Geochemical and mineralogical characterization of emeralds from La Arcadia mine, Colombia

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Abstract. Analyses were carried out on 514 emeralds, 439 from Colombia (15 from La Arcadia, 276 from other mines of Muzo district, 102 from other districts of the western belt and 46 from the eastern belt) and 75 from other countries, to find systematic trends or chemical composition characteristics that discriminate the Arcadia emeralds for provenance purposes. Principal Components Analysis (PCA) was carried out to compare La Arcadia mine against emeralds from other deposits around the world, mines from the eastern belt, mines from other districts, and mines of the same district. Additionally, petrographic analysis was performed on 20 polished thin-sections of representative veins and breccias from the La Arcadia mineralization. The chemical composition of Colombian emeralds is characterized by a high concentration of Vanadium (>2000 ppm), however, La Arcadia emeralds have a lower concentration than other deposits from Colombia, also the elements that substitute for Al have low concentrations. Emeralds observed in La Arcadia are associated with a hydrothermal alteration that affected a conspicuous black level of siltstones and the typical paragenesis consist of dolomite, albite, mica and emerald in veins and breccias.

1 Introduction

Colombian emeralds are well known for their gem quality, Colombia is one of the World's largest producers of emeralds, along with Brazil and Zambia. One of the factors contributing to the high quality of Colombian emeralds is their style of mineralization, which is related to non-magmatic hydrothermal fluids. Sedimentary host rocks make the Colombian deposits unique. In contrast, emeralds from Brazil and Zambia were formed by processes linked to igneous or metamorphic activity and generally the emeralds are found in the metamorphic "black walls" or pegmatitic veins.

The Colombian emerald deposits are distributed in two belts, eastern and western, the former contains the districts of Chivor, Gachala and Macanal, the western belt groups the districts of Maripí, Coscuez, Peñas Blancas, Yacopí and Muzo-Quipama. The latter is one of the most remarkable districts in terms of quality and gem production. The most extraordinary emeralds have been found there and, moreover, this district produces the trapiche variety. Emerald mineralization occurs within calcareous mudstones layers in marine rocks of Lower Cretaceous age. The relevant zones correspond to brecciated hydrothermally altered shales transformed by evaporitic brines. These are associated with veins containing sulfides, albite, carbonates, quartz and emeralds.

The principal elements in emerald are beryllium, aluminum, silicon and three key chromophore elements (chromium, vanadium, and iron). In Colombian emeralds the percentage of iron is relatively low in comparison with emeralds from the rest of the world, whereas the concentrations of Cr and V differ depending on the belt.

International investment has increased in the last years improving the process of mining extraction and introducing new technologies. Most of the mines remain, however, largely artisanal using traditional mining methods. Production has, however increased. 2020 production was estimated at 2.083.134 ct (Esmeralda 2021), contrasting with a rough emerald exportation of 807.507 carats in 2014.

The purpose of this study is to contribute new information on these emerald deposits. Relevant observations on paragenetic sequence, geochemical composition, and emerald characteristics are presented for La Arcadia. Methods for discriminating the geographic origin of Colombian emeralds are presented.

2 Geological setting

The emerald deposits of Colombia are grouped within two parallel NE-SW-striking belts on the flanks of the eastern cordillera. They are commonly termed the Western emerald belt and Eastern emerald belt. The cordillera is the product of a back-arc basin in the Triassic-Paleogene period. A large quantity of sediments were deposited in the Lower Cretaceous. In the Cenozoic period, extensional tectonics became contractional and in the Neogene, the basin was controlled by thrust systems and ramp faults. This shortening episode was decisive for initiation of hydrothermal mineralization. (Branquet et al. 1999).

The La Arcadia deposit is located in Muzo district. (Fig. 1). The deposit is structurally associated with the southern prolongation of the Alto La Chapa-Borbur anticline, which is a regional fold controlled by three faults, Rio Minero Fault (southeast), the Rio Itoco Fault (southwest), both reverse faults, and the Peñas Blancas Fault (northwest), which is a strike-slip fault. (Pignatelli et al. 2015). The stratigraphic sequence in the area comprises four main formations. In chronological order, these are: Rosablanca Formation (three macro sequences of wackestones, boundstones, micrite with interacalations of lodolite); the Furatena Formation (thin layers of lodolites, claystones and siltstones); the Muzo Formation, principally composed of carbonaceous lodolites, calcareous lodolites and sporadic levels of limestones. The upper Formation is the Capotes Formation composed of thick layers of siliciclastic lodolites and siltstones. The calcareous lodolites from the

Muzo Formation are considered the emeralds host-rock, and it provides the chromophores elements (Reyes et al. 2006).

