

THE ROLE OF ORGANIC MATTER IN HIGH TEMPERATURE HYDROTHERMAL REGIMES

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INTRODUCTION

The generation of petroleum in basins involves accumulation of organic matter (OM), its gradual burial, diagenesis breakdown and maturation via biodegradation or thermal cracking processes within a 75-150°C "oil window" temperature range. In hydrothermal regimes, as illustrated by active submarine rift basins (Simoneit, 1985), transformation of OM in sediments by high temperature fluids, up to 360°C, is an effective and more rapid process than in conventional basins. The study of such systems are of great interest to understand sulfate-hydrocarbon redox reactions specially for the thermochemical sulfate reduction (TSR), because the hydrothermal fluid discharge contains base-metal sulfides, sulfates, carbonates and petroleum. Moreover, the existence of a thermal gradient induced between ambient and supercritical waters, permit to define the minimum temperature at which TSR reaction began. Hydrothermal experiments have shown that TSR take place at temperatures as low as 175°C whereas geological evidences suggest lower minimum temperatures, 100-140°C, as illustrated by the formation of the Pine Point Mississippi Valley type deposit (Powell and Macqueen, 1984). This paper deals with characterization of OM associated with the Colombian emerald deposition and its key role in TSR through high temperature hydrothermal regimes.

THE EXEMPLAR CASE OF COLOMBIAN EMERALD DEPOSITS

The Colombian emerald deposits are found within two narrow zones, located along the two major polyphased thrust limits of the Eastern Cordillera (EC), corresponding to the original borders of an huge basin in Cretaceous time. The eastern zone consists of the mining districts of Gachalá, Chivor and Macanal and the western zone, of the districts of Coscuez, Muzo, La Palma-Yacopí. Both are contained in Early Cretaceous black shale (BS) series. Two distinct ages of formation of the emerald deposits have been obtained for the western and eastern emerald zones, respectively, 38-32 Ma for the Coscuez-Muzo mines (Cheilletz et al., 1994), and 65 Ma for the Chivor mine (Cheilletz et al., 1995). The deposits result from a two-stage cinematic process in which shortening tectonics affects the two borders of the EC, leading to decollement planes, thrusting, and thrust-fault related folds (Cheilletz and Giuliani, 1996). Stage 1 is characterized by decollement planes which focused the circulation of hydrothermal fluids inducing albitisation and calcitisation of the BS. This metasomatism leads to leaching of major (Si, Al, K, Ti, Mg, P), trace (Ba, Be, Cr, V, C, B, U) and REE-elements from the enclosing BS; this stage is accompanied by the development of a vein system filled by fibrous calcite and pyrite. Stage 2 is marked by the formation of breccias along thrust faults, and thrust related anticlines; it is characterized by

extensional vein sets and hydraulic breccia development filled by muscovite, albite, rhomboedral calcite and dolomite, pyrite and finally by the precipitation in drusy cavities of fluorite, apatite, parisite, REE-bearing dolomite, emerald and quartz.

Microthermometric, Raman-probe and SEM analysis demonstrate the presence of H₂O-NaCl-CaCl₂-KCl-CO₂-N₂ rich-brines trapped into emerald (Giuliani et al., 1992; Cheilietz et al., 1994; Ottaway et al., 1994), carbonate and pyrite (Giuliani et al., 1995). The trapping temperatures of fibrous calcite from stage 1 and rhomboedric carbonates and emerald from stage 2, are estimated respectively, at 150-200°C and 300°C (Cheilietz et al., 1994; Giuliani et al., 1995). Oxygen and carbon isotope composition of quartz and carbonates in all the deposits indicates a basinal formation water origin for the mineralizing fluid (Giuliani et al., 1992), data confirmed by Ottaway et al. (1994) for the Muzo mines. The $\delta^{34}\text{S}$ values of H₂S in solution in equilibrium with pyrite from emerald deposits (Giuliani et al., 1995) demonstrate the evaporitic origin for the mineralizing brines. Cation analysis of fluid inclusions by crush-leach technique (Banks et al., 1995) confirms that fluid in emerald, fluorite and quartz are derived from the dissolution of primary halite and are predominantly Na-Cl-Fe-Ca-K brines.

