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Analytical Note

Application of Laser Induced Breakdown Spectroscopy to the identification of emeralds from different synthetic processes ☆

G. Agrosì [a], G. Tempesta [a,*], E. Scandale [a], S. Legnaioli [b], G. Lorenzetti [b], S. Pagnotta [b], V. Palleschi [b], A. Mangone [c], M. Lezzerini [d]

[a] Department of Scienze della Terra e Geoambientali, University of Bari, Bari, Italy
[b] Institute of Chemistry of Organometallic Compounds, CNR, Pisa, Italy
[c] Department of Chemistry, University of Bari, Bari, Italy
[d] Department of Earth Sciences, University of Pisa, Pisa, Italy

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ABSTRACT

Laser Induced Breakdown Spectroscopy can provide a useful contribution in mineralogical field in which the quantitative chemical analyses (including the evaluation of light elements) can play a key role in the studies on the origin of the emeralds. In particular, the chemical analyses permit to determine those trace elements, known as fingerprints, that can be useful to study their provenance.
This technique, not requiring sample preparation results particularly suitable for gemstones, that obviously must be studied in a non-destructive way. In this paper, the LIBS technique was applied to distinguish synthetic emeralds grown by Biron hydrothermal method from those grown by Chatham flux method. The analyses performed by collinear double-pulse LIBS give a signal enhancement useful for the quantitative chemical analyses while guaranteeing a minimal sample damage. In this way it was obtained a considerable improvement on the detection limit of the trace elements, whose determination is essential for determining the origin of emerald gemstone. The trace elements V, Cr, and Fe and their relative amounts allowed the correct attribution of the manufacturer. Two different methods for quantitative analyses were used for this study: the standard Calibration-Free LIBS (CF-LIBS) method and its recent evolution, the One Point Calibration LIBS (OPC-LIBS). This is the first approach to the evaluation of the emerald origin by means of the LIBS technique.

1. Introduction

Emerald is a green variety of beryl, a mineral with an ideal chemical formula $Be_3Al_2(SiO_3)_6$. The green color is due to the trace amounts of chromium and sometimes vanadium. Natural emeralds from different localities are associated with different geologies, while synthetic emeralds from different manufacturers or from different synthetic processes have different ingredients.

Several papers have been published on the characterization of beryl by different techniques [1]. Moreover, considering the importance of the emerald variety in the gemmological market several studies were performed to identify the origin of the emeralds by examining their chemical composition and, in particular, their trace elements [2–6]. However, the analytical methods generally used in mineralogy such as Electron Micro Probe Analysis (EPMA) and Secondary Ion Mass Spectrometry (SIMS) for the light elements, require a detructive sample preparation and consequently they result not particularly suitable for gemstones, that obviously must be studied in non-destructive way. A feasibility study of Laser Induced Breakdown Spectroscopy (LIBS) without standards was previously carried out on other gemstones (in particular to other silicates very similar to Beryl) in order to obtain quantitative chemical data and comparisons with the results obtained with other techniques were made [7,8].

The purpose of this study is to evaluate the capability of the LIBS, to perform chemical analysis of synthetic emeralds in order to distinguish between different producers and growth methods. The analyses were performed detecting at the same time all the elements, also the light ones, in a non-destructive way. In addition, this study aims to compare quantitative analyses obtained by two different methods: the standard Calibration-Free LIBS (CF-LIBS) [9] and its recent evolution, the One Point Calibration LIBS (OPC-LIBS) [10].

From the chemical point of view, synthetic emeralds are characterized by relatively low amounts of foreign elements such as calcium (Ca), magnesium (Mg), copper (Cu), nickel (Ni), zinc (Zn) and iron (Fe). The coloring elements, chromium (Cr) and vanadium (V), are

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* Corresponding author at: Department of Scienze della Terra e Geoambientali, University of Bari, Via E. Orabona, 4, 70125 Bari, Italy. Tel.: +39 0805443450; fax: +39 0805442625.
E-mail address: gioacchino.tempesta@uniba.it (G. Tempesta).

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present in varying amounts. Basing on Si, Al, and Be amounts it is also possible to separate synthetic emeralds from natural emeralds: in the former the concentration of these elements approximates the ideal amounts, whereas in the latter these amounts are very variable. Tacking into account that the crystal structure of beryl (space group P6/mcc) consists of stacked six-membered rings of Si tetrahedra parallel to (0001), cross-linked by Be tetrahedra and Al octahedra to form a three-dimensional framework around six-membered ring channels, the complex cationic substitutions by "impurity ions" occur mainly in tetrahedral and octahedral structural sites.

Other substitutions changing the valence balance can also occur giving rise to charge imbalance that require the incorporation of alkali ions into the channels.

The evaluation of the concentration of the chromophores like Cr, V and Fe permits to distinguish among emeralds grown by different synthetic processes.

2. Samples

The studied samples grew by flux method (Chatham) and by hydrothermal method (Biron).

Flux growth is a method by which components of the gem material desired in the single crystal form are dissolved in a flux (solvent). A flux permits the growth to proceed at temperatures below the melting point of the solute phase with less sophisticated equipment. This reduction in temperature is the principal advantage of flux growth over growth from the pure melt. The Chatham method is still covered by industrial secret but from the literature data it results from the using of the lithium molybdate-vanadate flux with a nutrient of natural beryl or reagent-grade BeO, $BeCO_3$, Al_2O_3, and SiO_2, together with Cr_2O_3 or $LiCrO_4$ plus Fe_2O_3 as coloring agents.

