White Paper

Analysis of the 'Conflict Minerals' Columbite-Tantalite Using Laser-induced Breakdown Spectroscopy (LIBS)

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Background

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". 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. At present, the predominant supply of the world's columbite-tantalite ore comes from Brazil and Australia. 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 Democratic Republic of Congo (DRC) and adjacent areas. Although the overall production of Nb and Ta in Central Africa is relatively small at present, the illicit export and sale of columbite and tantalite from the DRC to European and North American markets has been cited as an important means by which the civil conflicts in Central Africa are being financed.

Current Situation

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.**

Proposal

We have investigated the use of laser-induced breakdown spectroscopy (LIBS) to meet this challenge based on the concept of 'geochemical fingerprinting'. Laboratory scale validation of the technology will be completed (and published) by the middle of summer 2011.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 samples of the same kind from other locations. Identification is based upon the fact that the Earth's crust is compositionally heterogeneous and that minerals forming within the crust will reflect that intrinsic geographic heterogeneity. 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. a 'chemical fingerprint') of any material in real-time. LIBS has already been proven to work in the field for other applications.

Columbite-tantalite samples from North America, South America, Africa, and Asia have been examined by LIBS using laboratory-based and field portable instruments. The data was analyzed using chemometric techniques such as partial least squares discriminant analysis (PLSDA) to demonstrate that LIBS can rapidly distinguish different geographic sources with LIBS spectra with high levels of certainty. A paper describing the preliminary studies has recently appears (Harmon, R.S., Shughrue, K.M., Remus, J.J., Wise, M.A., East, L.J., Hark, R.R. "Can the provenance of the conflict minerals columbite-tantalite be ascertained by laser-induced breakdown spectroscopy?" *Anal. Bioanal. Chem.*, **2011**, DOI 10.1007/s00216-011-5015-2). Additional work with a larger, more geographically diverse and fully validated sample suite and optimization of spectral acquisition parameters is currently underway. Samples of processed coltan ore from actual areas of conflict in central Africa are also being obtained for testing.

LIBS holds great promise as a means to provenance "conflict" coltan as well as other conflict minerals found in abundance in the region such as cassiterite (tin ore), wulframite (tungsten ore) and gold. The buying rules related to Congolese minerals recently adopted by the global electronics industry have caused considerable hardship in the region for hundreds of thousands of people involved in the mining industry in that region. This makes finding a solution to the traceability problem all the more imperative.

Following the current on-going technical (R&D) investigation, the research team proposes a 6 month Engineering and Demonstration effort (T&E) to mature and demonstrate the Applied Spectra Inc field-portable LIBS instrumentation in mining and ore processing sites world-wide.

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Introduction


Figure 1: Map of where conflict minerals can be found in the Democratic Republic of the Congo (DRC) [http://conradiator.wordpress.com/].

Niobium (Nb) and tantalum (Ta) are rare metals of high commercial value. The primary natural occurrence of Nb and Ta is in the complex oxide minerals **columbite and tantalite**, which form a solid-solution series having the general composition $[(Fe,Mn)(Nb,Ta)_2O_6]$. 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 Democratic Republic of Congo (DRC) and adjacent areas (Figure 1).

The **Dodd-Frank Wall Street Reform and Consumer Protection Act** passed in July 2010 by the U. S. Congress requires publically traded companies in the United States that manufacture products utilizing *conflict minerals*, 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" and describe measures taken to identify the source and chain of custody of such minerals. Analytical methods utilizing immobile laboratory-based instrumentation have been used to successfully categorize coltan ores but, at present, there is no technique by which an analysis to determine the place of origin of coltan ore can be accomplished in the field.

A study was initiated to determine if **laser-induced breakdown spectroscopy (LIBS)** could meet this challenge based on the concept of 'geochemical fingerprinting'. LIBS is a versatile method of atomic emission spectroscopy that allows for rapid chemical analysis (Figure 2). This attribute of LIBS, together with its **field-portable potential**, makes the technology an appropriate choice for this geochemical application.

The LIBS emission spectrum (Figure 3) provides a unique chemical signature of a material that can be used to discriminate geological specimens originating in one place from samples of the same kind from other locations. It has already been demonstrated that this approach works well for analysis and geographic discrimination of other geomaterials.

Figure 2: Schematic of the LIBS experimental set-up.

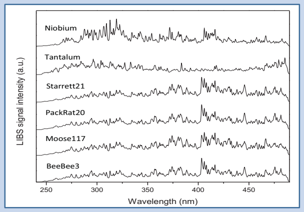

Figure 3: LIBS emission spectra for niobium and tantalum metals and representative examples of coltan spectra from North American samples.

