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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Analysis of the ‘Conflict Mineral’ Coltan-Tantalum by using Laser-induced Breakdown Spectroscopy (LIBS)

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Introduction

Nickleum (Nb) and tantalum (Ta) are rare metals of high commercial value. They are components of the military-grade tantalum cathodes used in electronics devices and are critical to many areas of Central Africa. Ta is one of 80 of the world’s 94 reserves located in the eastern portion of the Democratic Republic of Congo (DRC) and adjacent areas [Figure 1].

The Dodd-Frank Wall Street Reform and Consumer Protection Act signed in July 2010 by the US Congress requires publicly traded companies in the United States that manufacture products utilizing conflict minerals, including tantalum, to disclose where such minerals come from. To report whether such materials “find origin in the Democratic Republic of the Congo or an adjoining country,” describe the mine or quarry of origin, and determine the country of origin of the minerals, geologists must be able to identify the mineral constituents in a product.

A study was initiated to determine if laser-induced breakdown spectroscopy (LIBS) could meet this challenge based on the concept of “geological fingerprinting.” LIBS is a versatile method of atomic emission spectrometry that allows for rapid chemical analysis. This attribute of LIBS, together with its field-portable potential, makes the technique an attractive choice for the geophysical 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 works well for analysis and geographic discrimination of ore materials.

A preliminary study was conducted using several coltan-tantalum sample sets from locations in North America (Figure 5). 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 99% was achieved. While this demonstrated that LIBS could be used to pronounce coltan-tantalum minerals found in North America a similar 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.

A Portable LIBS instrument was used to determine if results comparable to those achieved with a laboratory instrument were possible. The PLSDA-GEU (Applied Spectra, Inc.) is a full-featured LIBS instrument housed in a watertight, rugged pelican case on wheels. It is designed as a rapid screening tool for large-diameter. The system uses Fourier transform infrared spectroscopy (FTIR) and a high-power Nd:YAG laser to establish the sample position for subsequent LIBS analysis. A portable LIBS instrument was used to determine if comparable results could be achieved with a laboratory instrument. LIBS was used to analyze a wide range of sample sets from North America, South America, Africa, and Asia. The results of this study were consistent with the findings from the laboratory analysis.

Results and Discussion

As observed in Figure 3, the majority of the coin samples have similar LIBS spectra. Due to the high degree of spectral similarity, chemometric analysis using multivariate statistical analysis techniques such as PLSDA and PCA were found to be successful in identifying the samples. The results of the study showed that LIBS has potential for the analysis of coltan-tantalum materials.

Conclusion

A suite of coltan-tantalum 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 these 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 it may be possible to perform “conflict mineral” provenance with a robust global LIBS database can be developed. Sample of processed ore from one or more actual areas of conflict in central Africa are currently being obtained from our collaborators. Analysis of coltan-tantalum 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 be also used in conjunction with PLSDA (least-squares discriminant analysis) plots to identify the elements responsible for the discrimination. Further optimization of the instrumentation and collection parameters is underway.

References


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Table 3: LIBS data classification results for analysis of new coin samples obtained using the PLSDA-GEU portable LIBS instrument.