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14. ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) offers a means of rapidly distinguishing different geographic sources for a mineral because the LIBS plasma emission spectrum provides information on the chemical composition (i.e. geochemical fingerprint) of a geomaterial. An application of this approach with potentially significant commercial and political importance is the spectral fingerprinting of "conflict minerals" such as columbite–tantalite ("coltan"). Following a successful pilot study of a columbite–tantalite suite from North

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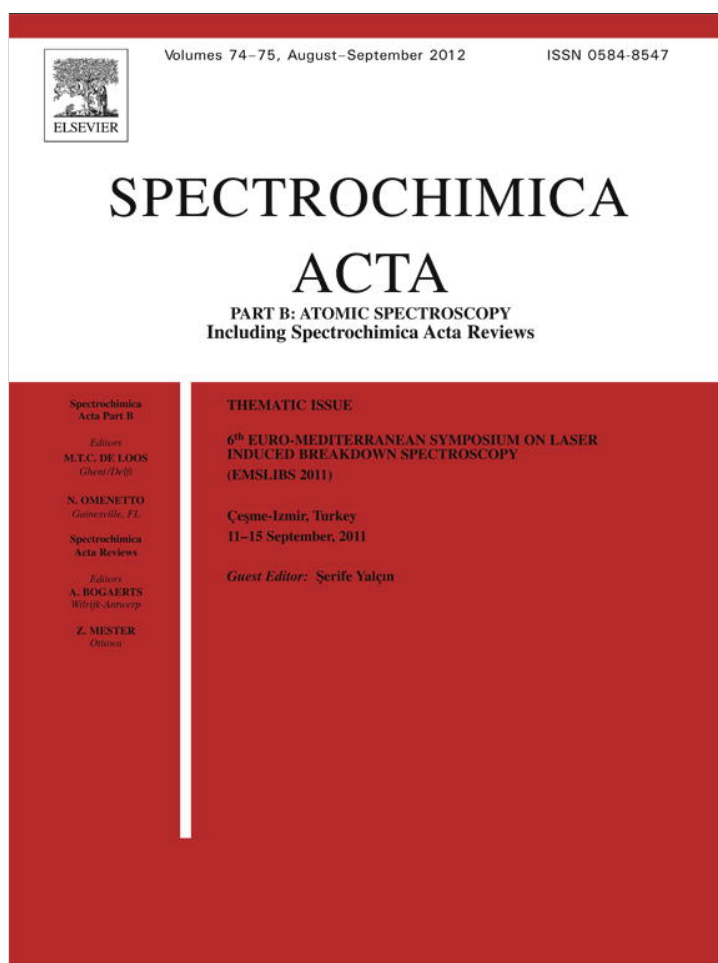
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Analytical Note

Geographical analysis of "conflict minerals" utilizing laser-induced breakdown spectroscopy

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1. Introduction

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 $[(Fe,Mn)(Nb,Ta)_2O_6]$. These minerals have high commercial value due to the technological and industrial importance of niobium (used in the manufacturing of steel alloys) and tantalum (essential for the production of capacitors used in consumer electronics such as laptops and cell phones) [2]. Columbite–tantalite mineralization occurs in association with granitic pegmatites [3] and derivative placers deposits formed from their fluvial erosion. At present, the predominant supply of the world's columbite–tantalite ore comes from Brazil and Australia, but the Democratic Republic of Congo (DRC) and its eastern neighbors also have substantial columbite–tantalite resources [4]. The illicit export and sale of these minerals, also known as "coltan," are one of several potential revenue streams for the combatants engaged in civil conflict in the DRC since the late 1990s [5]. For this reason, columbite–tantalite, as well as cassiterite, wolframite, and gold, are referred to as "conflict minerals."

Controlling the income from the sale of coltan from conflict regions involves concerted effort by government agencies and industry [6]. The United States Financial Regulation Bill of July 2010 holds all U.S. companies accountable for where they purchase raw materials and components used to manufacture their products. The legislation asks corporations to release documentation outlining what steps they are taking to prevent the purchase of conflict minerals [7]. However, efforts to accomplish this without harming legitimate mining operations in other areas of the DRC and surrounding Great Lakes region of central Africa require analytical methodology that can be used in the field to reliably distinguish between minerals obtained from different places at a very early stage of the commercial chain, which ultimately leads to the amalgamation of material from multiple sources for processing. Melcher et al. [2,8] have developed a successful laboratory-based protocol utilizing scanning electron microscopy (SEM) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to match a sample of columbite–tantalite obtained from a given mine site with samples from the same mine cataloged in a database.

