

Chromium and vanadium from host rock to emerald: tracing differences between the two main emerald zones in Colombia and their gemological implication

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Abstract. We have analyzed 1321 samples of emerald, euclase, carbonates, micas and host rocks from the Western and Eastern emerald belts in Colombia: 738 from the Western emerald belt (WEB); and 583 from the Eastern emerald belt (EEB). Results enable trends in chemical composition to be identified, and the pathways followed by key elements in emerald formation to be identified. Colombian emeralds are distinguished chemically by lower concentration of iron. The Cr/V ratio in EEB emeralds is 3:1, it is 1:1 in WEB. This contrasts with host rock compositions where the Cr;V ratio is near 1:1 in both belts. Nevertheless, next to emerald there are several minerals able to catch the elements leached from the host rock and that could be a key role in the characteristic emerald's chromophores concentration from both zones and it could generate into different hues in emeralds.

1 Introduction

Emerald is a gem variety of beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$. The color of emeralds is due to the content of trace elements such as chromium (Cr), vanadium (V) and iron (Fe) (Schwarz and Schmetzer 2002). Colombian emeralds can be distinguished by their relation of Cr /V and their low concentration of Fe (Cedeño et al. 2015). The two zones are recognized worldwide for the quality and beauty of their emeralds.

The presence of other minerals coexisting with emeralds, including carbonates, micas and euclase [$\text{BeAlSiO}_4(\text{OH})$], can incorporate the same trace elements. This can influence the characteristic ratio of the chromophore elements that provide the color to the emeralds in each zone. In consequence emeralds from the both zones display differences in color, WEB emeralds have a yellow-green hue, whereas EEB's emeralds have a blue-green hue (Fig 1). The purpose of this work is therefore to provide mineral chemistry data that can be used to identify the possible pathways taken by these two key elements (Cr and V) in the formation of emeralds from their host rocks to the mineralization and suggest exploration geochemical indicators.



Figure 1 A. Emerald samples from the EEB B. Emerald specimens from the WEB.

2 Geological setting

Colombian emerald deposits are sediment-hosted and occur within two parallel, elongated belts along the NE trending Eastern Cordillera. The belts share similar features and the deposits are located in both flanks of the Cordillera, these are called the Eastern and Western Emerald Belts (Fig. 2).

The most striking differences between the two belts are the compositions of the host rocks, their age, and the tectonic settings of the mineralization. In the EEB, the emerald-bearing veins are hosted in a stratiform brecciated level predominantly composed of gray albitites. Mineralization took place at 65-67 Ma. and it was controlled by an extensional structural style. In contrast, mineralized veins and breccias in the western belt are hosted by organic-rich black shales and were emplaced in a compressional tectonic regime. There is, however, no agreement on the age of mineralization. Published ages are between 12 to 67 Ma. (Cheilletz et al. 1994; Mantilla et al. 2008; Romero et al. 2000).

The host-rocks leached and released elements like beryllium, chromium, vanadium, all essential for emerald formation. Emeralds are formed in hydrothermal breccias and veins displaying strong alteration (albitized and

carbonatized) composed of calcite-dolomite, albite and pyrite.

The circulation and mixing of basinal fluids with evolved evaporitic brines generated thermochemical reactions that are controlled by the organic-rich host rocks. These processes lead to the release of the essential chemical components for emerald formation (Giuliani et al. 1993-1995; Ottaway et al. 1994). In consequence, the mineralization of the Colombian emeralds is linked to a particular paragenetic sequence with four stages in the following order: the pre-mineral stage compresses the alteration of the host rock, the first one is the albitization(albite, micas, fibrous calcite, among others), the second is the carbonatization (rhombohedral calcite, dolomite, micas and sulfides) this stage is related to the emerald crystallization and the third one includes posterior mineralization (euclase, baryte, posterior calcite, gypsum, pyrophyllite, fluor-apatite and supergene minerals).

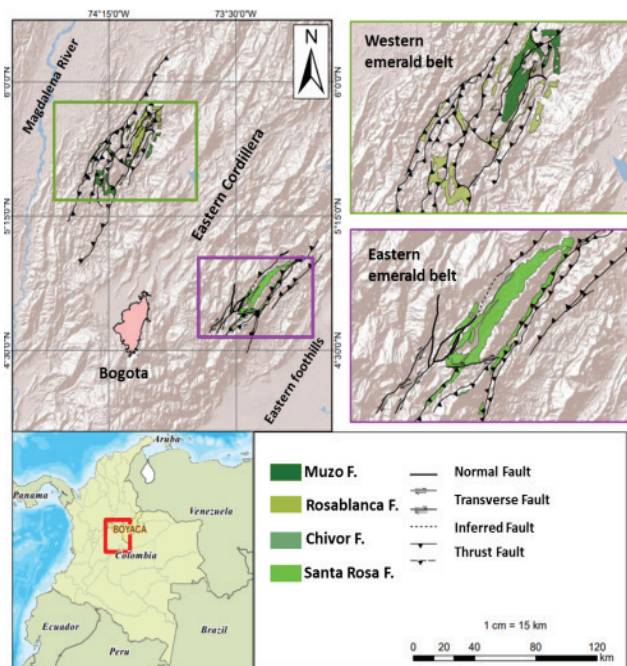


Figure 2 Location of the two emerald belts (EEB and WEB) in the Colombian Cordillera

