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μ-SRXRF characterization of Brazilian emeralds

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Abstract. The aim of the present study is to characterize emeralds from different mines of Brazil by using Synchrotron Radiation X-ray Fluorescence Microanalysis (μ-SRXRF). The advantage of this technique is that we can analyze a homogeneous, inclusion free area of the stone with the microbeam to distinguish the elemental fingerprint according to the provenance of the emerald. A total of 47 samples belonging to 5 different Brazilian mines were studied in this work and 28 elements were identified. By means of Principal Component Analysis (PCA) it is possible to build different groups according to the provenance of the stones, which allows to assign samples of unknown origin to the according mine.

1. Introduction

Emerald is one of the most important precious stone used in jewelry and therefore one of the most imitated gems, synthetic or simulated, as well as one of the principal items on the illegal trade of gems [1,2]. Belonging to the Beryl group, its chemical formula is Be_3Al_2 (Si_6O_{18}). Their purity, in terms of mineral inclusions, is one of the factors that determines the commercial value and also serves as proof of authenticity. The green color is associated with the presence of elements as chromium, iron, and in some cases vanadium. These trace elements can be used as fingerprint and can therefore be a guideline to determine the region of origin. Nowadays, Brazil is the largest producer, by volume, of emeralds with many important mines located mainly in the southeast and northeast of the country [3,4]. The emeralds are processed by domestic cutters or foreign buyers take the rough stones to cutting facilities in their own countries [5].

In the present study 47 natural emeralds from 5 different mines were analyzed. The occurrences are from Goiás state (Santa Terezinha de Goiás(St) and Minaçu(M)), Minas Gerais state (Nova Era(N) and Belmont(B)) and Tocantins state (Tocantins(T)).

2. Experimental Procedures

The set of stones were analyzed with μ-SRXRF (μ-Synchrotron Radiation X-Ray Fluorescence) at the BAM*line*, the beamline of the Federal Institute for Materials Research and Testing [6,7] for hard X-rays at the electron storage ring BESSYII in Berlin. The measurements were performed in homogeneous areas, free of inclusion to distinguish the elemental fingerprint of the emeralds.

The samples are small emeralds whose sizes range from 0.4 cm to 2.0 cm where some are in their raw form and others are cut having polished surface. Visually it is not possible to classify the samples according to their source. There are only few changes in the color of emeralds ranging from shades of light to dark green. The stones were all mounted on the same holder in a way that a flat surface of each stone was facing up towards the detector and on the same plane. For stones with cuts, one of the flat surfaces and for rough stones the flattest available surface was chosen for irradiation.

Excitation energies of 10 and 20 keV were used and the emitted fluorescence radiation was detected with a silicon drift detector (SDD). The acquisition time was 60s per point and the beam size was 0,5mm with a total of 4 points per sample having no relevant statistical fluctuation. Spectrum evaluation was performed with the Axil software package [8].

By using an excitation energy of 10keV we were able to identify 16 elements (Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, and Cs) and with 20 keV 12 additional elements (Ga, Ge, Se, Br, Rb, Sr, Y, Zr, Nb, W, Pb and Bi) could be detected.

Naturally, not all elements were found in each sample, some were even found in only one sample but all were present in the model used for the analysis. A typical spectrum obtained is shown in figure 1. In this figure is shown the Kα or Lα lines of some elements as example.

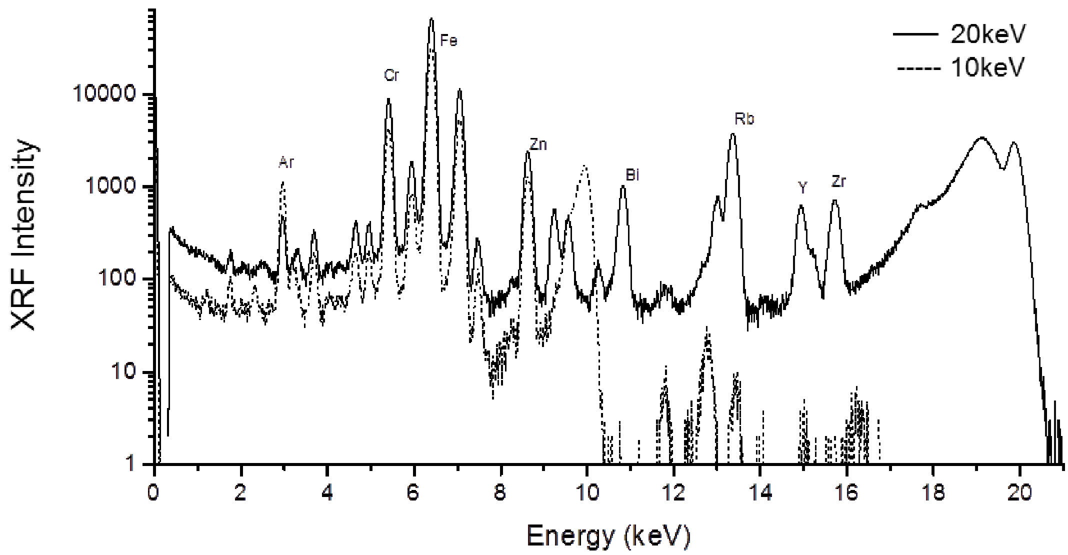

Figure 1. Typical spectra obtained by SRXRF technique for emerald sample with excitation energies of 10keV (dashed line) and 20keV (solid line).