In a previous study [9], Harmon et al. (2011) demonstrated that columbite–tantalite samples from three locations in North America could be distinguished using advanced signal processing of the laser-induced breakdown spectroscopy (LIBS) emission spectra. In

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this paper, it was argued that the LIBS spectrum provides a unique chemical signature of a material, its geochemical fingerprint, and that this information can be used to discriminate geological specimens originating in one place from samples of the same kind from other locations. This idea of geochemical fingerprinting 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 inherent geographic heterogeneity. The approach of Melcher et al. [2,8] is principally based on quantitative elemental and isotope analysis to detect these differences while the LIBS methodology described in a variety of papers [9–12] relies on a qualitative comparison of the relative variation in elemental composition between samples. In order to verify and extend the preliminary results of our previous study we undertook analysis of a larger and more geographically diverse sample suite.

2. Experimental procedure

For this follow-up study, 57 samples from 37 locations around the world were obtained from private, government, and commercial sources and used for analysis without any preparation (Table 1). These samples come from specific granite pegmatite fields from 14 countries in Africa, Asia, Australia, North America and South America. Each field is unique in its geologic environment, mineralogical makeup, and geochemical character. This heterogeneity is reflected in the variety of major elements (Ta, Nb, Fe, Mn) and 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 [$FeNb_2O_6$], manganocolumbite [$MnNb_2O_6$], ferrotantalite [$FeTa_2O_6$], and manganotantalite [$MnTa_2O_6$] [13–15].

The analyzed samples are representative of the natural range of compositions for columbite-group minerals. However, individual crystals may exhibit fine-scaled chemical zoning of Fe–Mn or Nb–Ta, localized modification of composition due to the altering effect of migrating fluids, or contain included mineral phases (e.g., hematite, wodginite or cassiterite) with compositions significantly different from the host columbite–tantalite — all of which are commonly observed textural features [3]. These features may be present when attempting to use LIBS data to discriminate columbite–tantalite samples based on their provenance and have the potential to complicate the statistical analysis.

The sample suite was analyzed using a commercial LIBS unit (RT100-HP, Applied Spectra, Inc.). This instrument employs an Nd: YAG laser operating at 1064 nm with a 5 ns pulse width and 1–20 Hz variable repetition rate. It includes a Czerny–Turner spectrograph/ICCD detector fitted with a 600 grooves/mm grating that provides ~0.25 nm spectral resolution across the 250 to 490 nm spectral window used in this experiment. This spectral range was chosen to encompass many of the intense emission lines for the major elements known to commonly substitute in the columbite group minerals. The integration time was 3 μs with a gate delay of 2 μs and a laser repetition rate of 3 Hz. The laser spot size and irradiance were approximately 150 μm and 25 GW/cm^2, respectively. Not all of the parameters were systematically optimized for coltan samples but they were consistent with values used previously for analysis of other minerals. [9–12].

Sampling was accomplished under ambient atmosphere using a 2×2 mm grid pattern with 0.5 mm spacing. The analysis was performed over the space of several days during which time the instrument was deemed to be reliably stable based on prior empirical evaluation. For each of the four locations in the grid, 15 laser pulses were used to clean the sample surface and then data for the next 25 laser pulses were retained for analysis to provide a total of 100 emission spectra per sample grid. The ablation depth and aspect ratio of the craters formed after 40 laser pulses were estimated via

microscopic observation using a stage micrometer to be approximately 50 μs and 0.2, respectively. In most cases, the samples were analyzed only once. However, some pieces of coltan were sampled at three locations (20 examples) and a few at four, five or eight separate spots (one example of each) to afford additional spectra.