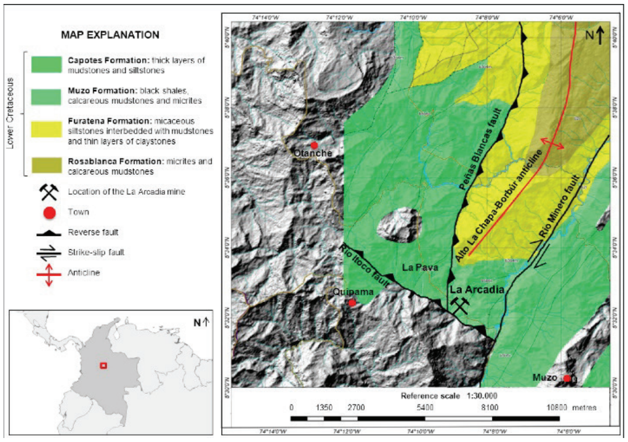


Figure 1. Generalized geological map of the La Pava emerald Mine

3 Material and methods

Four tunnels in La Arcadia mine were studied, we described the main features including the macroscopic mineralization, the host rock description, and structural trends. We recollected forty samples; the twenty most representative samples were selected to elaborate polished thin sections. Fifteen rough emeralds specimens were recollected from the La Ventana Tunnel, these emeralds are light green with homogeneous color, the length varies between 5 to 15 mm. In addition, we compare these specimens with 276 emeralds from the same district, with 102 emeralds from the same belt, 46 emeralds from the eastern belt and 75 emeralds from different countries. In the emerald samples, a chemical composition analysis was carried out through the XRF method.

Petrography. 20 Thin sections were analyzed in a Axio Scope.A1 ZEISS microscope with 5x, 10x, 20x and 50x magnification.

Energy- Dispersive X-Ray Fluorescence (XRF): The chemical composition of each sample was collected with a PANalytical – EPSILON 5 instrument. Data was processed using Epsilon 5 Software. Sample preparation was not necessary. The elements analyzed were S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Ga with a manual entry of 13.15 wt% Be.

Statistical Analysis: The data were processed and analyzed using R software. The function PCA from the FactoMineR was used for the PCA. Data visualization was made using the Factoextra package and ternary plots were made using the 'ggtern' package.

4 Results

4.1 Mineralization

Five mineralization assemblages were recognized according to their temporal, textural and geochemical features (Fig. 2).

The pre-mineral stage comprises the alteration in the host rock, which was mainly composed of quartz. However, due to hydrothermalism, the quartz was replaced by albite. Besides, other minerals crystallized in this stage as tourmaline, xenotime and monazite. The first stage corresponds to the extensive mineralization of albite (Albitization), the plagioclase is present in the rock-vein contact in paragenesis with quartz, apatite, and very fine crystals of xenotime (sometimes displayed as inclusions in albite), this stage commonly fills fractures in the host rock. The second stage is defined by the abundant presence of carbonization divided in two substages, scratchy calcite and a posterior rhombohedral calcite, including rutile overlaying albite crystals, and sulfides as pyrite, chalcopyrite, pyrrhotite and sphalerite usually found in veins with thickness greater than 2 cm.

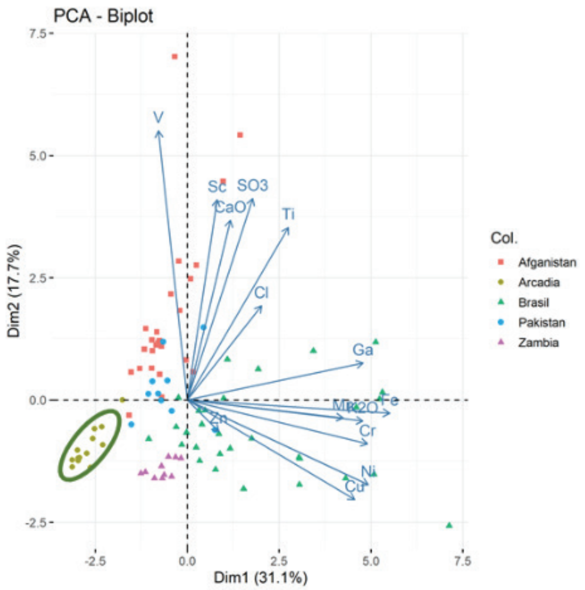
The third mineral assemblage in the veins includes dolomite, which displays euhedral crystals, frequently with albite inclusions. Other minerals such as albite and mica are also present. This stage includes emerald occurrence as anhedral crystals exhibiting a light green – deep green color and exceptional brightness. A superimposed late-stage contains gypsum occasionally filling open spaces exhibiting light-gray crystals. Goethite is part of a supergene oxidation that affects the sulfides.

