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AGE AND SULPHUR ISOTOPE SIGNATURES OF BRAZILIAN AND COLOMBIAN EMERALDS

G. Giuliani [1-2], A. Cheilletz [1-3], G. Féraud [4], J-L. Zimmerman [1], V. Carillo [5], F. Rueda [5], J. Baker [6] and R. Montigny [7]

Introduction

In south America, emeralds are found only in Brazil and Colombia (Fig.1) which are amongst the firsts in the world in emerald quality and production. This last proceeds from two contrasted emerald vein type deposits, currently quoted[1,2] in the classification for emerald deposits. In Brazil, emeralds are hosted by greenstone terranes mostly in highly metamorphosed cratonic areas[3,4]. The mineralization belongs to the biotite-schist beryl type where the sources of beryllium, chromium and vanadium necessary to form the green variety of beryl are likely found in juxtaposed pegmatites and metamorphic-mafic rocks[5,6]. However, neither pegmatites nor ultramafic rocks are found in the vicinities of Colombian deposits: emerald is hosted by carbonate veins located within black shales of the Cretaceous-Eocene basin of the Eastern Cordillera[7,8].
Today, an hydrothermal model is proposed for the genesis of Brazilian and Colombian emeralds [4,9,10]. However, the age of formation of these deposits is unknown and controversies still exist concerning the origin of the mineralizing fluids: a magmatic versus metamorphic versus sedimentary source is always debated.
In this paper, we present the first ages of two major Brazilian and Colombian emerald deposits, and the results of sulphur isotopic investigation on sulphides coeval to emerald precipitation with the aim to identify the possible sources of sulphur.

1 - Centre de Recherches Pétrographiques et Géochimiques, UPRA CNRS 6821, BP. 20, 54501 Vandoeuvre-lès-Nancy Cedex, France.
2 - ORSTOM, Département TOA UR1H, 213 rue La Fayette, 75480 Paris cedex 10, France.
3 - Ecole Nationale Supérieure de Géologie, BP. 452, 54001 Nancy cedex, France.
4 - Institut de Géodynamique, URA CNRS 1279, Université de Nice, Parc Valrose, 06034 Nice cedex, France.
5 - MINERALCO S.A., calle 32, n° 1307, Bogotá, Colombia.
6 - Geologisch Institut, Nieuve Prinsengracht 130, 1018 VZ, Amsterdam, the Nederlands.
7 - E.O.G.P.S., 5 rue Descartes, 67084 Strasbourg, France.

Figure 1 : Map of South America showing the location of the eastern and western emerald zones of Colombia and the main emerald deposits of Brazil (solid circle).

Geological setting

The Carnaíba and Socotó emerald deposits (Brazil)

These two deposits are located in the Bahia State at the proximity of the Transamazonian (2.0 Ga) Carnaíba and Campo Formoso granites[11], respectively. The mineralization is developed at the expense of Early Proterozoic metamorphosed utramafic rocks and juxtaposed pegmatite intrusives. Both pegmatite and serpentinite were pervaded by metasomatic fluids[4,6], inducing the formation of plagioclasite (rock derived from the metasomatism of pegmatite and composed mainly by plagioclase) and phlogopitite (rock derived from the serpentinite and composed mainly of phlogopite), respectively. These metasomatic rocks display a clear zoning from the central pegmatite intrusive to the enclosing serpentinite, forming a metasomatic column (see Fig.3). Emerald is found either within plagioclasite or within phlogopitite in which spinel (chromite) has disappeared during the metasomatic leaching of the rocks .

Two stages of mineralization are evidenced in the deposits[12]: the first corresponds to the formation of the emerald-bearing phlogopitite with the precipitation of emerald, molybdenite, scheelite and apatite; the second, is characterized by the formation of molybdenite-muscovite-bearing quartz veins which crosscut the first stage.

The Colombian emerald deposits

They define two emerald-bearing zones situated along two major polyphased thrust limits of the Eastern Cordillera which correspond to the original borders of the Cretaceous-Eocene basin[13]. The deposits are located within the Lower Cretaceous black shales series. The mineralization is hosted within breccias, networks of extension fractures and pockets related to hydrofacturing[9]. The hydrothermal circulations induced albitization, carbonatization and pyritization halos developed around the mineralized structures[14]. Emerald occurs within calcite-dolomite-pyrite veins.