Many of the analytes were chips from larger pegmatite specimens that contained both matrix material and veins of the minerals of interest. The automated X–Y–Z stage, ablation spot guiding laser and CMOS camera imaging system of the RT100-HP instrument were therefore used to correctly position the sample. The roughness of the surface varied among samples but the instrument has an active focusing system that refocused the laser onto the surface each time the stage moved to a new grid location.

The classification model used for the analysis of the data was partial least squares discriminant analysis (PLSDA) [16–18]. PLSDA is a supervised, linear regression technique that uses a set of labeled training pulses to learn a set of coefficients that map between the LIBS spectra X and designated labels Y and maximize the covariance between the X and Y. The linear regression is performed in a lower-dimensional subspace, with the dimensionality of the subspace being a variable that must be set by the operator. To examine classification performance independent of the value of this parameter, the PLSDA methods were run using a variable number of PLS components that ranged from 10 to 100. The specific implementation of PLSDA used in this study was based on the SIMPLS solving method [19]. All signal processing work was performed using a commercial software package (MATLAB 7.13 with Statistics Toolbox 7.6, The MathWorks Inc., Natick, MA, 2000).

The classification experiments were set up using 15-fold cross-validation with whole spectra (a total of 1024 data points) [20]. The spectra were divided into 15 groups of approximately equal size. In 15-fold cross-validation, one group of spectra is sequestered while the remaining groups are used to develop a model for classification; the classification model is then applied to the sequestered group of spectra to estimate labels. The process is re-run for 15 iterations until each group of spectra has served as the hold-out test set. The k-folds cross-validation approach allows maximum use of the available data, since every spectrum appears in the test set and contributes to the overall calculation of classification performance. This reduces the probability of overtraining that occurs when simultaneously using the same spectra in training and testing but does not eliminate it. K-folds cross-validation has been shown to provide a less robust result for some classification tasks than cross-validation schemes that divide groups based on samples rather than spectra (e.g. leave-one-sample-out [21]); however many of the localities in the available data set were represented by a single sample which prevented use of a leave-one-sample-out cross-validation scheme.

3. Results and discussion

This study was designed to determine if the previous successful classification analysis of coltan samples using LIBS [9] could be replicated using a larger, more geographically diverse library of ores. As observed in Fig. 1, the coltan samples have visually similar LIBS spectra. The high degree of spectral similarity and complexity of the spectra prevented simple visually-based classification of the samples. Thus, a cross-validated statistical classification study was designed to determine whether the LIBS spectra contained sufficient information to discriminate between columbite–tantalite having different geographic origins. The data were analyzed using subspace projection techniques and chemometric methods to generate classification results.

Four sets of class labels were developed and the PLSDA results showing the percent of correctly assigned labels for classification tasks are shown in Fig. 2. The number of components (latent

Table 1
Sample labels indicating the location, sample number (where applicable), and putative mineral type (C = columbite, T = tantalite) plus PLSDA results showing the percent of correctly assigned labels for classification tasks based on country, country and mineral type, location, and sample.

