

### Emerald

Emerald with lapis-lazuli is the oldest known gemstone, having been mined since ancient times in Egypt and probably in Bactria and Scythia. Emerald is rarer than diamond and may have a value thousands of times that of gold. Colombia produces 60% of the world's emeralds (total world production in 1986 was estimated to be 15 million carats), followed by Zambia (15%), Brazil (10%), Russia (5%), Madagascar (3%), Zimbabwe (2%), and Pakistan and Afghanistan (together 5%). Colombian emeralds are prized for their exceptional color, clarity, and carats, as are those from Afghanistan, and to a lesser extent Zambia and Russia. The mineralogical and gemological properties that are normally used to determine the origin of emeralds are their optical features (refractive indices and birefringence), density, adsorption spectra (ultraviolet and near-infrared), internal characteristics (growth phenomena and solid and fluid inclusions), and chemical composition. The diagnostic value of these properties is often restricted because there may be an overlap for emeralds originating from different deposits. However, a combination of mineralogical and gemological properties can be used, in many cases, to accurately identify emeralds from specific localities. Nevertheless, gemological features are often insufficient to certify the ori-

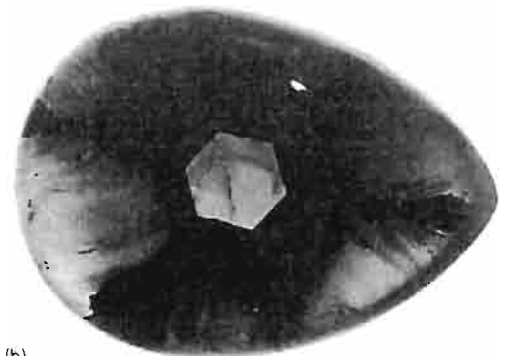
gin of gems, especially emeralds of excellent quality that are poor in inclusions. Thus, doubt or ambiguity always exists when determining the geographical origin of cut or carved emeralds removed from the environment in which they formed.

**Formation.** Emerald is the green variety of beryl (see *illus.*), beryllium aluminum silicate ( $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ) with trace amounts of chromium and vanadium, which produce its characteristic color. Emerald is rare because chromium (and vanadium) and beryllium have antagonistic geochemical behavior in the Earth. Chromium is concentrated in mafic rocks from the mantle (the zone of the Earth located under the continental or oceanic crust), while beryllium has an affinity for the continental crust and concentrates in granitic magmas. The formation of emerald necessitates the bringing together of chromium (and vanadium) and beryllium in the same geological site.

Two types of emerald deposits have been recognized worldwide: One type is associated with granites and pegmatites (rocks composed of quartz, feldspar, and mica, with crystals sometimes having a size of several meters). These emeralds result from the circulation of hot alkaline fluids that developed an alteration halo around pegmatite veins. The fluids, at temperatures between 400 and 600°C, dissolve the main constituents of pegmatite (beryllium) and mafic rock (chromium and vanadium), transforming the two rocks into plagioclase (rock composed of white feldspar rich in sodium) and phlogopite (biotite schist). Thus chromium dissolved from



(a)



(b)

Colombian trapiche emeralds, from the Coscuez mine. (a) Crystallized within black shale. The width of the trapiche crystal on the left is 4 cm. (b) 48-carat gemstone showing solid and fluid inclusions. (Photograph by Omar Bustos)

the mafic rock and beryllium dissolved from the pegmatite are concentrated in phlogopitite and plagioclase where emeralds have crystallized. Emeralds of this type occur in most of the deposits of the world (Zambia, Brazil, Madagascar, Russia, Zimbabwe, Australia).

The other emerald type is linked to plate tectonics (thrusts, faults, and shear zones) affecting chromium- and vanadium-bearing rocks. These emeralds correspond to deposits hosted by (1) mafic rocks from the mantle, such as the Brazilian deposits of Santa Terezinha de Goiás and Itaberaí, the emerald mines of Djebel Sikait, Zabara, and Umm Kabo in Egypt, the Pakistani (Swat-Mingora), and the Austrian (Habachtal) emeralds; (2) metamorphic rocks of sedimentary and magmatic origin, as in the Pansjhir valley (Afghanistan); and (3) sedimentary rocks, such as the black shales of the Colombian deposits. The chromium and vanadium in these emeralds were extracted from source rocks by fluids at temperatures between 300 and 600°C. The source of the beryllium in these deposits is still in debate, with the exception of the Colombian emeralds, the beryllium for which is from the black shales in which they are found.

