
THE CHEMICAL DISTINCTION OF NATURAL FROM SYNTHETIC EMERALDS

By Carol M. Stockton

The chemical characteristics of natural and synthetic emeralds were studied in order to identify differences that could be used to separate them from one another. Thirty-eight natural emeralds from 20 localities and 11 synthetic stones from six manufacturers (flux and hydrothermal growth processes) were analyzed by microprobe and X-ray fluorescence. The results revealed a complex collection of chemical constituents that reflect the different environments in which natural and synthetic emeralds form. The present study agrees with the limited number of analyses previously reported for both materials. Thus, a new method of distinguishing natural from synthetic emeralds is now available for use in gemology when more conventional methods prove inadequate.

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The gemological techniques now used to separate natural from synthetic emeralds—primarily refractive index, fluorescence, and inclusions—do not provide solutions for all current situations, especially in the case of stones that lack inclusions. Moreover, the rapid advances being made in the manufacture of synthetics are almost certain to reduce the usefulness of these gemological tests even further. Consequently, a detailed analysis of major and minor-element chemistry of natural and synthetic emeralds was conducted to determine the possible existence of essential differences in the chemical compositions of these materials in order to provide gemology with additional means of distinction.

The theory that one can distinguish chemically between synthetic and natural gem materials is based on the premise that natural gems incorporate a variety of nonessential chemical components from the natural environments in which they are formed that are not present in the manufacture of their synthetic counterparts. Conversely, elements that are not associated with the natural environment for minerals are frequently incorporated into the artificial environments created for the growth of synthetic crystals.

The results of a small preliminary sampling of natural and synthetic emeralds indicated that there was support for the idea of chemical distinction and that more extensive work was justified. In addition, a recent article by Schrader (1983) provided further evidence that natural and synthetic emeralds have significant chemical differences. Although Schrader's paper is a summary of a more thorough study, it is not conclusive and demonstrates the need for additional work, especially since his study included natural emeralds from only seven localities and omitted hydrothermally grown synthetics.

Another recent article (Hänni, 1982) presented chemical data on a number of natural and synthetic emeralds, but

TABLE 1. Localities of the natural emeralds and manufacturers of the synthetic emeralds discussed in this article (from this and two previous studies).

Country/method of synthesis	Specific locality/ manufacturer	Stockton (49 stones)	Schrader (1983) (58 stones)	Hänni (1982) (43 stones)
Natural Emeralds				
Austria	Salzburg		+	+
Brazil	Santa Terezinha	+	+	
	Goiás	+		
	Bahia		+	
	Salininha		+	
	Minas Gerais		+	
Colombia	unknown	+	+	+
	Chivor	+	+	
	Muzo	+		
	unknown	+		+
Ecuador				+
Egypt (3rd century B.C.)		+		
Tanzania	Lake Manyara	+		
Norway	Eidsvoll	+		
Pakistan			+	+
Peru		+		
South Africa	Cobra Mine, Transvaal		+	
	Transvaal	+	+	+
U.S.A.	North Carolina	+		
USSR	Ural Mountains	+	+	
Zambia		+		+
Zimbabwe	Sandawana	+	+	+
Unknown		+		
Synthetic Emeralds				
Hydrothermal	Linde	+		+
	Regency	+		
	Biron	+		
Flux	Chatham	+	+	+
	Gilson	+	+	+
	Inamori	+	+	+
	Lens Lens		+	+
	Zerfass			+

there are some important disparities between Hänni's data and the information obtained from this study. A discussion of both Schrader's and Hänni's data as well as those of other researchers is included with the presentation of results obtained in the current study.

Chemical data on emeralds are relatively scarce, and the wide ranges of sources, colors, and qualities of this gem also suggest that extensive analysis is advisable before any general conclusions can be reached. The work presented here both confirms Schrader's findings and introduces data for additional localities and synthetic manufacturers. The sum of these works thus establishes that natural emeralds can be chemically distinguished from their synthetic counterparts.