Location	Mineral type	Sample no.[a]	Percentage of correctly assigned labels			
			Country[b]	Country and mineral type[b]	Location[b]	Sample[c]
Afghanistan	T	1	100%	100%	100%	100%
		2				98%
Afghanistan, Kunnar	T	1			100%	100%
		2				100%
Australia, Western Australia	T	–	99%	100%	100%	100%
Brazil, Fumal	T	–	100%	97%	78% (Urubu 20%)	97%
Brazil, Urubu	T	1			98%	78% (94%)
		2				27% (80%)
Brazil, Minas Gerais	C	–		93%	100%	100%
Brazil, Minas Gerais, São José da Safira	C	1			99%	80% (89%)
		2				98%
DRC, Kivu	T	105008	78% (Namibia 21%)	78% (Namibia-T 23%)	100%	100%
DRC, Luwangashi	T	157219			100%	100%
Kenya, Nyanza	T	107892	23% (Namibia 75%)	21% (Namibia-T 78%)	100%	100%
Madagascar	T	–	99%	97%	100%	100%
Madagascar, Guilimane	T	104967			100%	100%
Madagascar, Ambockamasina	T	94115			97%	100%
Madagascar, Antsirabe-Betafo	C	B 12922		99%	100%	100%
		B 13640				100%
		B 13403				94%
		164825				100%
Madagascar, Tsarafara	C	–			100%	100%
Mozambigue, Morrua	T	170176	59% (USA 35%)	100%	97%	98%
Mozambique, Alto Lighona	T	133933			73% (Morrua 15%)	82% (96%)
	C	–		49% (USA-C44%)	84%	94%
Mozambique, Gile	C	R12980			68% (Zimbabwe 30%)	94%
Namibia	T	164979	65% (Mozambique	68% (Mozambique-T 17%,	99%	98%
Namibia, Donderhoek	T	B13409	23%, Zimbabwe 10%)	Zimbabwe-T 10%)	86% (Morrua 10%)	90%
Namibia, Karibib	T	120552			57% (Zimbabwe 42%)	100%
		R8635				98%
Nigeria, Dutsen Dushowo	C	14564	93%	94%	95%	99%
Nigeria, Bukuru	C	97753			70% (Dushowo 25%)	87% (100%)
Rwanda, Kibunga	T	107896	78% (Namibia 17%)	79% (Namibia-T 19%)	96%	99%
South Africa, Namaqualand	T	R5085	100%	100%	100%	100%
		B12883				100%
South Africa, Bushveld	C	104828		100%	100%	100%
Uganda, Mbarara	C	R8474	25%	51%	64%	99%
USA, California, Jacumba	C	1	99%	99%	95%	100%
USA, Colorado, Fremont	C	–			86%	91%
USA, Colorado, Jefferson	C	–			100%	100%
USA, Maine, Brunswick	C	1			100%	50% (67%)
		2				82% (96%)
		3				56% (70%)
		4				83% (89%)
		5				82%
USA, Maine, Greenwood	C	–			96%	99%
USA, Maine, Newry	C	–			100%	100%
USA, North Carolina, Spruce Pine	C	1			100%	98%
		2				73% (100%)
		3				55% (100%)
USA, Virginia, Amelia	T	1		99%	99%	56% (92%)
		2				85% (100%)
		3				53% (99%)
		4				66% (84%)
Zimbabwe	T	145503	100%	100%	100%	72% (100%)
		145504				82% (94%)
		R13775				96% (100%)

[a] Five or six character sample numbers are from the National Museum of Natural History.
[b] The identity and corresponding percentage of misclassified spectra (only ≥10%) are shown in parentheses.
[c] The values in parentheses correspond to the total percentage of spectra classified to the correct location.

variables) used by PLSDA to achieve maximal percent correct classification in cross-validation (PCCCV) was 50 for country-level classification, 55 for country and mineral type level-classification, 60 for location-level classification, and 65 for sample-level classification. PCCCV peaked between 90 and 95% for each of these classification tasks. The chance level of performance (i.e. the level of performance that can be achieved by a completely naïve classifier that just assigns the most common label to every shot) for these four tasks is 44%, 33%, 13%, and 7%, respectively.

The PLSDA classifier assigns a label to each LIBS spectrum, which can be viewed as the number of "votes" for the sample's class. Table 1 lists the percentage of spectra from each sample that was assigned to the correct class for each of the four classification tasks. The class identity is also shown for misclassified spectra with corresponding percentages equal to or greater than 10%. 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 12 out of 14 correct assignments
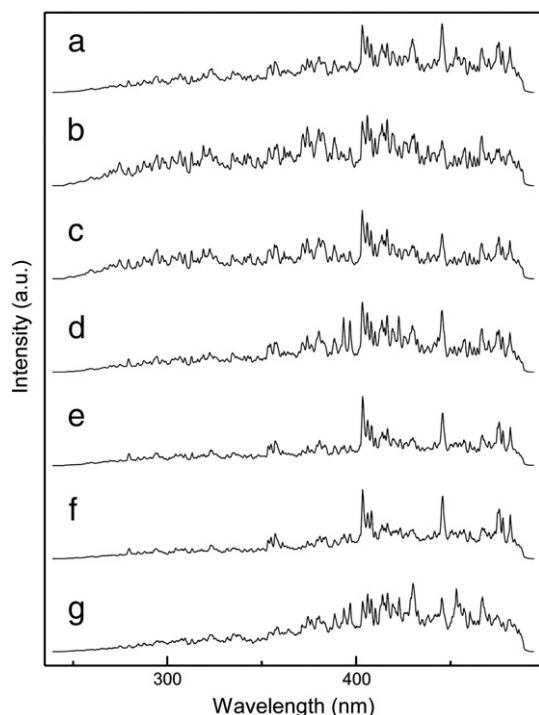
Fig. 1. LIBS emission spectra for representative coltan samples: (a) Madagascar, Tsarafara; (b) Brazil, Minas Gerais, São José da Safira; (c) Mozambique, Alto Lighona; (d) Afghanistan, Kunnar; (e) Zimbabwe, NMNH 145503; (f) South Africa, Namaqualand, NMNH R5085; (g) Democratic Republic of the Congo, Luwangashi, NMNH 157219.