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3. Results and Discussions

For the first analysis we generated column plots of elemental concentration for the comparison between the different samples. For some elements, such as Zn (10keV), Pb and Bi (20keV), it is possible to point to a small separation in the sample set as we can see at Figure 2. Using the results from the 10 keV measurements the group of samples originating from "Minaçu" can be separated from the other by their Zn content. With 20keV excitation energy the Bi and Pb concentrations can be evaluated. This allows the assignation of "Nova Era" and "Belmont" gems are characterized by a higher amount of Bi whereas the "Minaçu" and "Santa Terezinha" stones show higher presence of Pb in their composition.

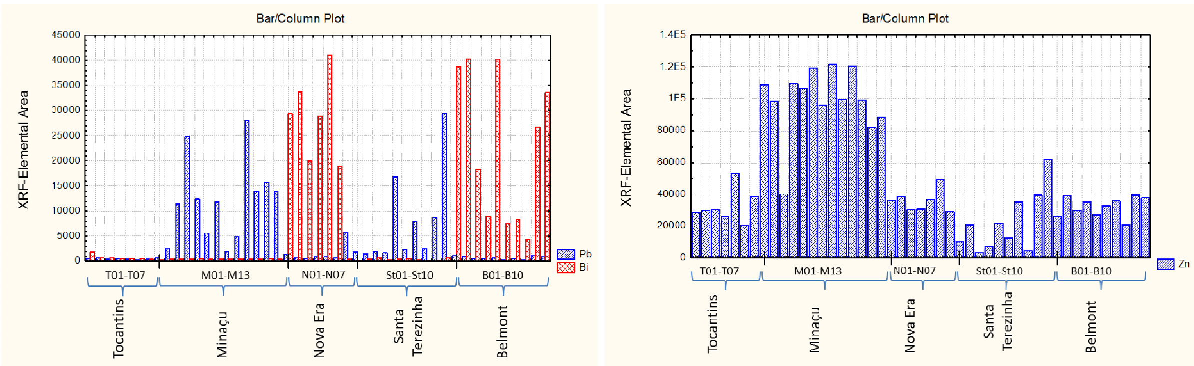
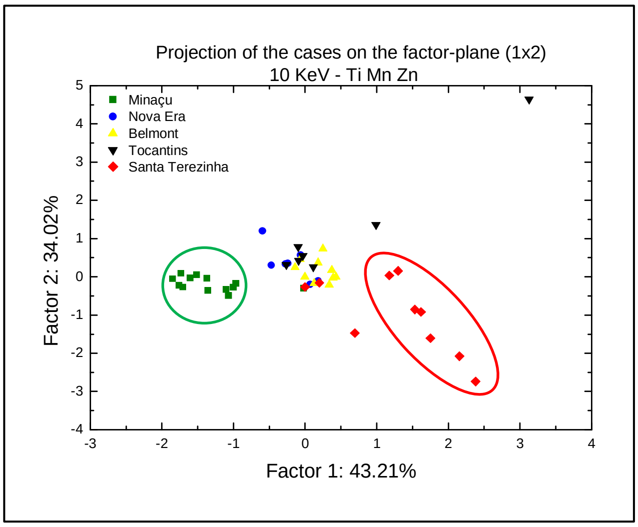


Figure 2. Column plot of intensity for emerald samples at 10 keV (Zn) and at 20 keV (Pb and Bi).

These histograms of peak areas are indicating a compositional difference between the samples from distinct places, but they are not conclusive. In order to verify the existence of the groups statistical PCA (Principal Components Analysis) was applied. The statistical analysis was carried out using the STATISTICA [9] software package. PCA reduces the number of original variables to a smaller number of representative variables, creating a factor space helping on their classification [10,11]. With these results the identification of clusters with similar characteristics with respect to these parameters is possible.

In the PCA, for the data measured with 10 keV excitation energy, the elements Ti, Mn and Zn were used as parameters. The result of this analysis is shown in the diagram in figure 3 on the left, where a separation of "Minaçu" and "Santa Terezinha" samples can be observed while there are no visible differences between the other groups. At the energy of 20 keV the elements Cr, Mn, Zn, Sr and Bi were used as parameters. In this case, a separation of the samples belonging to "Minaçu", "Santa Terezinha" and "Tocantins" can be detected, even if there are some exceptions.