K-Ar $^{40}Ar/^{39}Ar$ and dating

Age of Carnaíba and Socotó emerald deposits

K-Ar and $^{40}Ar/^{39}Ar$ measurements were performed on biotites and deuteric muscovites from the Carnaíba and Campo Formoso granites[15]. For the Carnaíba granite, biotites and muscovites provide isochrons with age of 1888 ± 32 and 1979 ± 28 Ma (2σ), respectively. For the campo Formoso granite, the biotites yield ages between 1875 ± 45 Ma and 1908 ± 47 Ma (2σ) and the muscovites yield ages of 1897 ± 34 Ma and 2040 ± 24 Ma (2σ). In contrast, phlogopites from emerald-bearing phlogopitites display K-Ar ages that spread between 1900 and 2000 Ma with an isochron of 1973 ± 20 Ma (2σ) for Carnaíba. Generally, the youngest biotite and phlogopite ages occur for chloritized samples. Since in Carnaíba, deuteric muscovites and chlorite - free phlogopites give similar K-Ar ages, 1979 ± 28 Ma and 1973 ± 20 Ma (2σ) respectively, we conclude that emerald mineralization is contemporaneous with the pervasive muscovitization of the granite. Bulk samples and individual grains from the phlogopitites of Carnaíba were dated[16] by $^{40}Ar/^{39}Ar$ as well as syngenetic solid inclusions trapped along growing zones of the emerald host crystal. In spite of the huge amount of excess ^{40}Ar detected in adjacent emerald, ages of 1951 ± 8 Ma and 1934 ± 8 Ma (1σ) were determined for the Trecho Velho and Braúlia emerald pits. A muscovite from the second stage of mineralization gave a plateau age of 1976 ± 8 Ma (1σ), which may correspond to a higher closure temperature of the K-Ar system during the cooling of the whole pluton and associated hydrothermal halo.

Age of Colombian emerald deposits.

Two emerald deposits from the western emerald zone (Fig.1), the Coscuez and Quipama-Muzo mines, have been dated by $^{40}Ar/^{39}Ar$ induction and laser microprobe methods on contemporaneous greenish Cr-V-bearing K-mica aggregates[17,18]. It consists of muscovite as a dominant phase ± kaolinite, ± paragonite, ± quartz, ± albite, and ± chlorite, pyrite and calcite. Contamination of the K-mica aggregates by wall-rock impurities was eliminated by in situ $^{40}Ar/^{39}Ar$ laser spot analysis.

Two distinct plateaus and spot fusion ages of 35 to 38 Ma and 31.5 to 32.6 Ma (Fig.2) were obtained for the Coscuez and Quipama samples,

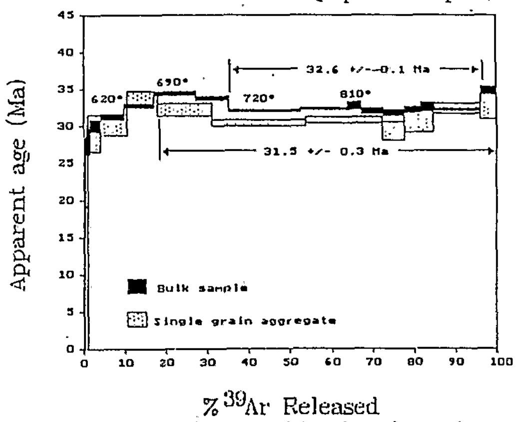

Figure 2: Induction (bulk sample) and continuous laser microprobe step heating (single grain aggregate) ages for the Quipama-Muzo muscovite.

respectively. These results give an unambiguous late Eocene to lower Oligocene age for the muscovite synchronous with emerald deposition. Concordant conventional K-Ar ages show that in spite of the small size of micas (< 0.5 mm), they did not suffer significant ^{39}Ar loss due to recoil during irradiation of the samples. Internal ^{39}Ar recoil may explain the slight disturbances observed on the age spectra.

Sulphur isotope data

Carnaíba and Socotó molybdenites

The $\delta^{34}S$ values of molybdenites related to quartz vein, plagioclasite, phlogopitite and metasomatized pegmatite are comprised between 2.95 to 3.53‰ (Fig.3). Molybdenites precipitate during the percolation of hydrothermal fluids