for country-level classification, 17 out of 19 for country and mineral type level-classification, 37 out of 37 for location-level classification, and 56 out of 57 for sample-level classification.

Country-level classification was anticipated to afford the lowest percentage of correctly assigned labels since political boundaries are not formulated on the basis of geology. The results were slightly better when the putative mineral type (i.e. columbite or tantalite) is taken into account. This is admittedly a somewhat arbitrary designation since columbite–tantalite minerals form a solid solution series with a corresponding range of chemical composition. However, misclassifications were always of the same mineral type as the assigned class (e.g. the misclassified spectra for the DRC samples, both of which were tantalite, were primarily confused with the tantalite samples from Namibia).

The location-level results show significant improvement, as would be expected when class labels reflect the different origin of the samples. For Mozambique, the Morrura pegmatite is part of the Alto Lighona pegmatite field, so it is not surprising that these two tantalite samples produce a 100% match for the country and mineral type-level classification and that the Alto Lighona tantalite is misclassified principally with the Morrua sample at the location- and sample-level.

The sample-level classification tasks afforded the best overall results with all but one of the samples being correctly labeled using the maximum-likelihood paradigm. The values in parentheses in the last column of Table 1 represent the total percentage when misclassifications are added in that correspond to the correct location-level classification. This suggests that samples from the same location are often so similar that they are easily "confused" for one another but rarely for another sample from a different location. The number of spectra available for each sample may have affected the classification results in that some samples for which only one set of data was obtained (e.g., Fumal, Mbarara and some of the samples from Mozambique and Namibia) probably suffered from undersampling while others seems to classify properly.

The less than perfect correlation of some samples may be due to factors such as (1) inadequate numbers of samples to correctly characterize the mineral deposit, (2) insufficient locality information
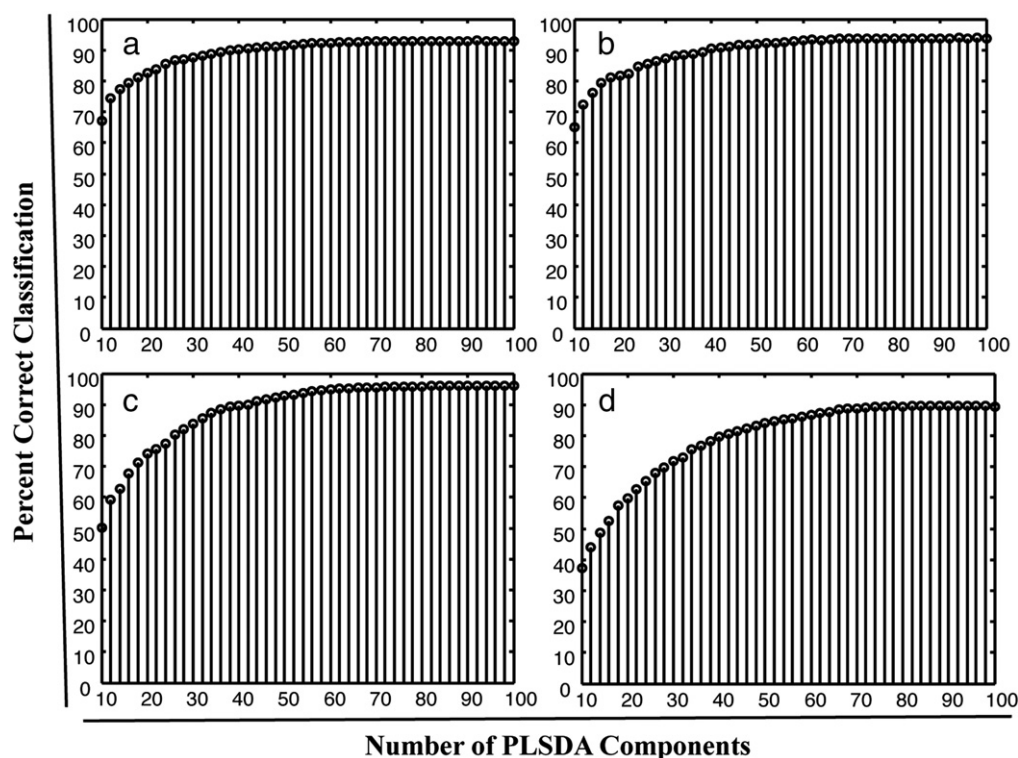

