

Can the provenance of the conflict minerals columbite and tantalite be ascertained by laser-induced breakdown spectroscopy?

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Abstract Conflict minerals is a term applied to ores mined in conditions of armed conflict and human rights abuse. Niobium and tantalum are two rare metals whose primary natural occurrence is in the complex oxide minerals columbite and tantalite, the ore of which is commonly referred to as coltan. The illicit export of coltan ore from the Democratic Republic of the Congo is thought to be responsible for financing the ongoing civil conflicts in this region. Determining the chemical composition of an ore is one of the means of ascertaining its provenance. Laser-induced breakdown spectroscopy (LIBS) offers a means of rapidly distinguishing different geographic sources for a mineral because the LIBS plasma emission spectrum

provides the complete chemical composition (i.e., “chemical fingerprint”) of any material in real time. To test this idea for columbite–tantalite, three sample sets were analyzed. Partial least squares discriminant analysis (PLSDA) allows correct sample-level geographic discrimination at a success rate exceeding 90%.

Keywords Laser-induced breakdown spectroscopy · LIBS · Conflict minerals · Columbite–tantalite · Coltan · PLSDA

Introduction

Niobium (Nb) and tantalum (Ta) are rare metals of commercial value, and the high demand for these elements has resulted in an increase in exploration programs to locate new ore deposits. The primary natural occurrence of Nb and Ta is in the complex oxide minerals columbite and tantalite [1], which form a solid-solution series having the general composition $[(\text{Fe},\text{Mn})(\text{Nb},\text{Ta})_2\text{O}_6]$. At present, the predominant supply of the world’s columbite–tantalite ore comes from Brazil and Australia [2]. However, columbite–tantalite occurs in many areas of Central Africa, with some 60% of the world’s Ta ore reserves located in the eastern portion of the Democratic Republic of the Congo (DRC) and adjacent areas [3]. Although the overall production of Nb and Ta in Central Africa is small at present (<1% of total global ore concentrate [2]), the illicit export and sale of columbite and tantalite from the DRC to the European and North American markets has been cited as an important means by which the civil conflicts in Central Africa are being financed [3]. A law passed in 2010 by the US Congress requires publicly traded companies in the USA that manufacture products utilizing conflict minerals,

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including columbite–tantalite (colloquially known as “coltan”), to report whether such materials “did originate in the Democratic Republic of the Congo or an adjoining country” [4] and to describe the measures taken to identify the source and the chain of custody of such minerals. Laboratory-based techniques involving SEM and LA-ICP-MS have been successfully used to categorize coltan ores [5], but at present, there is no analytical technique by which an analysis to determine the place of origin of coltan ore can be accomplished rapidly in the field.

This study investigated the use of laser-induced breakdown spectroscopy (LIBS) to meet this challenge based on the concept of “geochemical fingerprinting.” The idea is that the LIBS emission spectrum provides a unique chemical signature of a material that can be used to discriminate geological specimens originating in one place from the samples of the same kind from other locations. This hypothesis is based upon the fact that the Earth’s crust is compositionally heterogeneous, both horizontally and vertically, and that minerals forming within the crust will reflect that intrinsic geographic heterogeneity.

Methods

The columbite–tantalite samples selected for this pilot study come from three pegmatite locations in North America: (1) the Starrett pegmatite in southern Maine; (2) the BeeBee/PackRat pegmatite in San Diego County, California; and (3) the Moose pegmatite in the east-central Northwest Territories, Canada [6–12]. The 14 samples analyzed varied in shape, size, and color. Because many of the ores were chips from a larger pegmatite specimen that contained both matrix material and grains of columbite–tantalite, they needed to be correctly placed in the sample chamber to ensure that the mineral of interest was the portion being ablated. To improve the ease of handling and data collection for this preliminary investigation, the ore chips were embedded in polyester resin and polished in water to a flat surface for more consistent and reproducible LIBS analysis.