3 Material and methods

In this study, 1321 samples from the two belts were analyzed, 530 of which correspond to emeralds, 177 euclases, 65 samples of the host rock, 177 carbonates, and 372 micas. Chemical data for the host rocks were determined using Energy-dispersive X-ray fluorescence analysis (XRF) with a PANalytical - EPSILON 5 at CDTEC. Data were processed with Epsilon 5 Software.

Emerald analyses were performed by LA-ICP-MS at CODES (University of Tasmania). Electron probe microanalysis of micas, euclases, and carbonates was undertaken using a JEOL JXA-8230 super probe with

three WDS spectrometers at the National University of Colombia.

4 Results

Host rock samples were divided into two groups based on their spatial relationship with emerald mineralization. The first group is made up of host rock samples far from mineralization in which it is presumed that no alteration has occurred, the second group of rocks occurs beside the mineralization. Besides, data of different minerals; average concentration of mica from the first and the second stage, carbonates from the second stage, emerald, and euclase from a late stage are presented here (Table 1). In addition, dispersive graphics of the relation of Cr/V were made. (Fig. 3)

Table 1. Average concentration of the chromophores elements in different materials in each belt.

	WEB		EEB	
	Cr ppm	V ppm	Cr ppm	V ppm
Host-Rock	90	278	164	327
Altered Host-Rock	55	153	79	128
Mica	3202	9873	930	2756
Carbonates	44	327	80	282
Emerald	760	1320	4464	1866
Euclase	1326	514	249	267

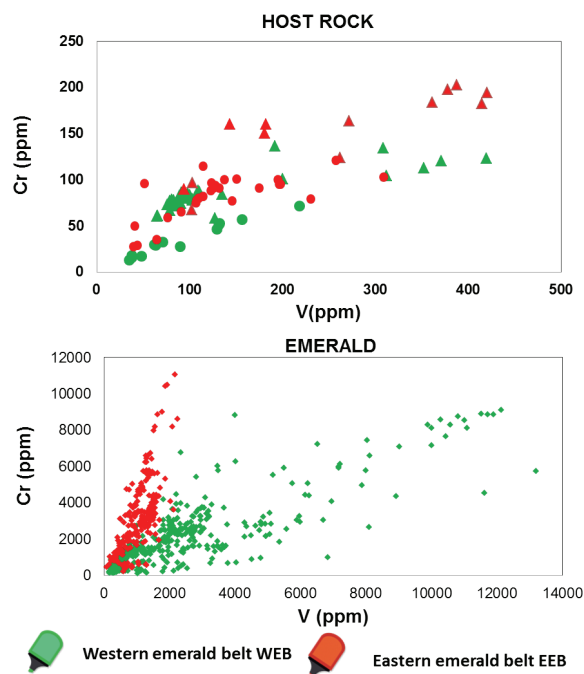


Figure 3 A. Concentration of chromium and vanadium element in the host-rock(altered-circle, not altered-triangle). **B.** Concentration of chromium and vanadium in the analyzed emerald specimens.

4 Discussion

The unaltered host-rock has presented high Cr and V concentration values that highlight respecting the average for crustal shales (Wedepohl 1991). Regarding the altered rock, the concentration of Cr and V decrease owe to the leaching processes mobilizing heavy elements.

Mica is the mineral with the highest capacity to trap chromophores, especially vanadium. The concentration of chromophores differs according to the stage. In the case of the WEB, the first stage has a Cr:V ratio of 1:4, and for the second stage, this ratio is 1,25:1. In the EEB in the first stage the ratio of Cr:V is 1:5, and in the second stage (in paragenesis with emerald) the Cr:V ratio is 1:2(Fig 3a). Hence, the fluid suffered geochemical changes due to the micas mineralization consumed a high quantity of V in the first stage (both belts), thus the fluid increase its saturation in chromium for the second stage, decreasing the ratio in EEB and equalizing the ratio in the WEB.

Emeralds from the EEB trap a major quantity of chromophores in comparison to the WEB. EEB emeralds have a higher concentration of Cr than V, the ratio in some cases reaches up to 3:1. Emeralds of WEB have a ratio close to 1:1, or in some cases, the V concentration is higher.

Carbonates present random values of concentration that do not permit finding a trend between the chromophores and their behavior in the mineralization (Fig 3b).