CHARACTERIZATION OF SEDIMENTARY AND HYDROTHERMAL ORGANIC MATTER RELATED TO EARLY CRETACEOUS BLACK SHALES AND EMERALD MINERALIZATION

The EC of Colombia corresponds, in its central part, to a fold belt which thrusts, on the East, the Llanos basin and on the West, the Magdalena basin. The Cretaceous sediments were deposited in a two arm basin, Tablazo-Magdalena at the west, and Cocuy at the east, separated by the Santander high. These basins were deformed and inverted at Cenozoic times. Fabre (1987) provides important estimations on burial and geothermal history of the EC basin during Cretaceous and Tertiary times. He showed that the basin formed by extension on a strongly thinned lithosphere which provoked a major thermal event coupled with intrusion of mafic magmatism. Fabre and Delaloye (1983), dated these different basic rocks and showed that an Early Cretaceous thermal episode developed from 118 to 93 Ma, up to the Albian-Cenomanian boundary. The vitrinite reflectance data from different portions of the Cocuy paleobasin (Fabre, 1987) indicate increase of maturity in sediments from Une (Albian; 0.5 <PR<1) to Macanal (Berriasian; 2.5 <PR<4.5) formations, as well as the presence of blackened pollens. Hébrard (1985, in Fabre 1987) evidences also the neoformation of pyrophyllite from detrital muscovite and quartz, and measured illite crystallinity up to 4.5. These data and the burial curves show that the basal section of the Cretaceous i.e., Macanal BS series, reached a temperature of 300°C (near the anchizone) until the Campanian. Rock-Eval realized on the Macanal (Cocuy basin) and Paja-Simiti BS (Barremian-Albian serie from Tablazo-Magdalena basin) which contain emerald mineralizations, confirm the overmaturity of OM (6<Hydrogen Index<61; 1<Oxygen Index<20; 0.2<TOC<1.1 %). The carbon isotopic composition of OM of the Macanal BS ($-28.2 < \delta^{13}\text{C} < -21.7$ ‰; mean: -24 ‰) is different from the isotopic composition of Paja-Simiti BS ($-22.2 < \delta^{13}\text{C} < -18.4$ ‰; mean: -20.5 ‰). This difference evidences the variation of sedimentation between the two arms basins: continental input from Guyana shield with precipitation of humic OM within the Cocuy basin versus marine mudstone within the Tablazo-Magdalena basin.

Carbonaceous hydrothermal material is closely associated with emerald mineralization (Giuliani et al., 1993b; Cheilietz and Giuliani, 1996). Petrographic investigations show that this material precipitated during the two stages of vein opening and until emerald deposition. Solid hydrocarbon (bitume) exhibits massive form (up to 2 cm in diameter) and sometimes infilled fractures. It shows conchoidal fractures and both in hand specimen and under the SEM, can present numerous hollow spheres and small voids ranging from 10 microns to 1 mm in diameter. Daughter mineral phases were identified in some bubbles as calcite, dolomite, anhydrite, vanadium-iron oxides, vanadium-rich muscovite, barite and zinc oxide. Bitumen has a low sulfur content (0.2 to 1.2 %) and important trace concentrations (V up to 2000 ppm, Zn up to 740 ppm, Cr up to 87 ppm, U up to 37 ppm and Mo up to 60 ppm). X-ray diffractograms display a broad band between 10 and 18 degrees defining the amorphous character of the material. The first order Raman spectra of bitumen display a band located around 1590 cm⁻¹, which corresponds to C-C vibrations in the aromatic layers, and a second broad band at 1350 cm⁻¹ which is attributed to defects in the graphite structure. The area ratio S 1590 / S 1350 is about 0.7. These data indicate a low structural degree of structural ordering and the non-graphitic character for the solidified

bitumen. The micro-transmission infrared microspectroscopy spectra show the lack of aliphatic and aromatic bands and the disappearance of oxygen species. These results added to Rock-Eval data (Hydrogen Index < 1; 19 < Oxygen Index < 61) confirm the important thermal cracking suffered by these bitumen. $\delta^{13}\text{C}$ values for bitumen range from -23.8 to -21.2 ‰ and are similar to those obtained for the OM in the BS. δD values are comprised between -73.2 and -122 ‰ and the H/C ratios are around 0.1. These isotopic data suggest a genetic relationship between OM and hydrothermal bitumen, and indicate the complete consumption of organic hydrogen during degradation of OM.

