

Sulfate Reduction by Organic Matter in Colombian Emerald Deposits: Chemical and Stable Isotope (C, O, H) Evidence

GASTON GIULIANI,

IRD, Institut de Recherche pour le Développement, and, CRPG-CNRS, UPR 9046, BP 20, 54501, Vandoeuvre Cedex, France

CHRISTIAN FRANCE-LANORD,

CRPG-CNRS, UPR 9046, BP 20, 54501 Vandoeuvre Cedex, France

ALAIN CHEILLETZ,

ENSG, Ecole Nationale Supérieure de Géologie, Rue du Doyen Marcel Roubault, BP40, 54501 Vandoeuvre Cedex, France, and, CNRS, UPR 9046, BP 20, 54501 Vandoeuvre Cedex, France

PIERRE COGET, YANNICK BRANQUET,

CRPG-CNRS, UPR 9046, BP 20, 54501 Vandoeuvre Cedex, France

AND BERNARD LAUMOMNIER

Ecole des Mines, 54042 Nancy, France

Abstract

Colombian emeralds occur within carbonate-silicate-pyrite veins and breccias in black shale-limestone-hosted deposits. They are contained within two zones, the eastern and western emerald zones, in the Eastern Cordillera. Mineralizing fluids were derived from the interaction of low-salinity fluids with primary halite and anhydrite. The source of beryllium is sedimentary and of sulfide sulfur is evaporitic. The presence of organic matter, as bitumen, in both the black shales and the emerald-bearing hydrothermal veins invites discussion of the role played by organic matter in thermochemical sulfate reduction, the mechanism proposed for H₂S production.

Organic matter is found in the orebodies in two forms: altered and unaltered. It is also found in primary fluid inclusions of emeralds. Rock-Eval analyses (hydrogen index <1; 19 < oxygen index < 61) as well the elemental H/C ratio (hydrogen index <1) confirmed the intense cracking suffered by the original organic matter. In hydrothermal bitumen, infrared microscopy revealed the absence of aliphatic and aromatic bands and the disappearance of oxygen functional groups.

The eastern emerald zone contains ¹³C-depleted carbonates (mean $\delta^{13}\text{C} = -11.3 \pm 1.3\text{‰}$, $n = 14$) with an homogeneous oxygen isotope composition range ($\delta^{18}\text{O} = 17.8 \pm 0.3\text{‰}$). The western emerald zone contains carbonates with relatively heavy $\delta^{13}\text{C}$ (mean $\delta^{13}\text{C} = -5.1 \pm 0.5\text{‰}$, $n = 25$) and notable $\delta^{18}\text{O}$ variation (17–23.8‰). In both emerald zones, ¹³C-depleted calcite points to thermochemical sulfate reduction by oxidation of organic matter, but most $\delta^{13}\text{C}$ values are heavier than predicted by thermochemical sulfate reduction. A model that mixes heavy CO₂ evolved from dissolution of local limestone and light CO₂ evolved by oxidizing organic matter explains the observed $\delta^{13}\text{C}$ range of carbonates. Variations in $\delta^{18}\text{O}$ of carbonate also reflect the local heterogeneity of the host rocks. Redox reactions produced HCO₃⁻ and H₂S; these compounds then reacted with the predominant cations (Fe²⁺ and Ca²⁺ extracted from the host black shale and limestones by the hydrothermal fluid) and induced calcite and pyrite precipitation.

The oxygen and hydrogen isotope compositions of fluid inclusions and structural waters of the gangue minerals and emeralds constrain the origin of the mineralizing fluids. The composition of these fluids was compared with the isotope composition of fluids in the Zipaquirá halite-bearing salt intrusions, which are near the emerald deposits. The calculated fluid $\delta^{18}\text{O}$ in equilibrium with calcite and dolomite (eastern emerald zone: $7.7 < \delta^{18}\text{O}_{\text{Fluid}} < 12.8\text{‰}$; western emerald zone: $8.2 < \delta^{18}\text{O}_{\text{Fluid}} < 17.8\text{‰}$) and emerald (eastern emerald zone: $15.5 < \delta^{18}\text{O}_{\text{Fluid}} < 17.1\text{‰}$; western emerald zone: $17.5 < \delta^{18}\text{O}_{\text{Fluid}} < 23.6\text{‰}$) are typical of metamorphic waters or highly evolved sedimentary formation waters (temperature of formation = 300°C). The high $\delta^{18}\text{O}$ H₂O values of the minerals suggest that the fluid may have been continuously enriched in $\delta^{18}\text{O}$ owing to exchange with limestones and black shales. In both emerald zones, the δD values of carbonates and quartz parental waters ($-64 < \delta\text{D} < -40.7\text{‰}$) are similar to those found for halite ($-66.4 < \delta\text{D} < -41.2\text{‰}$), whereas δD values of emerald, muscovite and albite are -51.4 to -7.1 per mil.

The increase in δD is interpreted as a consequence of mixing of fluids of different isotope composition during the mineralizing event. Two observations can be made about the O and H isotope ratios of fluid

inclusions and structural waters from salt, muscovite, albite, and emerald. In the eastern emerald zone, they indicate that the fluids from halite and aluminosilicates are the same and are the result of mixing of a meteoric water ($\delta^{18}\text{O} = -12.7\text{‰}$, $\delta\text{D} = -91.6\text{‰}$) with a fluid representing the previous mixture of a water with the Early Cretaceous evaporite brines. In the western zone, the isotope ratios do not show the covariation seen in the eastern zone. The $^{18}\text{O}_{\text{H}_2\text{O}}$ shift found in emerald and muscovite is interpreted to be the result of oxygen isotope exchange reactions with sedimentary formations during the precipitation of the silicate phase.