Figure 2. Paragenetic sequence of the mineralization in La Arcadia Mine.

4.2 Chemical composition

4.2.1 Comparison with emeralds of the world

PCA study was performed on the XRF data to identify provenance features. The plot (Fig. 3) shows that emeralds from La Arcadia differ from those rest elsewhere in the world if we consider all elements studied. This group has a considerately lower content of all elements, except V and Zn, than the rest of the samples. Some samples have similar characteristics to emeralds from Afghanistan but the different contents of Sc, Cr and Ti can help differentiate them. Moreover, the Brazilian emeralds are easily grouped because of their lower Sc and Ca. The ternary plot shows that La Arcadia emeralds have the highest V content and similar concentrations of Cr and Fe as the Brazilian specimens.



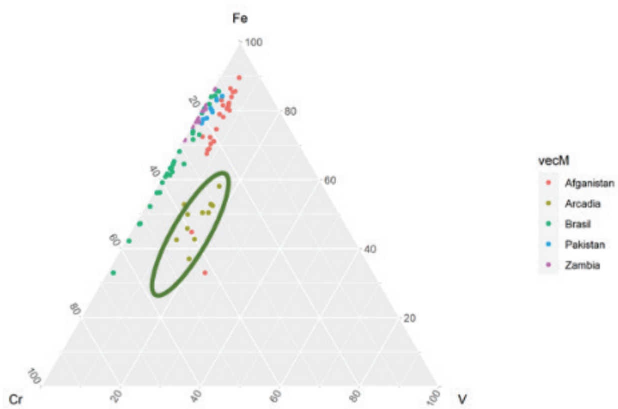
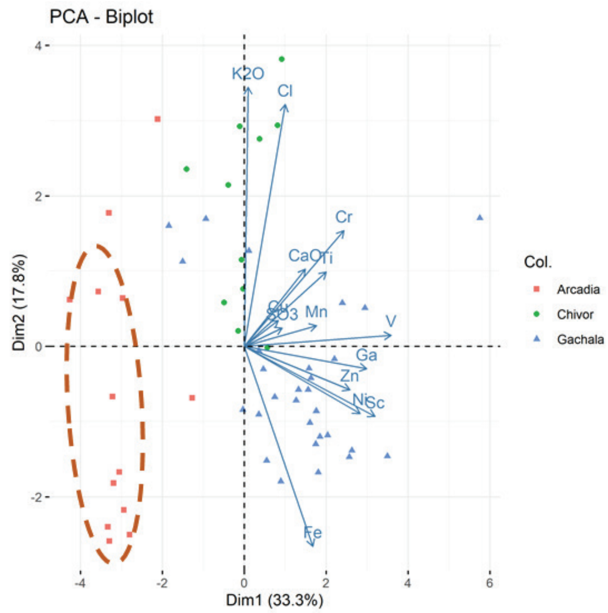


Figure 3. PCA results. **A**. Biplot of individuals from La Arcadia (Colombia), Afghanistan, Brazil, Pakistan and Zambia. **B.** Ternary plot considering Fe, Cr and V of individuals from La Arcadia (Colombia), Afghanistan, Brazil, Pakistan and Zambia

PCA results for the Arcadia and eastern belt samples (Fig. 4) shows that emeralds from the eastern belt have considerably higher contents of the elements studied. Samples from Chivor district have higher concentrations of Cl and K, and emeralds from Gachalá can be distinguished in most cases because they have higher content of Fe, Ni, Ga and Cr. The ternary plot shows a higher content of V in the Gachalá specimens, whereas examples from Arcadia and Chivor have similar V contents even though they can be differentiated by their Cr- Fe contents. Arcadia forms a group with higher Fe content whereas the Chivor group features greater Cr content.