The hydrothermal technique is a method to growth crystals from a solution in water at high temperatures and pressures in a small rotating autoclave that is lined with gold and carefully sealed. Normally a seed of natural colorless beryl is suspended by a platinum wire and it is used as germ for the growing emerald. To prevent the precipitation of chromophore such as Cr and V a concentrated hydrochloric acid is generally used [11].

The studied samples are rough stones (Fig. 1). The crystals are transparent and uniform in color and show planar surfaces and internal inclusions (solid and liquid). The inclusions in the Chatham synthetic emeralds, that are characteristically well-developed as hexagonal prisms, consist of clusters of dark red elongated isotropic crystals with high relief and two phase inclusions.

The characteristic inclusions for Biron are rare particles of gold, grayish white "bread-crumb" inclusions, phenakite crystals, fractures, veils and growth lines.

3. Experimental

The LIBS measurements were performed using the Modì (Mobile Dual-Pulse Instrument) by Marwan s.r.l (Pisa, Italy), in the 'Smart' configuration [12]. The instrument is equipped with a double pulse Q-Switched (Nd-YAG, $\lambda = 1064$ nm) laser, giving two collinear pulses with an energy of 60 mJ per pulse in 8 ns, at a maximum repetition rate of 10 Hz. The delay between the pulses can be varied from 0 μs (single pulse configuration) up to 60 μs. The use of the double pulse approach allows to obtain an enhancing of the emission line intensity [13].

The two laser beams were focused on the sample's surface using a 10 cm focal length lens.

The plasma radiation was collected using an optical fiber and analyzed with a double spectrometer (AvaSpec Dual-channel Fiber Optic Spectrometer) from Avantes, covering simultaneously the spectral interval between 190 and 415 nm (with spectral resolution of 0.1 nm) and between 390 and 900 nm (0.3 nm resolution).

The analyses were performed inside the internal experimental chamber of the instrument, using 60 mJ of energy per pulse, a delay between the two pulses of 1 μs. The LIBS spectra were acquired with a delay of 2 μs after the second pulse and were integrated for 2 ms. For each sample, four or five replicates were acquired in different points of the sample. For each point, a single spectrum was acquired. The LIBS spectra, after acquisition and storage, were qualitatively and quantitatively analyzed using a proprietary software (LIBS++), which implements the calibration-free method. Two different methods for quantitative analyses were used for this study: the standard Calibration-Free LIBS (CF-LIBS) method [9] and its recent evolution, the One Point Calibration LIBS (OPC-LIBS) technique [10].

The "One Point Calibration" is a new method for improving the reliability of quantitative analysis by Laser-Induced Breakdown Spectroscopy (LIBS). The method can be considered as a variation of the Calibration-Free LIBS approach; although not completely standardless, only one standard of known composition – and similar matrix to the ones to be analyzed – is needed. On the other hand, the One-Point Calibration approach allows the empirical determination of essential experimental and spectroscopic parameters whose knowledge is often imprecise or lacking; the result is a definite improvement of the trueness of LIBS analysis with respect to the traditional Calibration-Free approach.

The results on the application of the One-Point Calibration LIBS method show that the procedure, basically simple and as fast as the usual CF-LIBS approach, maintains all the advantages of the Calibration-Free method in terms of independence on the matrix effect while offering the possibility of compensating for the lack of precise information on crucial parameters which are essential for the application of the CF-LIBS analysis, and in particular the knowledge of the response curve of the spectrometer in the spectral regions more interesting for the LIBS analysis (and more difficult to measure experimentally), and of the spectral A_{ki} parameters. The additional requirement, with respect

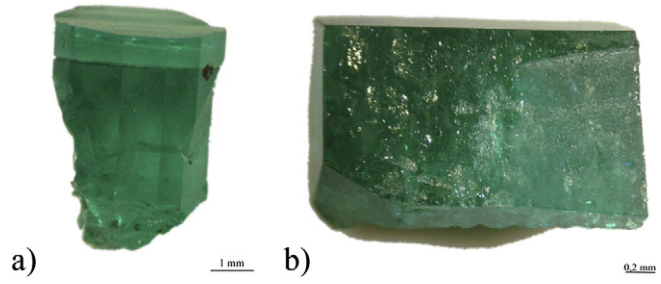

Fig. 1. Optical image of two representative samples: a) Chatham emerald; and b) Biron emerald.

Table 1
The quantitative analyses obtained from the Biron samples with the two methods, OPC and CF, normalized and compared with literature data and LA-ICP-MS results.

Biron emeralds				
Elementi wt.%	OPC	CF	LA-ICP-MS	Literature
Al	20.40 ± 0.82	19.89 ± 1.60	19.78 ± 1.31	20.84
Be	10.49 ± 0.71	10.93 ± 1.16	10.07 ± 0.44	10.21
Ca	1.03 ± 0.70	0.28 ± 0.19	0.04 ± 0.01	1.91
Cr	0.94 ± 0.03	1.36 ± 0.31	0.733 ± 0.07	1.06
Cu	0.058 ± 0.033	0.373 ± 0.261	–	0.106
Fe	0.62 ± 0.29	0.24 ± 0.09	0.018 ± 0.004	0.85
Ba	0.033 ± 0.022	0.008 ± 0.005	–	0.042
Mg	–	0.04 ± 0.025	–	0.021
Ni	0.053 ± 0.039	0.60 ± 0.31	–	0.021
Si	65.36 ± 1.30	64.42 ± 1.05	68.41 ± 4.92	63.59
V	0.958 ± 0.14	1.69 ± 1.10	0.906 ± 0.048	1.27
Zn	0.04 ± 0.02	0.14 ± 0.06	–	0.085