**Oxygen isotopes.** Oxygen is the most abundant chemical element in the Earth's crust and is the main constituent of emerald (up to 45% by weight). The variation among rocks of the isotopic ratio of the most abundant oxygen isotopes ( $^{16}\text{O} = 99.756\%$  and  $^{18}\text{O} = 0.205\%$ ) is commonly expressed as  $\delta^{18}\text{O}$  (per thousand, ‰), which is the relative difference between the  $^{18}\text{O}/^{16}\text{O}$  ratio of the sample and that of the Standard Mean Ocean Water (SMOW), whose  $^{18}\text{O}/^{16}\text{O}$  ratio is  $2.0052 \times 10^{-2}$ . Positive values of  $\delta^{18}\text{O}$  indicate higher  $^{18}\text{O}$  compared to SMOW, and vice versa. Extraction of oxygen from emerald can be performed under vacuum, using the oxidizer  $\text{BrF}_3$  (a destructive technique). In this technique, the oxygen released from emerald is converted to carbon dioxide ( $\text{CO}_2$ ) in a graphite furnace. The  $^{18}\text{O}/^{16}\text{O}$  ratio of the  $\text{CO}_2$  is then analyzed in a mass spectrometer. The overall reproducibility is 0.2‰. Natural emeralds collected from 62 deposits from 19 countries have been studied by this technique. Their  $\delta^{18}\text{O}$  values range from +6.2 to +24.7‰. Emeralds can be classified in three groups according to their  $\delta^{18}\text{O}$  values. The first group, with  $\delta^{18}\text{O}$  greater than +6.2‰ but less than +7.9‰, corresponds to emeralds from Brazil (Quadrilátero Ferrífero and Anagé districts), Austria (Habachtal,  $\delta^{18}\text{O} = +7.1 \pm 0.1\%$ ), Australia (Poona), and Zimbabwe (Sandawana). The second group, with  $\delta^{18}\text{O}$  greater than +8.0 but less than +12‰, encompasses most of the deposits in the world, such as those from Zambia, Tanzania, Russia, Madagascar, Egypt ( $\delta^{18}\text{O} = +10.3 \pm 0.1\%$ ), Pakistan (Kaltharo), and Brazil (Carnaíba and Socotó). The third group, with  $\delta^{18}\text{O}$  greater than +12‰, includes the emerald deposits from Brazil (Santa Terezinha de Goiás), Afghanistan, Pakistan (Swat-Mingora district), and Colombia (eastern zone,  $\delta^{18}\text{O} = +16.8 \pm 0.1\%$ , and western zone,  $\delta^{18}\text{O} = +21.2 \pm 0.5\%$ ).

The isotopic oxygen composition of emeralds also

can be determined by a near-nondestructive technique using an ion microprobe. In this approach, the  $^{16}\text{O}^-$  and  $^{18}\text{O}^-$  ions are sputtered off an emerald crystal by bombardment with  $\text{Cs}^+$  ions and negative ions, and analyzed in an ion probe mass spectrometer. Cut or crystal emeralds having flat surfaces can be analyzed after gold metallization. This technique allows the determination of the  $^{18}\text{O}/^{16}\text{O}$  ratio with a precision of  $\pm 0.4\%$  (1 sigma). The size of the craters produced on the emerald is about 10–20 micrometers in diameter and a few angstroms deep (that is, about  $2 \times 10^{-11}$  g sputtered for one analysis). These spots are invisible to the naked eye, so this method is considered nearly nondestructive and can be used on gems of high value.