LIBS, is a versatile method of atomic emission spectroscopy, allows for rapid chemical analysis and has been utilized for the study and geographic discrimination of different minerals [13–15]. This attribute of LIBS, together with its field-portable potential, makes the technology an appropriate choice for this geochemical experiment. In solid sample analysis, multiphoton bombardment of the sample surface by the laser radiation causes energy absorption, instantaneous heating, electronic excitation, and production of a high-temperature plasma. The ablation and vaporization of material result in dissociation into excited ionic, atomic, and molecular species. As the plasma cools, excited atoms, ions, and molecules emit light at their characteristic

wavelengths. The emitted light is then collected and analyzed spectrometrically, and the composition of the ablated material is ascertained from analysis of the emission spectrum. The samples were analyzed using a commercial LIBS unit (RT100-HP, Applied Spectra, Inc.) [16]. This instrument employs a 50-mJ Nd:YAG laser operating at 1,064 nm with a 5-ns pulse width and 1–20 Hz repetition rate. It includes a Czerny–Turner spectrograph/ICCD detector that has a dual grating turret: 600 grooves/mm for “low-resolution” analysis and 2,400 grooves/mm for “high-resolution” analysis, providing 0.2–0.3 and 0.05–0.1 nm spectral resolution, respectively.

Experimental parameters included a laser output of approximately 23 mJ, gate width of 3 μ s, gate delay of 2 μ s, and a repetition rate of 3 Hz. Emission spectra from 40 laser shots were collected at four spots on a 2 \times 2-mm grid for each sample. For each location in the grid, the first 15 “cleaning” shots were discarded and the data for the last 25 shots were used for analysis to provide a total of 100 emission spectra for each sample. Both the RT100-HP low-resolution and high-resolution gratings were utilized for this experiment. High-resolution data were collected for all 14 samples at two wavelength regions, 235–285 and 313–358 nm. After these data were collected, the samples were re-polished to provide a fresh surface for the low-resolution analysis, which covered the spectral range from 250 to 490 nm. These spectral regions were strategically chosen to encompass many of the intense emission lines for the major elements (Ta, Nb, Fe, and Mn) and the significant trace elements (e.g., W, Ti, Zr, Sn, U, Sb, Ca, Zn, Pb, Y, Mg, and Sc) known to commonly substitute in the crystal structure of the columbite group minerals ferrocolumbite [FeNb₂O₆], manganocolumbite [MnNb₂O₆], ferrotantalite [FeTa₂O₆], and manganotantalite [MnNb₂O₆; 17–22]. Spectra obtained from commercially available pure metals (e.g., Ta foil, >99.9%, and Nb foil, 99.8%, Sigma-Aldrich) were used to identify the location of major spectral lines of interest.

Analysis and results

The primary goal of the study was to determine whether LIBS could be used to ascertain the geographic origin of columbite–tantalite ores. Thus, to explore this question, a classification study was designed to determine whether the LIBS spectra contained sufficient information to discriminate between columbite and tantalite having different geographic origins. The high degree of spectral similarity and complexity of the spectra (see Fig. 1) prevented the visually based classification of the samples. Thus, the data were analyzed using subspace projection techniques and chemometric methods to generate classification results.

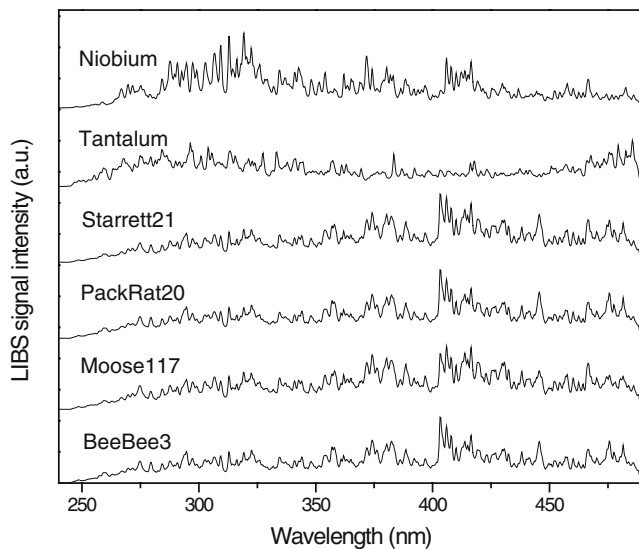


Fig. 1 Low-resolution LIBS spectra from 250–490 nm of niobium and tantalum with representative spectra of coltan samples used in this study (Starrett21, PackRat20, Moose117, and BeeBee3)

