COMUNICACIONES Nº 50 (1999): 55-58

OXYGEN ISOTOPES OF EMERALD: A RELEVANT TRACER FOR ITS GEOLOGICAL ORIGIN

GASTON GIULIANI[1]

[1] *IRD and CRPG-CNRS, BP20, 54501 Vandoeuvre, France (giuliani@crpg.cnrs-nancy.fr)*

KEY WORDS: Emeralds, pegmatites, oxygen, isotopes.

INTRODUCTION

Natural emerald, the chromium-vanadium-rich variety of beryl, is found in two types of deposit (Giuliani et al., 1997a, b): - (1) the type associated with pegmatites which concerns most of the deposits in the world. Emerald is hosted either by phlogopite schists or by plagioclasites formed at the expense of mafic-ultramafic rocks and pegmatites, respectively; - (2), the type linked to thrusts, faults and shear-zones contained in Cr-(V)-bearing rocks and disconnected from pegmatites. It concerns the Brazilian deposits of Santa Terezinha de Goiás and Itaberaí, the emerald mines of Djebels Sikaït and Zabara in Egypt, Afghan and Pakistan (Swat-Mingora) deposits, the emerald occurrence of Habachtal in Austria and the Colombian emerald deposits.

The present study describes, for the first time, the powerful tool of stable oxygen isotopes for deciphering the nature and the origin of emeralds. Furthermore, this work provides an opportunity to better constrain the oxygen-isotopic composition of emerald which depends on its geological setting, its parental host-rocks and the intensity of the fluid-mineral interaction. The $^{18}O/^{16}O$ ratios of emerald will allow the calibration of the CRPG-CNRS IMS 1270 ion microprobe that will provide new insights into the authentification of the origin of ancient rough and set emeralds.

SAMPLES AND ANALYTICAL METHODS

Emeralds used in this study were collected from 62 occurrences and deposits in 19 countries. The extraction of framework oxygen from emerald was done using standard techniques with BrF_5 as the reagent (Clayton and Mayeda, 1963). The oxygen released from 5 to 10 mg of emerald was converted to CO_2 in a graphite furnace at 750°C and the yields measured by a capacitance manometer. All the analyses were duplicated (sometimes triplicated) and standards (international : quartz NBS 28 , $\delta^{18}O$ = +9.6‰ or laboratory : quartz NL 615, $\delta^{18}O$ = +18.3‰) were measured for each experimental run. The $^{18}O/^{16}O$ ratio of CO_2 was analyzed on a gas-source spectrometer (VG 602D). The $\delta^{18}O$-values are presented in the conventional delta (δ) notation relative to SMOW standard. d (‰) = $[((R_{sample} / R_{standard}) - 1)] \times 10^3$, where R is the isotopic ratio $^{18}O/^{16}O$. The 1σ analytical precision is 0.2‰.

RESULTS

The $\delta^{18}O$-values of the emeralds studied range from +6.2 to +24.7‰. Asian emeralds have $\delta^{18}O$-values in the range +10.6 to +16.2‰. Pegmatite deposits of Khaltaro and Rajhastan have similar emerald $\delta^{18}O$-values, respectively +10.6 and +10.8‰, whereas Afghan (mean $\delta^{18}O = +13.5 \pm 0.1$‰) and Swat-Mingora emerald-bearing shear-zone deposits (mean $\delta^{18}O = +15.7 \pm 0.1$‰) have contrasted values.

Western Australian emeralds hosted by greenstone belts have $d^{18}O$-values (Poona and Menzies deposits, $+7.0 < \delta^{18}O < +9.0$‰) distinct from Eastern ones contained in meta-sedimentary formations (Torrington and Emmaville, $+9.9 < \delta^{18}O < +11.2$‰).

African emeralds have restricted $\delta^{18}O$-values ranges that overlap each other. Nevertheless, emeralds from Zambia ($+9.8 < \delta^{18}O < +10.4$‰), Zimbabwe ($+6.9 < \delta^{18}O < +8.0$‰) and Madagascar ($+8.5 < \delta^{18}O < +9.4$‰), which are the most prized in the international market, can be distinguished.

European emeralds have $\delta^{18}O$-values comprised between +6.9 and +10.8 ‰. Habachtal thrust-controlled emeralds have lower $\delta^{18}O$-values (mean = $+7.1 \pm 0.1$‰) than those related to pegmatite deposits from the Urals, Bulgaria, Norway and Spain.

