Current Research in Geology Applied to Ore Deposits. Fenoll Hack-Ali, Torres-Ruiz & Gervilla(eds)(1993). ISBN 84-338-1772-8 2nd Biennal SGA Meeting, Gramada, Spain, September 9-11, 1273 GEOCHEMISTRY AND ORIGIN OF THE EMERALD DEPOSITS OF COLOMBIA

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Abstract. The emerald deposits of Colombia are related to huge hydrothermal fluid infiltration vein networks which develop an intense sodium and carbonate metasomatic halo within the enclosing black shales. Leaching of major (K,Al, Si,Ti,Mg,P), trace (Ba,Be,Cr,Rb, Sc,U,V,B,C) and REE elements from black shales is accompanied by their partial redistribution as in-filling vein-system minerals. Oxygen isotope geochemistry of the hydrothermal carbonates and quartz indicates a strong enrichment in δ^{18} O of the waters in equilibrium with the mineralization (+10 $<\delta^{18}$ O H2O< +18‰), which correspond to metamorphic or basinal formation waters. The proposed model of emerald genesis involves a local sedimentary origin for beryllium and a metamorphic origin for the fluids.

INTRODUCTION

The emerald mineralization of Colombia consists of carbonate-pyrite breccia, veins, veinlets and pockets which are hosted by Lower Cretaceous black shales (BS). The ore formation is complex and involves a multiple stage process by the way of moderate temperature (300°c) fluid transfers through the sedimentary pile at 32-38 Ma (Cheilletz et al., 1993) without magmatic manifestation. The origin of the mineralizing fluids and the source of beryllium has been long time debated. A strong convergence appears concerning the removal of beryllium from the hosting-BS (Beus, 1979; Kozlowski et al., 1988; Giuliani et al., 1990a; Ottaway and Wicks, 1991) but not yet proved. The purpose of this paper is to add new geological and geochemical

The purpose of this paper is to add new geological and geochemical constraints to the emerald-forming process, particularly concerning the behaviour of major, trace and rare earth elements (REE) during fluid-rock interactions and to discuss the probable origin of the hydrothermal fluids through O-isotope geochemistry of gangue minerals as quartz and carbonates.

GEOLOGICAL SETTING

The Colombian emerald deposits are located within two narrow belts of the eastern Cordillera Lower Cretaceous sedimentary formations. The eastern belt includes the mining districts of Gachalá and Chivor, and the western belt, the districts of Coscuez, Muzo and La Palma-Yacopí. The mineralization is hosted by breccias, shear faults and tension gashes with hydrofracturing (Giuliani et 1., 1990b) acting as a major process of the fracture-system development. The ydrothermal fluid circulation is accompanied by an intense fluid-rock interaction and metasomatic alterations of the enclosing BS (Baker, 1975; Beus, 1979; Giuliani et al., 1990b) consisting in carbonatization, albitization and pyritisation halos developed around the emerald-bearing carbonate vein network. The carbonate and pyrite infilling of the vein system has been divided into three successive stages: (I) white fibrous calcite with cubic pyrite, albite and green micas, (II) rhomboedral-white to grey calcite or dolomite with cubic or dodecaedric pyrite, albite and quartz, (III) REE-dolomite, pyritohedral or dodocaedral pyrite, quartz, fluorite, parisite (in Muzo district). Stage III represents the main productive emerald period.

NEW GEOCHEMICAL DATA

Microscopic and X-Ray diffraction studies reveal that the BS around the neralized zones have undergone strong carbonatization and albitization. The .bitized BS (Ab BS) are composed mainly by albite (45 to 92% of the rock), micas (up to 20%), quartz (up to 19%) and pyrite (up to 10%). The calcitized BS (Ab-Ca BS) are composed by calcite and/or dolomite (5 to 55%), albite (25 to 45%), quartz (5 to 48%) and pyrite (up to 10%). The spatial relationships between Ab BS (albitites) and Ab-Ca BS is unknown, however, the stage of carbonatization appears evidently well developed around the carbonated breccia and vein systems.

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Figure 1-a: Al	./3-K versus	Al/3-Na diagram;
-b: Beryllium	versus Na/Al	diagram for the
deposits of	Chivor, El	Toro, Quipama,
Tequendama, La	Pava and Yac	opi.

