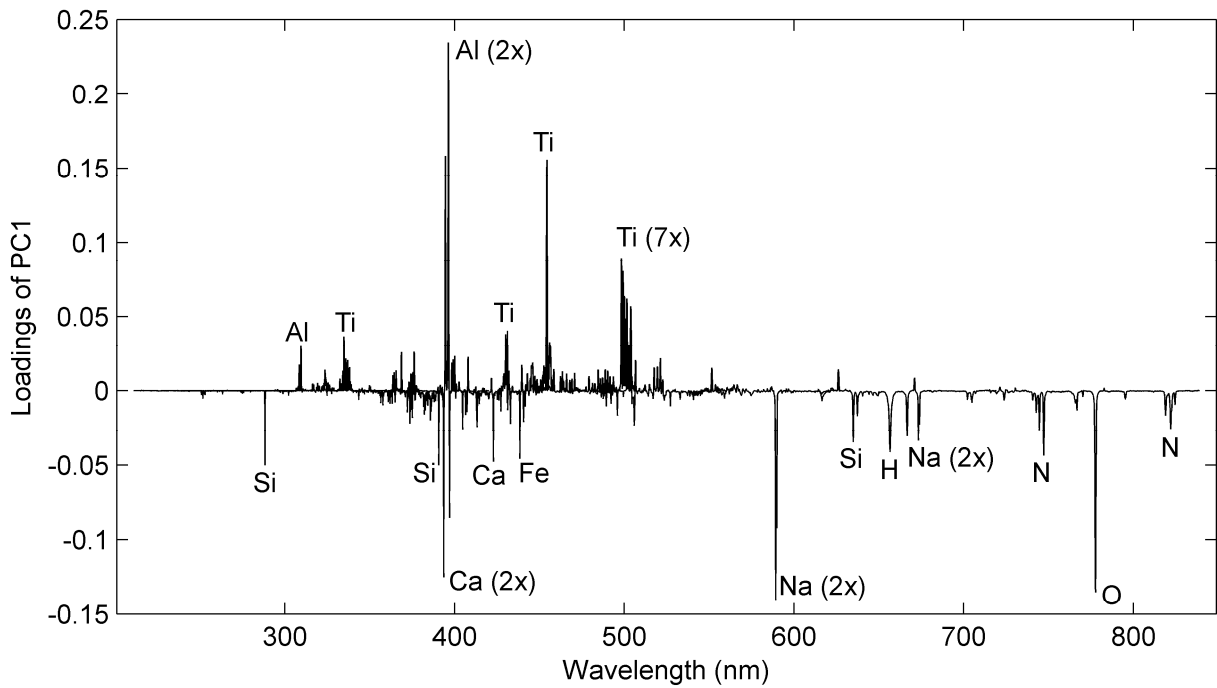


Figure 3: PCA loadings of PC1.

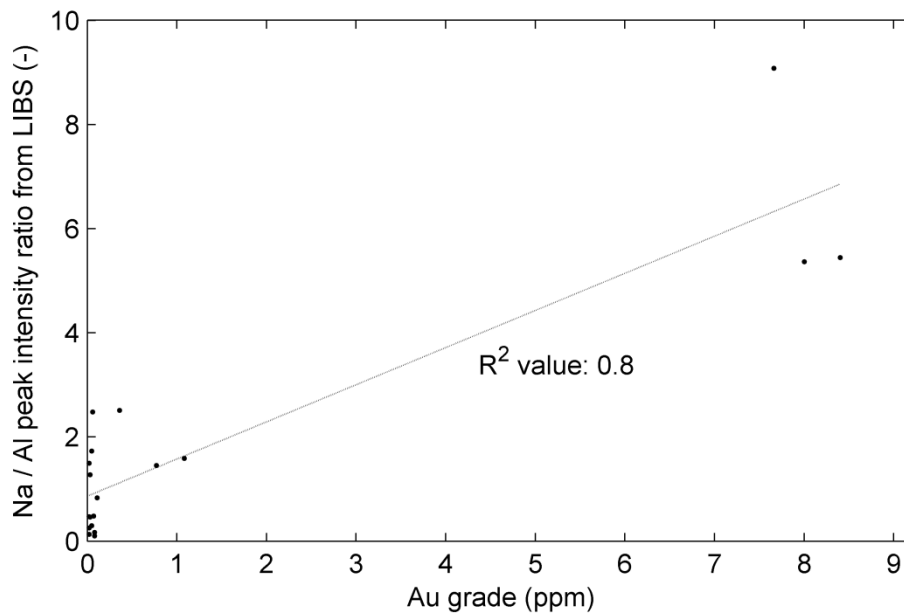


Figure 4: Na / Al peak intensity ratio from LIBS vs. Au grade from geochemistry.

Figure 4 presents a comparison between the Au grade of the samples and the averaged Na / Al peak intensity ratio from LIBS. It can be observed from this figure that a correlation with an R^2 value of 0.80 results between these variables. This means that the Na / Al peak intensity ratio from LIBS can be used to predict the Au grade of the samples. However, this result is based on a sample set of only 19 samples. Additional testwork is required to validate that this relationship persists for all the ore material that is mined from the deposit.

Discussion

The results showed that the LIBS technique is not able to directly detect the Au and Ag contents of the ore samples used in this study. It was also uncertain if the peaks that were identified for Au and Ag were correct since these peaks were only observed with a peak intensity that is just above the noise level. However, even if distinct peaks were found it would still be unsure if the detection of these elements can be used to characterize the economic value of the ore. This is because the LIBS peak intensities of many other elements also did not correlate with the geochemical data. This lack of correlation is likely produced by the heterogeneous composition of the ore material.

By applying a PCA to the LIBS dataset it was discovered that LIBS can be used to distinguish waste samples by using the spectra as chemical fingerprints of alteration mineralogy. This means that the occurrence of a certain LIBS spectrum can be used to predict whether a sample is more likely to be ore or waste. Classification models such as partial least squares discriminant analysis (PLS-DA) for example are available to achieve this (Sjostrom & Wold, 1986). Considering sample heterogeneity, an approach that utilizes

classification models would be more robust than one based on extracted compositional information. This is because a classification model will be less sensitive to the chemical matrix effects resulting from sample heterogeneity.

The results have shown that there is potential that an on-line LIBS system can be used to monitor of the economic value of the epithermal Au-Ag ores. However, characterizing the economic value will need to be based on indirect relationships between the Au and Ag grades and the alteration mineralogy. This is because the Au and Ag contents of the ore are below the detection limit of LIBS. Additional research will therefore be required to validate that the relationship between economic value and alteration mineralogy persists throughout the entire ore deposit that is mined.

Conclusions

The following conclusions were drawn from the testwork.

- The Au and Ag grades of the samples are below the detection limit of the LIBS setup that was used.
- Sample heterogeneity imposes difficulties for extracting quantitative compositional information from LIBS spectra due to signal intensity variations and chemical matrix effects.
- A relationship exists between the alteration mineralogy of samples and their Au content. Because of this the Na / Al peak intensity ratio from LIBS can be used to predict the Au grade of the samples.
- Classification models that use the LIBS spectra as chemical fingerprints of alteration mineralogy are considered to be the best approach for identifying sub-economic ore material. This is because these models will be less sensitive to the chemical matrix effects resulting from sample heterogeneity.
- There is potential that an on-line LIBS system can be used to monitor of the economic value of the epithermal Au-Ag ores by using the alteration mineralogy as indirect indicators.

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