The classification study was conducted using a leave-one-sample-out (LOSO) cross-validation approach and partial least squares discriminant analysis (PLSDA). Before processing, each spectrum was normalized by the sum of the raw data values so that after pre-treatment each spectrum equaled unity when summed across all wavelengths. In PLSDA, the high-dimensional spectral data are

projected into a lower-dimensional subspace onto latent variables that maximize the covariance between the projected data and the class labels. These projected dimensions are different from a principal component analysis (PCA) in that PLSDA is a supervised technique (i.e., it makes use of the sample labels), whereas PCA is unsupervised and projects the data without any awareness of the class membership of the different samples. The LOSO cross-validation experiment setup is more rigorous than a conventional k -folds cross validation (Remus, unpublished data). Due to the high correlation between shots collected from the same sample, the partitions of training and testing data in LOSO cross validation are constructed to exclude all test sample shots from the training data. Thus, each physical sample is tested using PLSDA models that have never “seen” data from that sample.

Table 1 lists the percentage of shots from each sample that was assigned to each possible class (i.e., geographic origin). The number of components used by PLSDA for each data set was chosen to minimize the root-mean-square error for cross validation (RMSECV). For these three data sets, the RMSECV-optimized number of PLSDA components varied from five components for the 250–490 nm low-resolution data to ten components for the 235–285 nm high-resolution data, and thirteen components for the 313–358 nm high-resolution data. While RMSECV and the percent correct classification rates shown in Fig. 2 are strongly correlated,

Table 1 Sample-level classification results for the three coltan data sets

Sample	Assigned Labels 235–285 nm (high resolution)			Assigned Labels 313–358 nm (high resolution)			Assigned Labels 250–490 nm (low resolution)		
	Moose	Starrett	BeeBee/PackRat	Moose	Starrett	BeeBee/PackRat	Moose	Starrett	BeeBee/PackRat
Moose102	100%	0%	0%	100%	0%	0%	100%	0%	0%
Moose104	100%	0%	0%	100%	0%	0%	100%	0%	0%
Moose113	100%	0%	0%	100%	0%	0%	100%	0%	0%
Moose114	100%	0%	0%	100%	0%	0%	100%	0%	0%
Moose117	100%	0%	0%	100%	0%	0%	100%	0%	0%
Moose121	100%	0%	0%	100%	0%	0%	100%	0%	0%
BeeBee3	0%	0%	100%	0%	24%	76%	0%	0%	100%
PackRat12	0%	55%	45%	0%	22%	78%	17%	25%	58%
PackRat20	0%	27%	73%	0%	7%	93%	0%	0%	100%
Starrett4	0%	100%	0%	0%	100%	0%	0%	100%	0%
Starrett5	0%	100%	0%	0%	100%	0%	0%	100%	0%
Starrett12	0%	100%	0%	0%	48%	52%	0%	100%	0%
Starrett21	0%	100%	0%	0%	93%	7%	0%	100%	0%
Starrett23	0%	53%	47%	0%	100%	0%	0%	100%	0%

For each sample, the table lists the percentage of shots from that sample that was assigned to each class (i.e., geographic location). The number of latent variables used in PLSDA for the 235–285 nm high-resolution data (left), 313–358 nm high-resolution data (middle), and 250–490 nm low-resolution data (right) was 10, 13, and 5, respectively. These values were selected using root-mean-square error from cross validation (RMSECV). The correct class for each sample is identified by bold text