A preliminary study was conducted using several columbite-tantalite sample sets from locations in North America (Figure 3). Using chemometric statistical data analysis techniques such as Principal Component Analysis (PCA) and Partial Least Squares Discriminant Analysis (PLSDA), **correct sample-level geographic discrimination at a success rate exceeding 90% was achieved**. While this demonstrated that LIBS could be used to provenance columbite-tantalite minerals found in North America a comparable study with a much larger, more geographically diverse data set was warranted. Additional samples from South America, Africa and Asia were therefore obtained and analyzed on a laboratory-based system and a field portable unit using optimized collection parameters.

Experimental

Experiments were conducted using commercial LIBS instruments provided by Applied Spectra, Inc. The RT100-HP (Figure 4) is designed for use in the laboratory. This instrument employs a 50 mJ Nd:YAG laser operating at 1064 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 2400 grooves/mm for 'high-resolution' analysis, providing 0.2-0.3 nm and 0.05-0.1 nm spectral resolution, respectively. The unit is a Class I laser device and can be safely operated without special eye protection.

A geographically diverse set of 24 samples of columbite-tantalite from 17 locations in North and South America, Africa and Asia was obtained from private, government and commercial sources and used for analysis without any prior preparation (Table 1).

Optimized experimental parameters for the collection of the LIBS data were: ~9 mJ laser output, 3µs gate width, 3µs gate delay, 15 Hz repetition rate, 40 shots per location, 15 cleaning shots, 2 x 2 grid with 0.5 mm spacing, and 600 grooves/mm grating (0.2-0.3 nm spectral resolution). After removing the cleaning shots a total of 100 spectra were used for subsequent chemometric analysis.


Figure 4: The RT100-HPLIBS laboratory-based LIBS instrument provided by Applied Spectra, Inc.

Table 1: Columbite-tantalite sample labels and descriptions for materials used in this study.

Location	Mine/Secondary Location	# of samples	Mineral
Amelia, Virginia*	--	3	Tantalite
"Afghanistan"	"Crystal Section"	2	Tantalite
Brunswick, Maine	"Starrett"	3	Columbite
Fremont County, Colorado*	Mica Lode Mine	1	Columbite
Greenwood, Maine	Gross Prospect	1	Columbite
Jacumba, California	"PackRat"	3	Columbite
Jefferson County, Colorado	Little Patsy Pegmatite, South Platte	1	Columbite; Samarskite-(Yb)
Kunnar, Afghanistan*	--	1	Tantalite
Minas Gerais, Brazil	--	1	Columbite
Maliaiza, Madagascar*	Tsarafara Pegmatite	1	Columbite
Newry, Maine	Dunton Mine	1	Columbite
São José da Safira, Minas Gerais, Brazil*	Single Euhedral Crystal	1	Columbite
Spruce Pine, North Carolina*	Spruce Pine	3	Columbite
Tumblestone from Madagascar	--	1	Tantalite with Hematite Mix
Zambesia, Mozambique*	--	1	Columbite

A portable LIBS instrument was used to determine if results comparable to those achieved with a laboratory instrument were possible. The PL100-GEO unit (Applied Spectra, Inc.) is a fully self-contained LIBS instrument housed in a watertight, rugged pelican case on wheels to withstand external shocks and allow for easy transport. This Class I device is powered by AC current or by battery and consists of a high power Nd:YAG laser and a CCD-based spectrometer with a 198 to 1005 nm spectral window. The spectral bandwidth is broader and the resolution is higher than the RT100-HP system. A total of 360 shots were obtained for seven samples (marked with an asterisk in Table 1) using either a 1.0 or 1.5 µs gate delay. After removal of cleaning shots, 315 spectra were utilized for subsequent data processing.


Figure 5: The PL100-GEO battery-operated field portable LIBS instrument (Applied Spectra, Inc.)

Results and Discussion

As observed in Figure 3, the majority of the coltan samples have visually similar LIBS spectra. Due to the high degree of spectral similarity, chemometric analysis using multivariate statistical analysis techniques, such as PLSDA and PCA, was necessary to determine if the sample groups differed significantly with regard to geographic location. Figure 6 shows the PCA for the LIBS data when samples are grouped by location. It is difficult to ascertain the degree of discrimination possible with such a large number of data points so the data was then processed through a PLSDA classifier that used 20 components to build a sufficiently robust model for analysis.

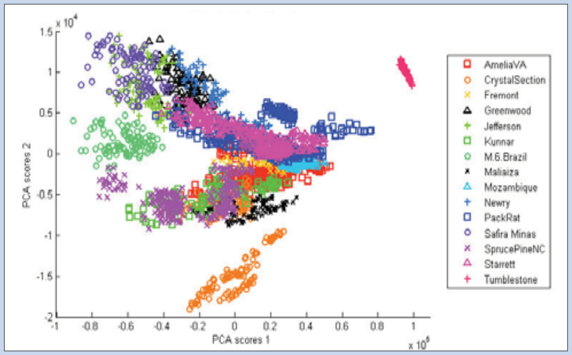

Figure 6: Principal Component Analysis result for 7,560 LIBS spectra of 24 columbite-tantalite samples from 17 locations.