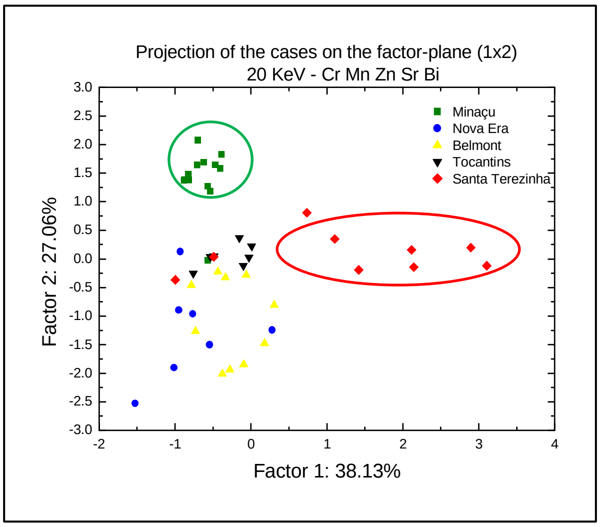


Figure 3. PCA analysis applied to SRXRF data of 57 emeralds stones. At 10keV, Ti, Mn and Zn were used as parameter. At 20 keV the elements Cr, Mn, Zn, Sr and Bi were used as parameter. The samples are listed according to their classification/mine.

The same result can be observed using a ternary graph of the elements Bi, Zn, Pb. In this graph the data was normalized by the samples to get a range between 0 and 1. The graph presents four groups which are in agreement with the information about the local origin of the stones, again with few exceptions. The samples from "Nova Era" and "Belmont" at the top of the graph form one cluster and cannot separated.

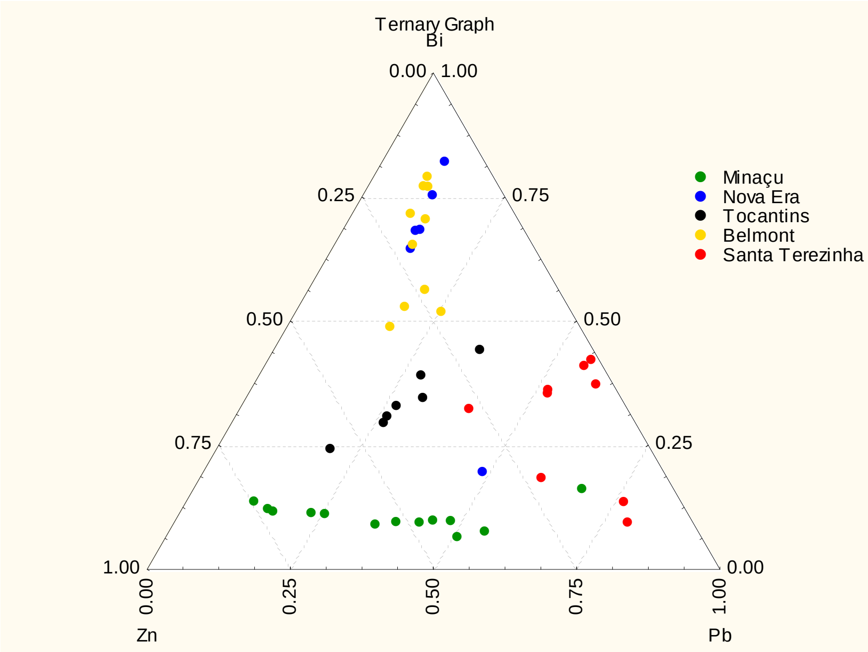


Figure 4. Ternary graph with the elements Zn, Pb and Bi at energy of 20keV.

With the data collected so for, the samples belonging to “Belmont” and “Nova Era” show a similar fingerprint. This result is conclusive given the fact that those two mines benefit from the same geological formation since they are just 10 km away from each other [12,13].

4. Conclusions

The analysis of emeralds using μ-SRXRF technique in inclusion-free areas, allows the determination of the elemental fingerprints. Characteristic elemental composition permits the assignment of each stone to the corresponding mine.

In this study, it was to differentiate the groups belonging to 3 mines, “Minaçu”, “Tocantins” and “Santa Terezinha”. The groups “Nova Era” and “Belmont” that are neighboring mines with the same geological formation cannot be distinguished. These results are valuable for the authentication of gems and the abatement of forgeries and the illegal trade.

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Reference

[1] K.Nassau, Journal of Crystal Growth 35 (1976), pg.211-222
[2] R.J.King, Geology Today, Vol.13, Issue 1, pg.37-40
[3] G Giuliani, L. J.H.D. Silva, P. Couto, Mineralium Deposita (1990), pg.57-64
[4] A.Lucas, Gems & Gemology, spring (2012), pg.73-77
[5] Puppim de Oliveira, J.A.; Ali, S.H., Resources Policy 36 (2011), pg.132.141
[6] H.Riesemeier et al, X-Ray Spectrometry, (2005) Vol34, issue2, pg.160-163
[7] W.Gorner et al, Insight, (2006) Vol48, issue9, pg 540.544
[8] P.van Espen et al, Chemometrics and Intelligent Lab. Systems, Nov (1986), pg.109-114
[9] StatSoft, Inc. (2004), STATISTICA, version 7. www.statsoft.com
[10] Jonathon Shlens, A Tutorial on Principal Component Analysis (2009)
[11] MINGOTI, S. A., Editora UFMG, 2007
[12] Preinfalk et al, J. of South America Earth Science 14 (2002) pg.867-887
[13] J. M.Watkins et al, Technical Report 56 (Relatório Técnico 56) P30_RT56