

The $^{18}\text{O}/^{16}\text{O}$ isotopic card of natural and synthetic emeralds: geological and archeological implications

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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 plagioclases 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 Itaberá, the emerald mines of Djebels Sikaït and Zabara in Egypt, Afghanistan and Pakistani (Swat-Mingora) deposits, the emerald occurrence of Habachtal in Austria and the Colombian emerald deposits.

Synthetic emeralds are re-creations of their natural counterparts and they are synthesized by flux-fusion and hydrothermal processes (Sinkankas and Read, 1986).

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 constrain better 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 $^{18}\text{O}/^{16}\text{O}$ ratios of emerald will allow the calibration of the CRPG-CNRS IMS 1270 ion microprobe that will provide new insights into the authentication 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. The $^{18}\text{O}/^{16}\text{O}$ ratio of CO_2 was analysed on a gas-source spectrometer (VG 602D). The $\delta^{18}\text{O}$ -values are presented in the conventional delta (δ) notation relative to SMOW standard and the 1σ

analytical precision is 0.2‰.

Results

Natural emeralds. Three oxygen isotopic groups corresponding to three sets of $\delta^{18}\text{O}$ -values are defined for natural emeralds: - the first group, in the range $+6.2 < \delta^{18}\text{O} < +8\text{‰}$, corresponds to emeralds from Brazil (districts of Quadrilátero Ferrífero: $\delta^{18}\text{O} = +6.8 \pm 0.4\text{‰}$ and Anagé: $\delta^{18}\text{O} = +7.2 \pm 0.3\text{‰}$), Austria (Habachtal, $\delta^{18}\text{O} = +7.1 \pm 0.1\text{‰}$), Australia (Poona, $\delta^{18}\text{O} = +7.2 \pm 0.2\text{‰}$) and Zimbabwe (Sandawana, $\delta^{18}\text{O} = +7.4 \pm 0.5\text{‰}$); - the second group, in the range $+8.0 < \delta^{18}\text{O} < +12\text{‰}$, concerns most of the deposits in the world as for example those of Zambia ($\delta^{18}\text{O} = +10.1 \pm 0.3\text{‰}$), Tanzania ($\delta^{18}\text{O} = +11.1$), Russia ($\delta^{18}\text{O} = +10.6 \pm 0.2\text{‰}$), Madagascar ($\delta^{18}\text{O} = +8.9 \pm 0.4\text{‰}$), Pakistan (Kaltharo, $\delta^{18}\text{O} = +10.6 \pm 0.05\text{‰}$), and Brazil (Carnaíba: $\delta^{18}\text{O} = +9.0 \pm 0.1\text{‰}$ and Socotó: $\delta^{18}\text{O} = +10.6\text{‰}$); - the third group, defined by $\delta^{18}\text{O} > +12\text{‰}$, includes the emerald deposits of Brazil (Santa Terezinha de Goiás, $\delta^{18}\text{O} = +12.2 \pm 0.1\text{‰}$), Afghanistan ($\delta^{18}\text{O} = +13.5 \pm 0.1\text{‰}$), Pakistan (Swat-Mingora district, $\delta^{18}\text{O} = +15.7 \pm 0.1\text{‰}$) and Colombia (Eastern emerald zone: $\delta^{18}\text{O} = +16.8 \pm 0.1\text{‰}$; Western emerald zone: $\delta^{18}\text{O} = +21.2 \pm 0.5\text{‰}$).

Synthetic emeralds. The $\delta^{18}\text{O}$ -values of synthetic emeralds obtained by flux process range between $+4.0$ and $+19.7\text{‰}$. With the exception of Chatham ($\delta^{18}\text{O} = +12.9 \pm 0.3\text{‰}$, $n = 3$), Zeffass ($\delta^{18}\text{O} = +9.25 \pm 0.05\text{‰}$, $n = 2$) and Hautefeuille and Perrey emeralds ($\delta^{18}\text{O} = +19.7 \pm 0.02\text{‰}$, $n = 3$), the isotopic values of emeralds derived by the other types of process are very variable. Thus, Lennix emeralds have values between $+4.0$ and $+8.8\text{‰}$ ($n = 2$), Gilson-Nakazumi between $+12.2$ and $+17.6\text{‰}$ ($n = 3$) and Inamori crystals between $+7.6$ and $+12.95\text{‰}$ ($n = 3$).

The $\delta^{18}\text{O}$ -values of hydrothermally synthesized emeralds are lighter than flux emeralds and vary between -9.0 and -0.95‰ . Regency emerald,

manufactured in the New Jersey (USA), has a $\delta^{18}\text{O}$ -value of -1.6% . Russian hydrothermal emeralds also have depleted ^{18}O -values: the analysed emeralds were manufactured in Novosibirsk as Taurus ($\delta^{18}\text{O} = -2.1$), Bukin ($\delta^{18}\text{O} = -0.95\%$) and Bidulite ($\delta^{18}\text{O} = -9.0\%$), and in Krasnoïarsk as Krasno ($\delta^{18}\text{O} = -6.3\%$). Biron emerald manufactured in Perth (Australia), has a $\delta^{18}\text{O}$ of -5.0% .

Discussion of the results

Geological implications. The first two $\delta^{18}\text{O}$ -groups ($+6.2 < \delta^{18}\text{O} < +12\%$) 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 $\delta^{18}\text{O}$ of these host rocks: $+5.0 < \delta^{18}\text{O} < +8\%$). The third emerald $\delta^{18}\text{O}$ -group characterized by $\delta^{18}\text{O}$ -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 ($+10 < \delta^{18}\text{O} < +25\%$) such as carbonated-talc schists (Santa Terezinha de Goiás deposit; $\delta^{18}\text{O}$ talc = $+10.8\%$), talc-magnesite schists (Swat deposit; $\delta^{18}\text{O}$ magnesite = $+17.9 \pm 1.2\%$), sedimentary and ultramafic formations (Afghanistan) or black shales and carbonates (Colombia; carbonates: $\delta^{18}\text{O} = +21.6 \pm 0.8\%$; shales: $+16.2 < \delta^{18}\text{O} < +19.3\%$). The different $\delta^{18}\text{O}$ -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 $^{18}\text{O}/^{16}\text{O}$ isotopic signatures, tend to modify the oxygen-isotopic composition of the pervasive fluid (Fallick *et al.*, 1994; Giuliani *et al.*, 1997b). This modification will depend on fluid-rock interaction intensity and buffering of fluid $\delta^{18}\text{O}$ may be achieved under low fluid-rock conditions.

Hydrothermal synthetic emerald result from a fluid-mineral interaction and its formation process looks like that of natural ones. Nevertheless, it grows in a water-dominant flow system and the $\delta^{18}\text{O}$ of the

fluid buffers the $\delta^{18}\text{O}$ of emerald under conditions of high fluid/mineral ratio. Indeed, the negative $\delta^{18}\text{O}$ -values found for these emeralds (between -9.0 and -1%) are depending on the $\delta^{18}\text{O}$ -values of the local meteoric water (tap water) used for their synthesis ($-10 < \delta^{18}\text{O} < -2\%$).

Archeological implications. The $^{18}\text{O}/^{16}\text{O}$ ratios of emerald obtained by classical 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 authentication 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: from Egypt, Afghanistan, Colombia, Urals, India or Pakistan? The $\delta^{18}\text{O}$ -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.

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