Provenance determination of sapphires and rubies using laser-induced breakdown spectroscopy and multivariate analysis

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ABSTRACT

Determination of gem provenance is a topic of research in the gemological community for financial, security, and societal reasons. Laser-induced breakdown spectroscopy (LIBS) and multivariate analysis have the potential to revolutionize the field of gem provenance. This study acquired LIBS spectra from 569 rough sapphire and ruby specimens from 21 localities in 11 countries. The spectra were analyzed using the multivariate technique partial least-squares regression (PLSR) in separate algorithms for sapphires and rubies. Each algorithm consists of a series of PLS models. Each model compares the spectra from a locality of interest to the spectra from all other localities in the database. Success rates, as determined by the percent of correct provenance identifications, are 98.9% (sapphire) and 96.0% (ruby) for country of origin and 97.9% (sapphire) and 95.4% (ruby) for deposit of origin. Individual deposits are not recognized by the concentrations of a few elements; rather, the unique compositional signature of each deposit consists of the ratios of many elements, primarily Ca, Zr, Fe, Ba, Mt, Ti, Sr, Si, Cr, H, C, and Li, some of which may reside in inclusions. This work demonstrates that determination of country or deposit of origin may be related to a quantitative measure with a high level of success.

Keywords: Ruby, sapphire, provenance, laser-induced breakdown spectroscopy, chemometrics

INTRODUCTION

The relationship between gem provenance (i.e., country or deposit of origin) and monetary value, combined with the difficulties in provenance determination, have fueled decades of gemological research and limited transparency in the gem industry. In 1990, Gemological Institute of America (GIA) chairman Richard T. Liddicoat explained the technical challenges that exist for determining the source of a gem with any amount of certainty (Liddicoat 1990). Despite his concerns with the ability and need to accurately determine provenance, demand from both the gem trade and the public for provenance certification has grown (Rossman 2009; Shor and Weldon 2009).

Demand has also risen for gem provenance determination because of socio-political concerns. In 2003, the U.S. banned trade with Myanmar through the Burmese Freedom and Democracy Act, citing concerns of human rights abuses in the country (U.S. Dept. of State 2008a). In a 2008 amendment, the Tom Lantos Block Burmese Jade Act of 2008 closed a loophole in the legislation, specifying that any rubies mined in the country could not be legally imported into the U.S. for commercial purposes (U.S. Dept. of State 2008b). To enforce sanctions such as these, a reliable method of determining the provenance of gems is required.

Gemstones from different localities possess different characteristics. Provenance has been determined using a combination of inclusion analysis, trace element geochemistry, special characteristics, and internal growth structures (Gübelin 1953; Gübelin and Koivula 1986; Ward 1995; Hughes 1997; Abduriyim and Kitawaki 2006b). It is evident that an objective and reliable technique needs to be developed to aid with provenance determination. A good example would be provenance studies for rubies and sapphires, which represent a high-value gemstone market complicated by a high volume of trade as well as a broad range of potential sources.

This pilot study uses spectra acquired with laser-induced breakdown spectroscopy (LIBS) from 569 ruby and sapphire specimens from 21 localities in 11 countries to demonstrate a highly successful method for determining the provenance of corundum samples. Sample availability ranged from as few as four to as many as 40 samples from a single deposit and the data are used to demonstrate the statistical need for a minimum sample size of ~30 gemstones. The method utilizes the multivariate statistical analysis technique partial least-squares regression (PLSR) to build a series of models that sequentially compares spectra from one region to all other regions. This method has proven successful in distinguishing between bacterial pathogens (Multari et al. 2010) and individual limestone beds (McMillan et al. 2012). Success rates, as determined by the percent of correct