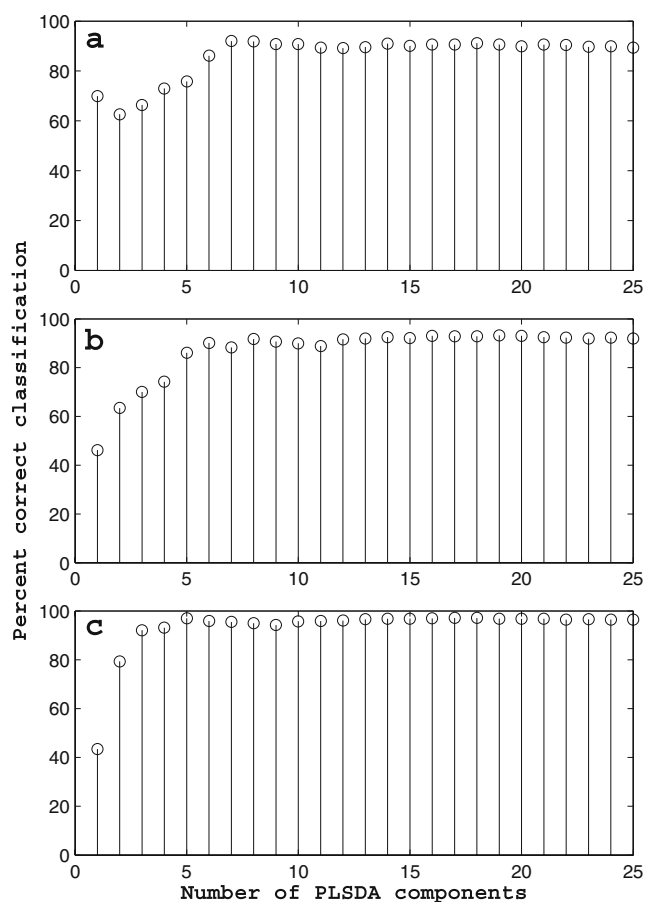


Fig. 2 Classification results for the BeeBee/PackRat, Moose, and Starrett LIBS data sets collected over different spectral ranges: (a) 235–285 nm high-resolution data, (b) 313–358 nm high-resolution data, and (c) 250–490 nm low-resolution data. Results are shown as the percentage of shots correctly classified (*y*-axis) as a function of the number of components (i.e., latent variables) used in the PLSDA classifier (*x*-axis)

they are not equivalent since RMSECV is calculated from the continuous scale outputs produced by PLSDA and correct classification rates from the discretized class label estimates. Therefore, in some cases, the correct classification rates may reach their peak level prior to the minimum RMSECV point, since the PLSDA model may be “close enough” to make most correct classifications while small refinements are still occurring for the RMSECV values.

The PLSDA classifier assigns a label to each LIBS spectrum, which can be viewed as “votes” for the sample’s class. A maximum-likelihood label can be assigned to each sample based on a plurality after aggregating the class estimates for all spectra from the sample. Using such an approach, there are 13 out of 14 correct sample-level classifications in the 235–285 nm data, 13 out of 14 correct sample-level classifications in the 313–358 nm data, and perfect classification results are achieved with the low-resolution broadband data.

The PLSDA discrimination of the three pegmatite suites on the basis of the low-resolution data is represented in Fig. 3 as a scatter plot of the first two latent variables (LV1 vs. LV2). These PLSDA projections graphically explain the classification results discussed above and clearly show that Moose samples are the most separable while there is a small degree of overlap between the Starrett and BeeBee/PackRat samples in this particular data projection. Much of the scatter of data points is attributable to the shot-to-shot variability of the spectra typically inherent in LIBS data combined with the heterogeneity of the mineral samples. The latter reason may explain the presence of the outliers, attributable to PackRat12, in the lower right hand corner of the plot since these samples were the most difficult to classify in all the three sets of data. Subsequent microprobe analysis confirmed that PackRat12 is extremely heterogeneous and displayed significant chemical zoning, due largely to varying niobium and tantalum concentrations and the presence of other mineral inclusions.