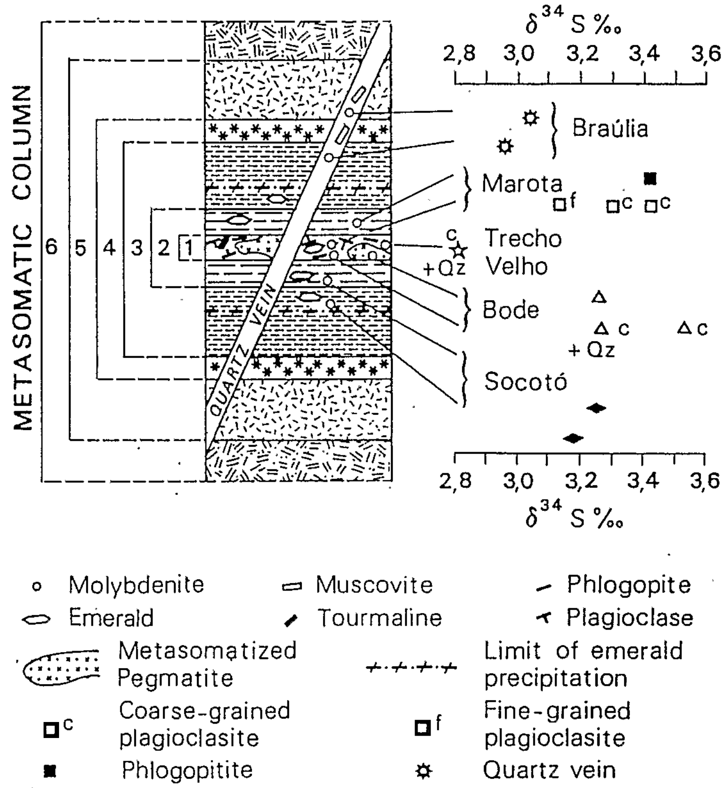

Figure 3 : Spatial relationship between emerald-molybdenite-bearing phlogopitites (metasomatic column of the first stage of mineralization) and molybdenite-bearing quartz veins (second stage of mineralization), and the corresponding $\delta^{34}S$ values (‰) of molybdenites from the Carnaíba and Socotó emerald deposits. The metasomatic column is composed by six zones which are from the central pegmatite vein to the hosting serpentinite rock: zone 1: pegmatite transformed into plagioclasite (albite, andesine in composition) with disseminated phlogopite and sometimes emerald and quartz; zone 2, corresponding to a coarse-grained phlogopitite with phlogopite, apatite, emerald and quartz; zone 3, composed by a fine-grained phlogopitite with an inner subzone where apatite and emerald precipitated, and an outer subzone with only spinel and phlogopite. In zone 3, the disappearance of emerald corresponds to the presence of spinel (chromite) within phlogopitite; zone 4, formed by an assemblage of phlogopite, spinel, and amphibole; zone 5, is composed by phlogopite, spinel, amphibole and talc; zone 6, representing the serpentinite which is composed of spinel, amphibole, talc, serpentine and chlorite.
Braúlia, Marota, Trecho Velho and Bode correspond to different prospecting pits of Carnaíba.

within both pegmatite and serpentinite. Sulphur can (1) result from leaching of previous sulphides of the pegmatite or, (2) be carried by the hydrothermal fluid. $\delta^{34}S$ of the different types of molybdenite are constant, indicating that the oxidation of the hydrothermal solution remained below the SO_2/H_2 boundary or constant. $\delta^{34}S$ melt of uncontaminated granitic magmas[19] are likely to be between - 3 and 3 ‰, and the resulting fluids with a $\delta^{34}S$ in the range of -3 ‰ to 7 ‰. The $\delta^{34}S$ values of molybdenites are within this suggested range, and a magmatic origin can be proposed either following hypothesis (1) or (2). The contamination of external wall-rock sulphur is avoided and the slight decrease in $\delta^{34}S$ for mobybdenites from phlogopitites to quartz-veins (deviation of 0.7 ‰) can be related to more acidic conditions (fluctuation of pH) prevailing during the precipitation of molybdenite in the quartz veins.

Colombian pyrites

The calculated $\delta^{34}S$ values of H_2S in solution in equilibrium with hydrothermal pyrite for a temperature of formation of 300°C, from six emerald deposits, range from 14.8 to 19.4 ‰ whereas sedimentary pyrite from the enclosing black shales yield a $\delta^{34}S$ of -2.4 ‰. The narrow range in $\delta^{34}S$ H_2S between the different deposits suggests, (1) an uniform and probably unique source for the sulphide sulphur, (2) the non participation of magmatic or sedimentary sulphur. Evaporitic sulphates are a likely source for heavy sulphur and the calculated $\delta^{34}S$ H_2S overlap the expected $\delta^{34}S$ range of Jurassic and Lower Cretaceous sulphates[20].
Fluid inclusions[18,21], oxygen[22], carbon[22] and sulphur isotopes[20] data give a typical evaporitic sedimentary signature for the mineralizing fluid and in consequence, promote a hydrothermal sedimentary model for Colombian emerald mineralization[18,22,23,24].

CONCLUSIONS

Brazilian and Colombian emeralds define two contrasted type of deposits which differ by their geological setting, tectonics, paragenesis and geochemistry.
Two distinct upper Eocene to lower Oligocene ages have been determined for the Colombian emerald deposits of Coscuez and Quipama-Muzo. These ages correspond to a strong shortening episode starting during the Eocene which is related to an acceleration of the convergence rate between the Nazca and South American plates. Thrusting and uplift of the Eastern Cordillera during late Eocene to Pliocene time appears younger than the emerald formation. An evaporite source for the NaCl-rich brines trapped within emerald crystals is constrained by the sulphur isotope data obtained on pyrites. Based on (1) oxygen, carbon and sulfur isotopes data, (2) geochemical profiles through the mineralized zones which show that leaching of major and trace elements (particularly Al, Be, Cr, V and REE) from the enclosing black shales is accompanied by their partial redistribution as infilling vein minerals[18,25] and (3) the chemical composition of the primary fluid inclusions ($NaCl-CaCl_2$-rich brines), a hydrothermal sedimentary model is proposed for the Colombian emerald genesis.
Carnaíba and Socotó emerald deposits yield Transamazonian ages (1980-1970 Ma) which are not separated in time with the granite and pegmatite emplacements. In Carnaíba, emerald mineralization is contemporaneous with the pervasive muscovitization which affected the juxtaposed granite. The sulphur signature of molybdenites is magmatic. Thus, Brazilian and Colombian emerald deposits differ considerably and the magmatic versus sedimentary origin for sulphur allows to propose a magmatic versus sedimentary origin for beryllium for these two contrasted type of deposits.

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