THE ROLE OF ORGANIC MATTER IN THE THERMOCHEMICAL SULFATE REDUCTION IN COLOMBIAN EMERALD DEPOSITS

Colombian emerald deposits have no magmatic connection and they can be considered as pyrite deposits hosted by carbonate veins, emerald being an accessory mineral. Sulfide-sulfur source is evaporitic but the chemical process responsible for the reduction of sulfate in sulfide is still in debate (Ottaway et al., 1994; Cheillett and Giuliani, 1996). The presence of both OM in the enclosing BS and in the hydrothermal carbonate-pyrite veins opens to discussion of the possible role of OM in emerald deposit. Four main conditions are necessary to establish that OM has played a key role on TSR (modified from Leventhal, 1990):

1- OM is now present in the ore body; it is the case in Colombian deposits where hydrothermal bitumen are found,

2- OM was present when the different stages of the hydrothermal system developed and at the time of ore formation: in fact, hydrothermal bitumen precipitated during stages 1 and 2 and are found as daughter minerals within primary fluid inclusions hosted by emerald,

3- two types of OM are present: in our case, original, i.e., OM in the BS, and hydrothermal, i.e., bitume in the veins. The organic-matter-bearing BS enclosing the emerald mineralization has suffered a thermal degradation due to burial and thermal history of the EC basin during Cretaceous time. The fluids related to emerald formation at Cenozoic times remobilized this OM provoking changes, differences in chemical composition and precipitation of bitumen,

4- the chemical change in the altered OM is compatible with TSR:

4.1- sulfate reduction implies always oxidation of OM. Oxidation of OM contained in the BS and subsequent carbonates precipitation in equilibrium with CO_2 would result in the formation of low $\delta^{13}\text{C}$ carbonates. $\delta^{13}\text{C}$ of the carbonates will depend on their temperature of formation and the initial isotopic composition of OM. Calcite-graphite $^{13}\text{C}/^{12}\text{C}$ fractionation factors were calculated using the calibration of Bottinga (1969). The difference of 4.5‰ in $\delta^{13}\text{C}$ found between OM from Macanal and Paja-Simiti (?) BS, implies that the $\delta^{13}\text{C}$ of carbonates from stages 1 and 2 of the eastern emerald zone are lighter than those of the western one. In fact, there are two isotopic populations of carbonates. The higher $\delta^{13}\text{C}$ values correspond to Coscuez, Muzo, Yacopí deposits ($-9.3 < \delta^{13}\text{C} < -0.4$ ‰). The more negative values are associated with the Chivor, Gachalá, Macanal mines ($-16.7 < \delta^{13}\text{C} < -3.1$ ‰). In conclusion, it appears that carbonates crystallized in equilibrium with organic carbon at temperatures determined by microthermometry,

4.2- a definitive change is a loss of hydrogen characterized by a lower H/C ratio or more by an aromatic structure. Rock-Eval analyses on both sedimentary and hydrothermal OM, coupled with hydrogen-carbon isotope data, have shown that organic hydrogen was consumed during the reduction.

The four main conditions for TSR reaction are checked in the case of Colombian emerald mineralization: OM acted as reactant and product, the chemical changes producing a considerable loss of hydrogen as shown by the low H/C ratio (H/C: 0.1) and the oxidation of OM produced large quantities of CO_2 necessary to form HCO_3^- .

Many reactions have been proposed for TSR and Machel (1987) summarized them in a global net balance exothermic reaction: hydrocarbon + $\text{SO}_4^{2-} \rightarrow$ altered hydrocarbon + bitumen + HCO_3^- + H_2S + CO_2 (?) + heat. Considering the different products found in the Colombian hydrothermal samples and the measured changes in chemical composition of OM, the following reaction is proposed to explain the role of OM in TSR (Cheillett and Giuliani, 1996): $\text{Ra}(\text{CH}_2\text{O})_2 + \text{SO}_4^{2-} \rightarrow \text{Rb} + 2\text{HCO}_3^- + \text{H}_2\text{S}$ where CH_2O represents a carbohydrate and R(a,b) large organic molecules. HCO_3^- and H_2S produced by the reaction reacted with Ca^{2+} and Fe^{2+} carried by the hydrothermal fluids to induce the precipitation of

calcite and pyrite i.e., $\text{HCO}_3^- + \text{Ca}^{2+} \rightarrow \text{CaCO}_3$ (calcite) + H^+ and $7\text{H}_2\text{S} + \text{Fe}^{2+} + \text{SO}_4^{2-} \rightarrow 4\text{FeS}_2$ (pyrite) + $4\text{H}_2\text{O} + 4\text{H}^+$.