For additional insight into the classification results, the PLSDA model that was used to generate the perfect sample-level classification results with the low-resolution data was further analyzed to determine which wavelengths were most important for identifying sample provenance. The largest magnitude PLSDA weightings (aggregated across all three classes) correspond to emission lines of anticipated major and trace elements of the columbite group minerals. The possible identity of these lines was determined using a ± 0.3 -nm search tolerance (to match the spectral resolution of the data) in a database generated from the spectra of 52 pure elements obtained on an RT100-HP instrument. Among the most significant weightings are

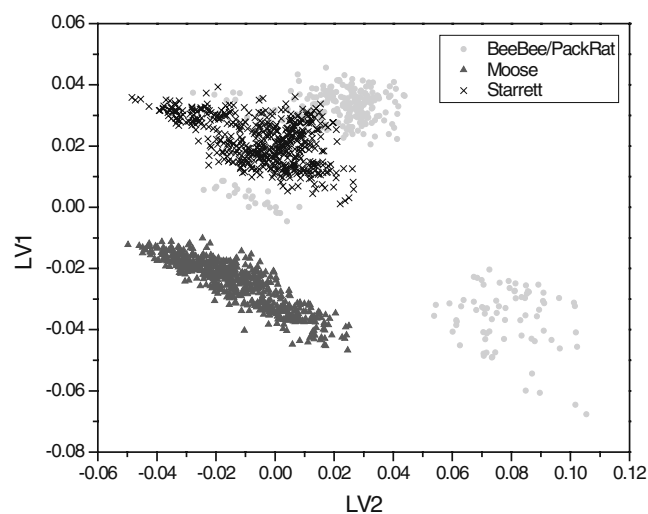


Fig. 3 Scatter plot of the first latent variable (LV1) versus the second latent variable (LV2) obtained from a PLSDA projection of 250–490 nm low-resolution LIBS spectral data of all BeeBee/PackRat, Moose, and Starrett samples

emission lines that correspond only to Fe(I) at 422.6 nm, Mn(I) at 443.5 and 472.0 nm, and Zr(II) at 318.3 nm. Other weightings were tentatively associated with more than one element, including Ta, Nb, Fe, Mn, Ti, W, and Zr. Examination of the raw data reveals differences in the intensities of the lines corresponding to the loadings. For example, the spectra of the Moose samples consistently have higher intensity than the other samples for the Fe(I), Mn(I), and Zr(II) lines identified above. Additional work is required to fully account for the high level of classification success but these preliminary results support the hypothesis that these minerals retain a unique crustal signature associated with the location of their formation.

Summary and future work

Niobium and tantalum are currently elements of high economic importance whose exploitation has become politically problematic. Given that the recent US federal legislation requires companies to report the sources of the columbite–tantalite used in their products, a method is needed to rapidly determine the place of origin for columbite–tantalite ores. As demonstrated in this pilot study, laser-induced breakdown spectroscopy has the potential to meet this need. Fourteen columbite–tantalite samples were analyzed from three pegmatite fields in North America that formed widely separated in space and time: the Starrett pegmatite of central Maine; the BeeBee/Pack Rat pegmatite in southern California; and the Moose pegmatite from the Northwest Territories, Canada. These three columbite–tantalite samples sets were analyzed by LIBS to ascertain if statistical analysis of the chemical information contained in the LIBS spectra could be used as a means of rapidly distinguishing different geographic sources of this economically important mineral series. LIBS spectra were collected at high resolution at two wavelength intervals, 235–285 and 313–358 nm, and at low resolution over the 250–490 nm wavelength range. These spectra were used in a statistical classification analysis (PLSDA) to determine sample geographic source. A >90% success rate was achieved, with the best performance observed for the low-resolution LIBS spectra. The fact that better discrimination was achieved using a broadband/low-resolution approach compared to a narrowband/high-resolution approach suggests that spectral range may be a more important parameter than spectral resolution, even for samples with elements that have a very large number of emission lines (e.g., Ta, Nb, Fe).

These promising preliminary results indicate that columbite–tantalite provenance can be ascertained by LIBS analysis and suggest that additional work with a larger, more geographically diverse data set and optimization of

spectral acquisition parameters is warranted. It remains to be determined if the high level of correct classification obtained with a PLSDA model based on three classes can be extended to the larger number of classes associated with a more geographically diverse set of localities. Ultimately, it may be possible to provenance conflict coltan in the field, provided a robust global LIBS database can be developed. Going forward, samples from Central Africa, Australia, and Brazil, plus other regions of the world, will be carefully analyzed for this purpose.

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