Representative rock-types of several deposits from the different mining districts were chemically analyzed by ICP spectrography at the CRPG (Vandoeuvre). The diagram Al/3-K versus Al/3-Na (Fig.1a) underlines the albitization and carbonatization trends of the BS. Breccia lies on the albitecarbonate joint confirming that albite is still precipitating with carbonates during the main ore-forming process. A geochemical major and trace elements profile realized through the mining gallery from El Toro (Gachalà district, Fig.2) shows that albitization is well developed in the immediate outer zone

■ BS

X "Kaolin"

Ab-Ca BS

• Ab BS

A B-AbBS

* B-BS - B- Kaolin



Figure 2. Major and trace elements behaviour of a mining gallery from El Toro mines (eastern emerald belt).

Sketch Map of El Toro horizontal mining gallery

(G4) of an emerald-free calcite vein (G6). In G4 zone, the increase in Na is acompanied by decreases of K, Al, Ti, Si, Mg and P from the BS (density BS= 2.45; ds Na-Ca BS= 2.44); G5 shows an increase of Ca and Mg relatively to G4. Comparison of trace elements distribution in the BS and within G4 and G5 zones (Fig 2), evidences an intense leaching of almost all trace elements from the BS with huge depletion in Ba,Be,Cr,Rb,Sc,U,V,B,Th and organic carbon. These observations can be generalized to the other emerald deposits (Giuliani et al., 1990a) with particular emphasis of the progressive leaching of Be at the same time as the BS metasomatic albitization (Fig.1b).

The REE behaviour during the fluid-rock interactions and the development of the metasomatic alteration halos has been particularly emphasized. The shape of the REE patterns of the Ab-Ca and Ab BS looks like those of BS. However, they are depleted in light REE (LREE), especially Ce and Nd. The REE patterns of the vein-filling minerals show (Fig.3): (1) calcite from stage II is LREE



Figure 3. REE patterns of veinfilling minerals associated to the stage III of a emerald-bearing carbonate vein from Quipama mine (Cincho workings, Muzo District).

depleted relative to the BS. This behaviour is typical of calcite and dolomite from stages I and II of the whole deposits. It indicates that the solutions must have been initially LREE depleted, considering that fractionation of REE between calcite and brine is low (Graf, 1988); (2) the parisite deposition in the coeval association of parisite, fluorite, dolomite and emerald (stage III), provokes the depletion of \sum REE and LREE in the fluid. In consequence, emerald and fluorite have the same Eu anomaly as parisite (Eu/Eu*= 0.30) but are both LREE depleted. Besides, fluorite is HREE enriched meanwhile emerald shows exactly the opposite pattern. Dolomite and emerald present, excepted for the Eu anomaly (Eu/Eu*dolomite= 0.65) and their total REE concentrations, the same pattern, especially concerning the LREE.

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Oxygen isotope studies of quartz and carbonates associated with emerald from Cincho, Coscuez, Yacopí, Tequendama and Chivor mines were realized at the CRPG (Giuliani et al., 1992). The data show a strong enrichment in 1^8 O (Fig.4).



Figure 4. δ^{18} O data of the carbonates and quartz from the studied deposits. The δ^{18} O data in equilibrium with quartz and calcite are calculated at ^250, 270 and 300°C. a: Fractionation factors of Bottinga and Javoy (1973), b: fractionation factor of Clayton and Mayeda (1972) applied to all the others quartz. 1= calcite stage I; 2= calcite stage II The δ^{18} O from the different types of carbonates varies over a range of 2.2‰ for the all of the samples and appears more variable for quartz (4‰). The waters in equilibrium with the mineralization are generally enriched in 18 O (+10‰ < δ^{18} O < +18‰) for a temperature of formation estimated at 300°C. The calculated δ^{18} O H₂O for the different deposits yield values of metamorphic waters or basinal formation waters. In contrast, the δ^{18} O H₂O are higher than the values measured in such waters (T<150°C) and imply that the δ^{18} O is controlled by the lowtemperature sedimentary origin of the metasediments. Following these results, the origin of the fluids can be considered as metamorphic. Stor. L.

CONCLUSIONS

The emerald deposits of Colombia are characterized by a strong fluid-rock interaction process leading to sodium and carbonate metasomatism of enclosing BS which conversely are leached in major, trace and REE elements, redeposited as in-filling vein minerals. The depletion in Al,Si,Be,Cr and V particularly evidences a wall-rock BS source for these elements recovered within the crystallochemical structure of emerald in the vein system. Therefore, a model based on a local sedimentary origin for Be can be proposed for the genesis of emerald. The origin of the hydrothermal fluids responsible of cationic transfers has been approached by oxygen isotopic measurements. The calculated δ^{18} O H₂O for carbonates and quartz indicate values of metamorphic or basinal formation waters. Considering the 300°C temperature of emerald formation, these fluids are considered to be of metamorphic origin with high δ^{18} O values being controlled by the low temperature sedimentary origin of the metasediments.

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