**Trade routes.** The recent examination by ion microprobe of a set of historical emeralds has revealed unexpected origins, hinting at previously unknown trade routes for the gems. Four emeralds from the Nizam of Hyderabad (India), cut in the eighteenth century in India, were analyzed; three of them came from Colombia and one originated from Afghanistan. This result contradicted their proposed origin as old-mine emeralds from long-lost Indian mines, and showed that Afghani mines had been exploited as early as the eighteenth century, although their recorded discovery was in 1976. In another study, four emeralds belonging to the National Museum of Natural History in Paris were examined. The oldest is an emerald set in a Gallo-Roman earring which originated from Swat in Pakistan, a region along the ancient silk road route. The 51.5-carat emerald, mounted in the Holy Crown of France by Louis IX in the thirteenth century, was shown to have come from Habachtal in Austria. The other two emeralds, belonging to the eighteenth-century French mineralogist René Just Haüy, originated in Austria and Egypt. These results showed that during ancient times emeralds of Pakistan and Egypt were traded by way of the silk route. These two places and Austria were the only sources of emeralds. After the discovery of the Colombian mines by the Spaniards in the sixteenth century, a new trade route was established via Spain to Europe and India. Emeralds of exceptional quality have been cut in India since the Bobur Moghul dynasty and sold as old-mine emeralds worldwide. One emerald, property of the Mel Fisher Maritime Heritage Society, was recovered from the Spanish galleon *Nuestra Señora de Atocha*, which sank off the Florida coast in 1622. The galleon was coming from Colombia, but isotopic analysis of the emerald demonstrated that the crystal came from the old Tequendama mine, exploited during Pre-Colombian times.

**Tracing the sources of gemstones.** Other techniques can be used to determine the geographic origin of precious gemstones. An ion-beam technique, external beam proton-induced x-ray emission (PIXE), is suitable for chemically analyzing gems. The ion beam is external (diameter of the proton beam on target is less than 0.5 mm), and the sensitivity is excellent for the analyses (even in trace amounts) of the

transition elements (vanadium, chromium, titanium, iron, magnesium) that are found in emerald. The chemical composition obtained from artifacts compared to a collection of standards from different well-known sources allows in many cases the probable identification of their geographical origin. This technique has been applied successfully to antique jewelry by ion-beam analysis at the Laboratoire de Recherche des Musées de France at the Palais du Louvre in Paris.

Another technique used to identify emerald origin is Fourier-transform infrared spectroscopy. An infrared beam is transmitted through the crystal, and an absorption spectrum representing the nature of impurities and the water, carbon dioxide, and nitrogen content is obtained. Comparison of the different absorption bands found for the gem is compared to emerald standards from known world sources. This technique is nondestructive. The geographic determination of emeralds by infrared spectroscopy is used at the Laboratoire Environnement et Minéralurgie in Nancy, France.

For background information see BERYL; EMERALD; GEM; INFRARED SPECTROSCOPY; MASS SPECTROMETRY; MINERAL; MINERALOGY; OXYGEN; PRECIOUS STONE in the McGraw-Hill Encyclopedia of Science & Technology.

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Bibliography. T. Calligaro et al., PIXE/PIGE characterisation of emeralds using an external micro-beam, *Nucl. Instrum. Meth. Phys. Res. B*, 161-163, 769-774, 2000; D. Giard et al., *L'émeraude*, Association Française de Gemmologie, CNRS et ORSTOM Editions, AFG Press, Paris, 1998; G. Giuliani et al., Les gisements d'émeraude du Brésil: Genèse et typologie, *Chronique de la Recherche Minière*, 526: 17-61, 1997; G. Giuliani et al., Oxygen isotope systematics of emerald: Relevance for its origin and geological significance, *Mineralium Deposita*, 33:513-519, 1998; G. Giuliani et al., Oxygen isotopes and emerald trade routes since antiquity, *Science*, 287: 631-633, 2000; E. Gubelin and J. Koivula, *Photoatlas of Inclusions in Gemstones*, 2d ed., ABC Editions, Zurich, 1986; La gemmologie, *Analisis Mag.*, 23(1):10-54, 1995; J. Sinkankas, *Emeralds and Other Beryls*, Chilton Book, Radnor, PA, 1981, reprinted by Geoscience Press, Tucson, 1989.

Giuliani Gaston. (2002).

Emerald.

In : McGraw-Hill yearbook of science and technology : comprehensive coverage of recent events and research.

New York : McGraw-Hill, 92-94.