Fig. 2. Classification results for four different sets of class labels: (a) 14 classes organized by country; (b) 19 classes organized by country and putative mineral type, with samples from different sites in the same country being placed in the same class if the mineral types were identical and in separate classes if the mineral type differed; (c) 37 classes organized by location; and (d) 57 classes for sample-level classification. Results are shown as the percentage of spectra correctly classified (*y*-axis) as a function of the number of components (i.e. latent variables) used in the PLSDA classifier (*x*-axis).

which could lead to errors in the initial selection of class labels, (3) inaccuracies related to samples whose chemistry is poorly characterized or (4) textural and/or chemical heterogeneity within and between samples from a single deposit. The role of geology in assuring a meaningful classification also cannot be disregarded. In part, the chemical character of columbite-group minerals reflects the bulk composition of the parent pegmatite (essentially an exceptionally coarse-grained, rare-element enriched granite) in which it crystallized. The chemistry of the pegmatite, which can be extremely variable, reflects the source material from which it is derived and is subject to modification by various geologic processes during and after crystallization. Thus, such a complex history could potentially introduce some degree of uncertainty into the results of the statistical analysis.

Despite this potential natural complication, it is significant that most coltan samples are classified correctly. These results suggest that LIBS analysis can reasonably distinguish between specific coltan deposits within a limited area. However, because most states or countries will have multiple pegmatite fields within their political borders, and each pegmatite field may have a unique geochemical signature, care must be taken when extrapolating the results to large geographical domains on the scale of regions, states, or countries.

For additional insight into the classification results, the PLSDA models were further examined to determine which wavelengths were most important for correctly assigning class labels. Fig. 3 shows a plot of the wavelength (*x*-axis) versus the variance of the PLSDA weightings (*y*-axis) for the sample-level classification.

The largest magnitude weightings (calculated with 40 components and aggregated across all classes) were expected to correspond to emission lines of anticipated major and trace elements of the columbite–tantalite group minerals. The possible identity of these lines was determined using a range of 250–490 nm and a ±0.3-nm search tolerance (to match the spectral resolution of the data) in a database generated from the LIBS spectra of pure elements obtained on an RT100-HP instrument. This approach provides possible assignments of the lines and is a built-in feature of the instrument's software. The results, which are summarized in Table 2, were relatively consistent across the four classification tasks.