CONCLUSIONS

The geochemical study of OM in the Colombian emerald deposits provided new informations and confirmed previous data on the degree of maturity of the Early Cretaceous BS of the EC and the burial history of the ore-filled area. It constraints also the possible role of OM on the mode of formation of emerald ore bodies. Bitumen appears to have been derived locally from the transformation of OM from sediments by high temperature hydrothermal fluids, up to 300°C. The question of genetic relationships between sulphides, OM and bitumen is solved. Sulfate-hydrocarbon redox reactions occurred at high temperature as described in active submarine rift basins, and isotopic evidences are suggestive of the effective role of OM in the formation of hydrogen sulfide necessary to produce sulfides (pyrite). The mechanism proposed involves the reaction between sulfate of evaporitic origin and OM, without the production of an intermediary elemental sulfur, to produce hydrogen sulfide. This redox reaction process has been already verified experimentally and invoked in disseminated or stratiform base metals or Mississippi Valley type deposits.

REFERENCES

- Banks D.A., Yardley B.W.D., Giuliani G., Cheillett A. and Rueda F. 1995. Chemistry and source of the high temperature brines in the Colombian emerald deposits. Mineral deposits, Pasava, Kribek & Zak (eds), Balkema, Rotterdam, 557-560.
- Bottinga Y. 1969. Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite-carbon dioxide-graphite-methane-hydrogen-water vapor. *Geochim. Cosmochim. Acta*, 33, 49-64.
- Cheillett A., Féraud G., Giuliani G. and Rodriguez C.T. 1994. Time-pressure-temperature constraints on the formation of Colombian emeralds: a laser-probe and fluid inclusion study. *Econ. Geol.* 89, 2,362-380
- Cheillett A., Giuliani G., Zimmermann J.L. and Ribeiro-Althoff A.M. 1995. Ages, geochemical signatures and origin of Brazilian and Colombian emerald deposits: a magmatic versus sedimentary model. Mineral deposits, Pasava, Kribek & Zak (eds), Balkema, Rotterdam, 569-572.
- Cheillett A. and Giuliani G. 1996. The genesis of Colombian emeralds: a restatement. *Mineralium Deposita* (in press).
- Fabre A. 1987. Tectonique et génération d'hydrocarbures: un modèle de l'évolution de la Cordillère Orientale de Colombie et du bassin des Llanos pendant le Crétacé et le Tertiaire. *Arch. Sc. Genève*, 40, 2, 145-190.
- Fabre A. and Delaloye M. 1983. Intrusiones básicas cretácicas en las sedimentitas de la parte central de la Cordillera Oriental. *Geol. Norandina*, 6, 19-29.
- Giuliani G., Sheppard S.M.F., Cheillett A. and Rodriguez, C.T. 1992. Fluid inclusions and $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$ isotope geochemistry contribution to the genesis of emerald deposits from the Oriental Cordillera of Colombia. *C. R. Acad. Sci. Paris*, 314, série II, 269-274.
- Giuliani G., Cheillett A., Arboleda C., Carrillo V., Rueda F. and Baker J. 1995. An evaporitic origin of the parent brines of Colombian emeralds: fluid inclusion and sulfur isotope evidence. *Eur. Journal of Mineralogy* 7, 151-165.
- Leventhal, J.S. 1990. Organic matter and thermochemical sulfate reduction in the Viburnum trend, Southeast Missouri. *Econ. Geol.*, 85, 622-632.
- Machel H.G. 1987. Some aspects of diagenetic sulphate-hydrocarbon redox reactions. *Geol. Soc. Special Pub. "Diagenesis of Sedimentary sequences"*, Marshall J.D. (eds), 36, 15-28.
- Ottaway T.L., Wicks F.J., Bryndzia L.T., Kyser T.K. and Spooner E.T.C. 1994. Formation of the Muzo hydrothermal emerald deposit in Colombia. *Nature*, 369, 552-554.
- Powell T.G. and Macqueen R.W. 1984. Precipitation of sulfide ores and organic matter: sulfate reactions at Pine Point, Canada. *Science*, 224, 63-66.
- Simoneit B.R.T. 1985. Hydrothermal petroleum: genesis, migration and deposition in Guaymas basin, *Can. J. Earth Sci.*, 22, 1919-1929.