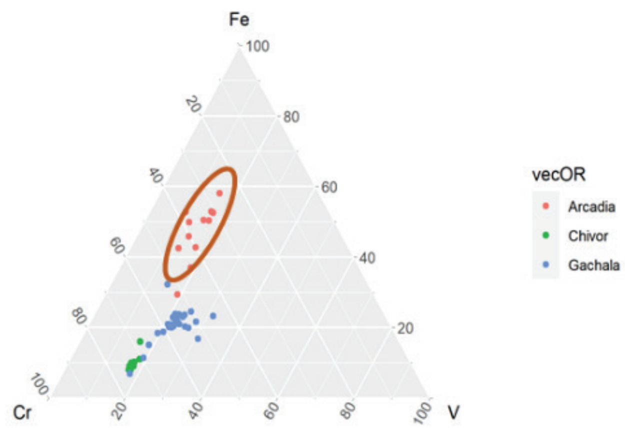


Figure 4. PCA results. **A**. Biplot of individuals from La Arcadia (Western belt), Chivor and Gachalá district (eastern belt). **B**. Ternary plot considering Fe, Cr and V of individuals from La Arcadia (Western belt), Chivor and Gachalá (eastern belt).

Based on the PCA results, the Arcadia emeralds are distinguished from the rest of the western belt by their lower content of Ga, Mn and Cl. On the other hand, La Pita has the greater Cl content. In the case of Peñas Blancas, the ratio of Cr to V is near 1:1. The ternary plot shows that the concentration of V is the lowest in Arcadia, thus making a differentiation among this district and the other districts of the western belt possible (Fig. 5).

From the PCA biplot, it is evident that is impossible to discriminate emeralds from Arcadia from emeralds from mines in the same district (Fig. 6), even though the Arcadia specimens have the lowest content of Ga. In the ternary plot, it is notable that Arcadia emeralds contain the least V and the Cr/Fe ratio is near 1:1. Samples from Futuro, Tunel 5 and Retorno are the most similar to Arcadia individuals.

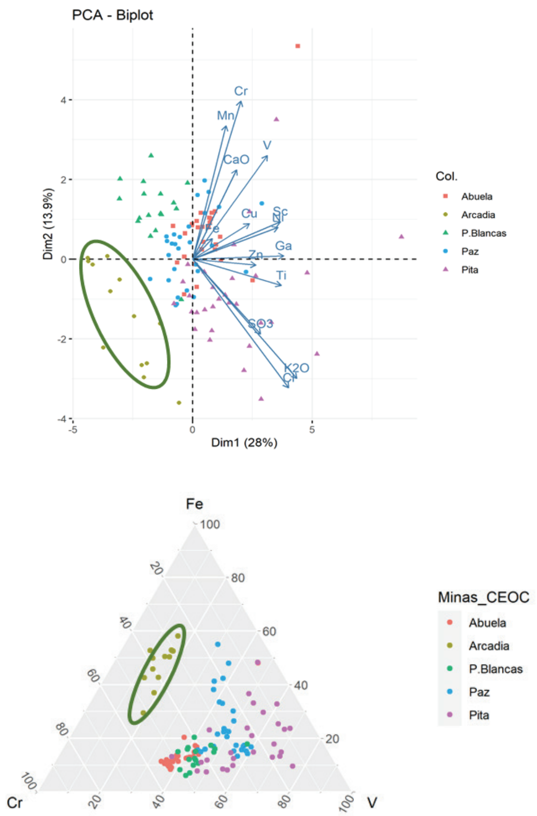


Figure 5. PCA results. **A.** Biplot of individuals from La Arcadia (Muzo district), La Abuela (Coscuez district), Peñas Blancas (Peñas Blancas district), La Paz (Coscuez district), La Pita (Maripì district). **B.** Ternary plot considering Fe, Cr and V of individuals from La Arcadia (Muzo district), La Abuela (Coscuez district), Peñas Blancas (Peñas Blancas district), La Paz (Coscuez district), La Pita (Maripì district).