The weightings correspond to emission lines for major and trace elements expected in coltan samples, such as Nb, Ta, Fe, Mn, Ti, W, and Mg. These are the same elements that were identified in the weightings found in the preliminary study [9], though some of wavelengths are not identical. Of particular interest in the present study is
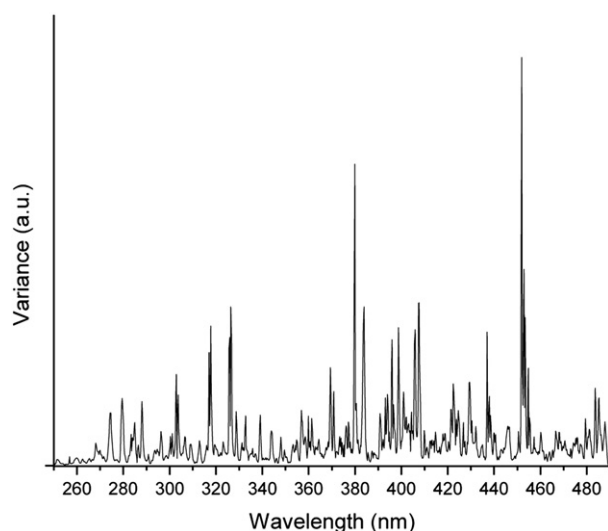
Table 2
Combined top PLS weightings for four PLSDA classification tasks performed using data from a laboratory-based LIBS instrument with possible element assignments. The values were obtained using 40 PLS components.

PLS loadings (nm)	Wavelength from database (possible element assignment)
279.3	279.5 (Mg)
	279.7 (Ta)
317.8	317.81 (Zn)
	317.93 (Ca)
379.9	379.81 (Nb)
	379.95 (Fe)
398.7	398.78 (Gd)
	398.79 (Yb)
	398.98 (Ti)
407.4–407.6	407.44 (W)
437.0	436.97 (Gd)
	436.84 (Nb)
451.7–452.9	451.85 (Lu)
	451.96 (Gd)
	452.28 (Gd)
	452.3 (Nb)
	452.34 (Nb)
	452.7 (Y)
	453.3 (Ti)
483.6	483.53 (Gd)
	483.69 (Y)

the possible significance that rare-earth elements (REE — the lanthanides and yttrium) may play in the discrimination of samples.

It is known that varying levels of REE enrichment can be found in some granitic pegmatites, where they are typically concentrated in the primary accessory minerals monazite, xenotime, fergusonite, euxenite, samarskite and gadolinite. Several of the most significant weightings found in this study may correspond to emission lines associated with Y, Gd, Yb and Lu (see Table 2). Though the density of emission lines in typical columbite–tantalite spectra is high and some lines almost certainly overlap at the resolution used in these experiments we were able to see evidence that REE's are actually present in the samples. For example, Gd has a series of intense lines between 302 and 337 nm and corresponding emission lines are observed in many of the spectra though they are weak. REE data for columbite-group minerals occurring in pegmatites are infrequently reported [22–25] and generally occur in very low concentrations. Gadolinium has been found to occur as a trace element in some columbite–tantalites with amounts <250 ppm [26,27]. Given that the LIBS limit of detection for Gd was estimated to be much less than 100 ppm for a sample deposited on a quartz substrate [28] it is entirely reasonable that we are observing Gd emission lines in our spectra. Additional work involving elemental analysis using microprobe techniques or LA-ICP-MS is required to confirm the presence and relative percentage of the REEs in these and other columbite–tantalite samples.

4. Conclusion

A diverse suite of columbite–tantalite samples from North America, South America, Africa, and Asia was analyzed by LIBS using a laboratory-based instrument to ascertain if multivariate 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. Chemometric analysis using the PLSDA classification model with *k*-folds cross-validation was employed to achieve correct place-level geographic classification at success rates between 90 and 100%. The possible role of rare-earth elements (REEs) as a factor contributing to the high levels of sample discrimination was also identified. These encouraging results provide further support for the hypothesis that columbite–tantalite minerals retain the unique crustal signature associated with the location of their formation, support the findings described in our preliminary paper [9] and point the way to future studies.

Fig. 3. Plot of spectral wavelength (nm) versus variance of the PLS weightings (arbitrary units) for the sample-level classification.

In order to ensure sufficient sampling of the chemical heterogeneity of pegmatite mineral deposits, allow for the use of the more robust leave-one-sample-out cross-validation scheme in the PLSDA classification model and reduce the possibility that inadequate locality information may lead to inaccuracies in the initial selection of class labels, it will be necessary to use an even larger sample suite that has been characterized using standard analytical techniques (e.g. microprobe analysis, XRD, LA-ICP-MS). To determine what LIBS can achieve realistically in comparison to other schemes for classifying minerals the limit of detection, level of precision and other analytical figures of merit need to be established.

Acknowledgments

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