Euclase corresponds to the late stage, also contains concentrations of Cr and V. In contrast to emerald, EEB euclases have Cr:V ratios of 1:1, and in the WEB, the ratio can be 1:3, the concentration of vanadium tend to be higher, commonly up to 2000 ppm. (Fig. 4).

The mineralizing fluid undergoes changes as it evolves through the different stages of mineralization: first, it captures the chromophores elements from the host rock, mobilizing them to a first stage in which they are trapped (especially vanadium) by minerals such as mica, thus leaving a fluid with less vanadium content, which is reflected in the micas of the second stage and in the emeralds (mainly in the EEB). Finally, in the later stage, the Cr and V concentrations in euclase are equalized in the EEB, whereas in the case of WEB the Cr: V ratio is 2:1 due to vanadium could be trapped by phyllosilicate minerals as pyrophyllite in later stages.

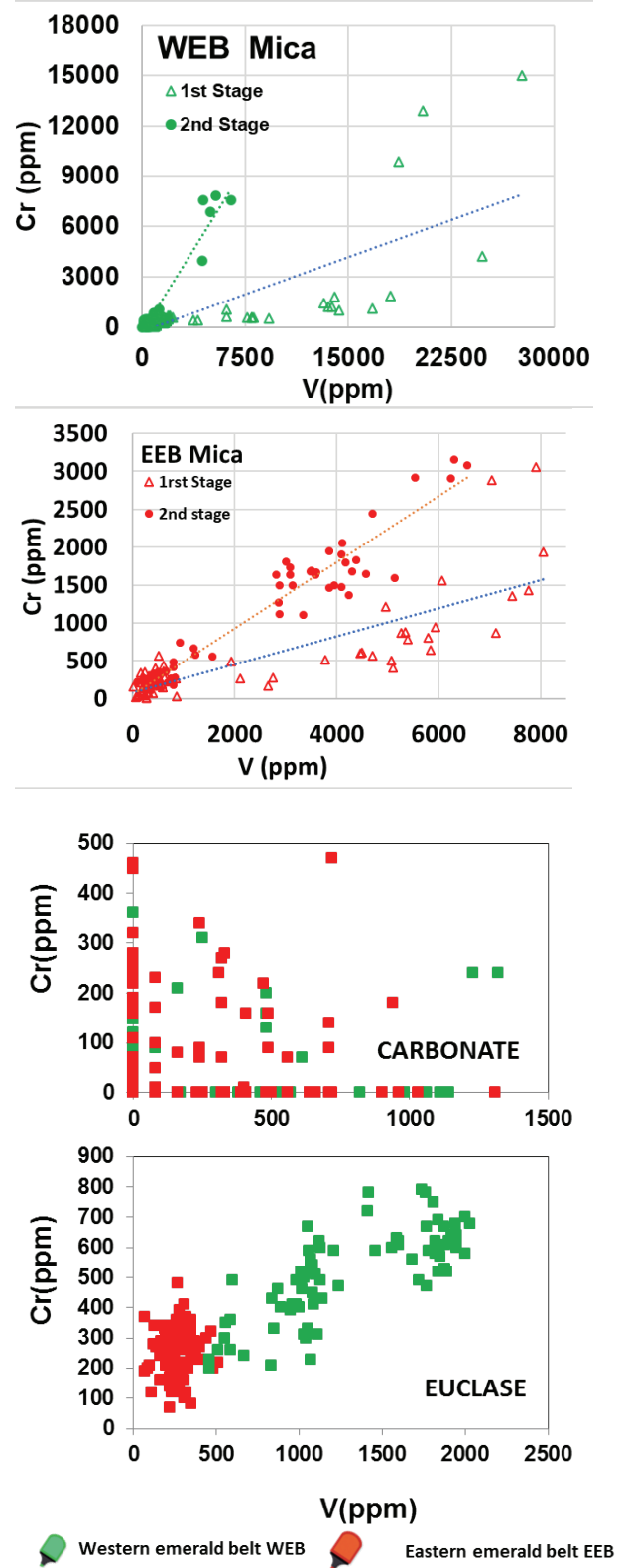


Figure 4 A,B. Concentration of chromium and vanadium in micas. C. concentration of chromium and vanadium in carbonates D. concentration of chromium and vanadium in euclases

5 Conclusions

The geochemical study of micas shows that it could be an indicator mineral in exploration to identify the emerald-bearing veins, thus the micas from the second stage have a particular fingerprint owe to the chromophores relation near to 1:1 in the WEB and 1:2 (Cr: V) in the EEB.

Negative Cr and V anomalies in the host-rock evidence a relation with the presence of mineralized zones, hence a lateral geochemical study of the rock is suggested, as it could delimit possible host zones for mineralization.

The famous and exotic colors of Colombian emeralds; the yellowish-green emeralds from the WEB, and the blueish-green emeralds from the EEB are linked to the relation of the chromophores Cr:V.

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