5 Conclusions

Our petrographic analysis showed that the mineralization in La Arcadia mine is associated with a level of black siltstone albitized as a result of alteration by hydrothermal fluids. Emeralds are found in veins and breccias compositionally dominated by a third mineralization stage predominantly composed of dolomite, mica and previous albite.

The uniqueness of Colombian emeralds is linked to their genesis, normally the content of V is even higher than the emeralds associated with a mafic genesis, besides emeralds from other deposits contain a higher content of elements from mafic/ultramafic rocks as Sc and Cr. Another feature to be highlighted is the lowest content of Ga in La Arcadia, actually the Al substitution is low and thus the concentration of elements that substitute for Al is low too.

La Arcadia emeralds are distinguishable by lower V contents than in districts from the eastern belt. The content of chromophores is relatively low in La Arcadia emeralds in comparison with the rest of the western belt districts. However, it cannot be differentiated from those from other mines in the Muzo district. La Arcadia, Retorno, Tunel 5 and Futuro mines are geographically close and share similarities in chemical composition. due to similar genesis.

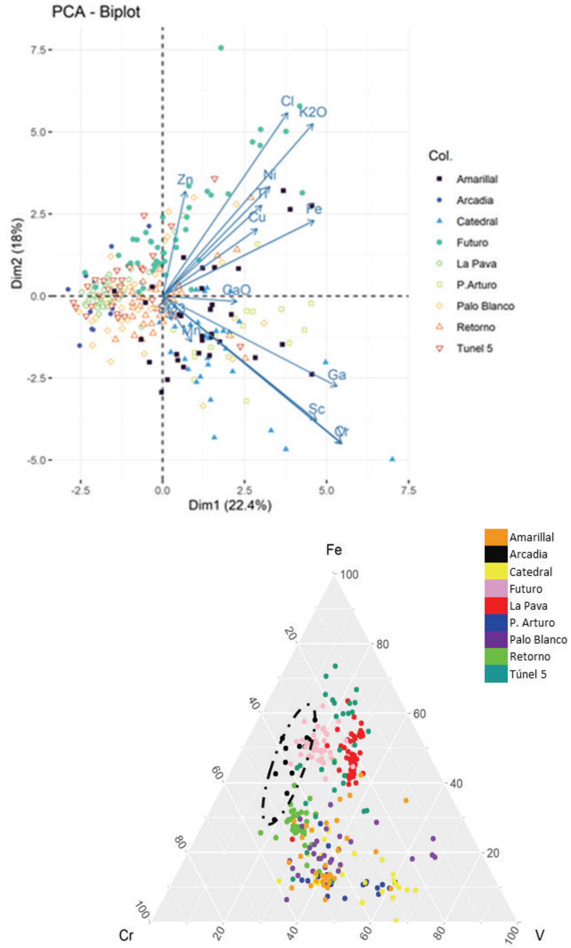


Figure 6. PCA results. **A.** Biplot of individuals from Muzo district: La Arcadia, Amarillal, Catedral, Futuro, La Pava, Puerto Arturo, Palo Blanco, Retorno and Tunel 5 **B.** Ternary plot considering Fe, Cr and V of individuals from Muzo district: La Arcadia, Amarillal, Catedral, Futuro, La Pava, Puerto Arturo, Palo Blanco, Retorno and Tunel 5.

Acknowledgements

This study was supported by the National Emerald Federation (FEDESMERALDAS), the association of Colombian Emerald Producers (APRECOL), the Colombian association of trade in emeralds (ASOCOESMERAL), Colombian Association of Emerald Exporters (ACODES) and the Ministry of Mines and Energy.

References

Branquet Y, Laumonier B, Cheilletz A, Giuliani G (1999) Emeralds in the Eastern Cordillera of Colombia: Two tectonic settings for one mineralization. Geology 27:597–600.

Esmeralda (2021). Un planeta en crisis. (2422-0906), p 14

Pignatelli I, Giuliani G, Ohnenstetter D, Agrosi G, Mathieu S, Morlot C, Branquet Y (2015) Colombian trapiche emeralds: Recent advances in understanding their formation. Gems & Gemology 51:222–259.

Reyes G, Montoya D, Terraza R, Fuquen J, Mayorga M, Gaona T (2006) Geología del Cinturón Esmeraldífero Occidental Planchas 169, 170, 189 y 190. Ministerio De Minas Y Energía Instituto Colombiano De Geología Y Mineria Ingeominas.