After full cross validation, a confusion matrix (Table 2) was created. In this table, the actual sample ID correctly is compared against the designated model class (i.e. geographic location). The number of spectra that were correctly assigned to each of the possible classes (i.e. geographic group) is compared to the total number of spectra for a given sample. All but one of the cells along the diagonal are highlighted in dark green to represent correct classification at the 85% or higher level. The pink cells correspond to spectra that are incorrectly classified. The discrimination study found that the vast **majority of the samples could be correctly discriminated by geographic source with very high confidence**. The **false positive (Type I error) and false negative (Type II error) rates are typically 0%**. Only the Starrett (12.4%) and PackRat (5.0%) have poor false negative rates but this may be due to the interference of matrix minerals associated with these paerticular samples. These results confirm that LIBS is an appropriate method for discriminating columbite-tantalite samples.

Table 2: PLSDA sample classification results analysis of 24 columbite-tantalite samples from 17 locations from around the world. Green boxes represent correct classification at 85% or higher and pink boxes correspond to a misclassification result.

	Model Classes														
Test Samples	Amelia, VA	Crystal Section	Fremont	Greenwood	Jefferson	Kunnar	Minas Gerais Brazil	Maliaiza	Mozambique	Newry	Packrat	Safira Minas	Spruce Pine, NC	Starrett	Tumblestone
Amelia, VA	300/300	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Crystal Section	0	200/200	0	0	0	0	0	0	0	0	0	0	0	0	0
Fremont, CO	0	0	100/100	0	0	0	0	0	0	0	0	0	0	0	0
Greenwood	0	0	0	99/100	0	0	0	0	0	0	0	0	0	1/100	0
Jefferson	0	0	0	0	100/100	0	0	0	0	0	0	0	0	0	0
Kunnar	0	0	0	0	0	92/100	0	0	0	0	8/100	0	0	0	0
Minas Gerais Brazil	0	0	0	0	0	0	100/100	0	0	0	0	0	0	0	0
Maliaiza	0	0	0	0	0	0	0	100/100	0	0	0	0	0	0	0
Mozambique	0	0	0	0	0	0	0	0	100/100	0	0	0	0	0	0
Newry	0	0	0	0	0	0	0	0	0	94/100	2/100	0	0	4/100	0
Packrat	0	0	0	0	0	0	0	0	0	0	285/300	0	0	15/300	0
Safira Minas	0	0	0	0	0	0	0	0	0	0	0	100/100	0	0	0
Spruce Pine, NC	0	0	0	0	0	0	0	0	0	0	5/300	0	295/300	0	0
Starrett	0	0	0	0	0	0	0	0	0	0	37/300	0	0	263/300	0
Tumblestone	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100/100

Using a smaller yet geographically diverse sample set, the portable LIBS instrument was able to correctly classify the coltan according to geographic origin. Figure 5 shows the PCA results which show substantial clustering of the samples with some outliers. However, **the PLSDA confusion matrix (Table 3) shows only *a single misclassification* among 2,205 spectra**.

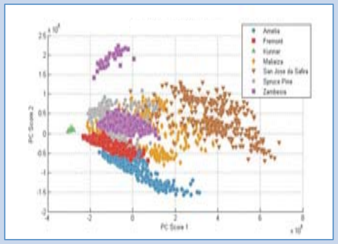

Figure 6: Principal Component Analysis result for 2,205 LIBS spectra of coltan samples from 7 locations obtained using a portable LIBS instrument.

Table 3: PLSDA sample classification results for analysis of seven coltan samples using the PLS100-GEO portable LIBS instrument

	Model Classes						
Test Samples	Amelia	Fremont	Kunnar	Maliaiza	Minas Gerais	Spruce Pine	Mozambique
Amelia	315/315	0	0	0	0	0	0
Fremont	0	314/315	1/315	0	0	0	0
Kunnar	0	0	315/315	0	0	0	0
Maliaiza	0	0	0	315/315	0	0	0
Minas Gerais	0	0	0	0	315/315	0	0
Spruce Pine	0	0	0	0	0	315/315	0
Mozambique	0	0	0	0	0	0	315/315

Conclusions and Future Work

A suite of columbite-tantalite samples from North America, South America, Africa, and Asia was analyzed by LIBS using laboratory-based and field portable instruments 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. Chemometric analysis was used to determine that geographically diverse samples can be properly classified using LIBS with high levels of certainty. These promising results suggest that still more work with a larger, fully validated sample set is warranted and that is may be possible to provenance "conflict" coltan provided a robust global LIBS database can be developed. Samples of processed coltan ore from actual areas of conflict in central Africa are currently being obtained from our collaborators. Analysis of coltan samples using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) will allow a quantitative comparison between the two laser ablation techniques. This will also be used in conjunction with PLSDA loadings plots to identify the elements responsible for the discrimination. Further optimization of the instrumentation and collection parameters is likewise underway.

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