South American emeralds are characterized by a wide range of $\delta^{18}O$-values. Colombian emeralds have the highest oxygen-isotopic compositions found worldwide and their $\delta^{18}O$-range permits one to distinguish easily emeralds from the Eastern zone (Chivor mining district: mean = $+16.8 \pm 0.1$‰) to those from the Western zone (Muzo, Peña Blanca and Cosucez districts: mean = $+21.2 \pm 0.5$‰). In Brazil, emeralds related to pegmatites have a systematic $\delta^{18}O$ inter-deposit variability ($+6.2 < \delta^{18}O < +12.1$‰) and those related to shear-zone-type deposits have a restricted $\delta^{18}O$ range ($+12.0 < \delta^{18}O < +12.4$‰).

DISCUSSION OF THE RESULTS

Geological implications. The first $\delta^{18}O$-group ($+6.2 < \delta^{18}O < +12$‰) include the granitic-pegmatite-related emerald type deposits and two thrust- and shear zone-controlled emerald deposits (Austria and Egypt), all found in Cr-(V)-bearing mafic-ultramafic rocks. Emerald is contained within phlogopite schists developed in serpentinites or talc-schist rocks (range of $\delta^{18}O$ of these host rocks : $+5.0 < \delta^{18}O < +8.0$ ‰). The second emerald $\delta^{18}O$-group characterized by $\delta^{18}O$-values >

+12‰, corresponds to thrust and shear-zone-controlled emerald type deposits which are disconnected from granites and pegmatites. Emerald is contained in ^{18}O-rich rocks (+10.0 < δ^{18}O < +25.0‰) such as carbonated-talc schists (Santa Terezinha de Goiás deposit; δ^{18}O talc = +10.8‰), talc-magnesite schists (Swat deposit; δ^{18}O magnesite = +17.9 ± 1.2‰), sedimentary and ultramafic formations (Afghanistan) or black shales and carbonates (Colombia; carbonates : δ^{18}O = +21.6 ± 0.8‰; shales : +16.2 < δ^{18}O < +19.3‰). The different δ^{18}O-values obtained for emeralds are the result of fluid rock-interaction linked to pervasive fluid-flow systems affecting contrasted geological environments. The hydrothermal fluid is always channeled by fractures which crosscut rocks of variable chemical composition such as granites and pegmatites, mafic-ultramafic rocks, sedimentary or metamorphic formations. These different types of rocks which have different ^{18}O/^{16}O isotopic signatures, tend to modify the oxygen-isotopic composition of the pervasive fluid (Fallick et al., 1994; Giuliani et al., 1998). This modification will depend on fluid-rock interaction intensity and buffering of fluid δ^{18}O may be achieved under low fluid-rock conditions.

Archeological implications. The ^{18}O/^{16}O ratios of emerald obtained by mass spectrometry will allow the calibration of the CRPG-CNRS IMS1270 ion microprobe (which requires only 2.10^{-11} g of material with a beam of 1 to 5 microns diameter) that will provide new insights into the authentification of the origin of ancient emeralds, in particular to map out the route of emeralds since Egyptian times and to test the myth or reality of the emeralds known as «old mines». These emeralds are found in the ancient treasures of Teheran, Delhi and Istanbul and a debate is opened on their geographic origin: Egypt, Afghanistan, Colombia, Urals, India or Pakistan ? The δ^{18}O-values range of the emeralds from these different deposits is very restricted and consequently, the IMS1270 ion microprobe will be used for deciphering the origin of these "old mines" emeralds.

REFERENCES

Clayton RN, Mayeda TK (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. Geochimica Cosmochimica Acta, 27, 45-32.

Fallick AE, Schorscher HD, Machado GAA, Monteiro MMG, Ellam RM (1994) A review of stable isotope (d^{18}O, dD) studies of emerald deposits in Brasil. In: Annual Meeting Mineral Deposits Study Group, Exeter, GB, p. 411.

Giuliani G, Cheilletz A, Zimmermann J-L, Ribeiro-Althoff AM, France-Lanord C, Féraud G (1997a) Les gisements d'émeraude du Brésil: genèse et typologie. Chronique de la Recherche Minière, 526, 17-61.

Giuliani G, France-Lanord C, Zimmermann J-L, Cheilletz A, Arboleda C, Charoy B, Coget P Fontan F, Giard D (1997b) Composition of fluids, dD of channel H_2O and $d^{18}O$ of lattice oxygen in beryls: genetic implications for Brazilian, Colombian and Afghanistani emerald deposits. International Geology Review, 39, 400-424.

Giuliani G, France-Lanord C, Coget P, Schwarz D, Cheilletz A, Branquet Y, Giard D, Pavel A, Martin-Izard A, Piat D H (1998) Oxygen isotope systematics of emerald - relevance for its origin and geological significance. Mineralium Deposita, 33, 513-519.

Sinkankas J, Read P (1986) Beryl. Butterworths Gem Books (ed), 225 p.