MATERIALS AND METHODS

The collection compiled for this study includes 38 natural emeralds from 20 different localities

and 11 synthetic emeralds that represent six different manufacturers. All are either cut gems or gem-quality rough specimens. An attempt was made to sample as many localities and manufacturers as possible; a list of these specific sources is provided in table 1. In addition, the collection represents as broad a variety of colors as could be found that still lie within the range generally accepted as emerald (figure 1).

The emerald specimens were analyzed for Na₂O, K₂O, MgO, CaO, MnO, FeO, Al₂O₃, V₂O₃, Cr₂O₃, SiO₂, and Cl by a MAC electron microprobe at an operating voltage of 15 KeV and beam current of 0.05 μ A. This provides only partial analyses (less than 100% total), because the light elements, most importantly Be and Li, cannot be detected by the microprobe. The raw data were corrected by the Ultimate program (Chodos et al., 1973). Microprobe results were checked and additional trace elements identified by qualitative energy-



Figure 1. A representative sample of natural and synthetic emeralds from the study collection. The stones pictured range from 0.50 to 1.91 ct and originate from the following sources (left to right): Santa Terezinha de Goiás (Brazil), Lake Manyara (Tanzania), Biron (hydrothermally grown synthetic), Chatham (flux-grown synthetic), natural (country unknown), and two stones from Colombia (specific localities unknown). Photo by Michael Havstad.

dispersive X-ray fluorescence spectrometry (EDXRF) with a Kevex 0700 system.

DISCUSSION OF RESULTS

The results of the chemical analyses of the study collection are summarized in table 2. Major elements include Al_2O_3 and SiO_2 . Minor elements, for the purposes of this study, are those present in oxides below 10.0 wt.% but above microprobe detection limits (≤ 0.1 wt.%): Na_2O , MgO , FeO , V_2O_3 , Cr_2O_3 , and Cl . Trace elements then, are those present in quantities below the microprobe detection limits (i.e., determined by EDXRF).

The oxides measured by microprobe fall into two categories: (1) those that provide no information useful for distinguishing natural from synthetic emeralds; and (2) those that, at certain levels of concentration or in conjunction with other elements present or absent, provide means of separation. Among the oxides measured, V_2O_3 and Cr_2O_3 fit the first category and thus can be disregarded.

Chemical components that fall into the second category mentioned above provide us with reliable means of identification in most cases. In the samples analyzed here, chlorine (Cl) was found

in all the hydrothermal synthetics, but in no other emeralds examined. It was detected at trace to minor levels and reportedly comes from the chloride hydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) that is used to supply chromium as a coloring agent (Nassau, 1980, p. 151).

The remaining major and minor chemical components are present in ranges that partially overlap for natural and synthetic emeralds. Na_2O , MgO , and FeO are all present in greater quantities in natural emeralds than in the synthetics. Na_2O was found in amounts not exceeding 0.1 wt.% in synthetics but up to 2.3 wt.% in natural emeralds, therefore suggesting that quantities appreciably greater than 0.1 wt.% indicate natural origin. Likewise, the presence of MgO and FeO in amounts that notably exceed 0.1 wt.% is characteristic of natural emerald. Smaller quantities of Na_2O , MgO , and FeO , however, provide no diagnostic information.

Al_2O_3 and SiO_2 supply additional information about origin. In natural emeralds, Al_2O_3 ranges from about 11.7 wt.% to 18.2 wt.%, while in both types of synthetics it invariably exceeds 18.0 wt.%. Similarly, SiO_2 ranges from approximately 63.3 wt.% to 66.5 wt.% in the natural specimens,

but exceeds 65.6 wt.% in all the synthetics. Thus, amounts of Al₂O₃ and SiO₂ below those found in synthetics (18.0 wt.% and 65.7 wt.%, respectively) are indicative of natural origin and probably reflect the greater amounts of minor and trace elements usually included in the composition of natural emeralds.

Qualitative analysis by EDXRF revealed the presence of a number of elements at the trace level that provide additional evidence of natural or synthetic origin. From the data listed in table 2, one can see that several elements identified at trace and minor levels in many of the natural emeralds were not found at corresponding levels in any of the synthetic emeralds examined here. On the other hand, only one element (rhodium) found in synthetics at the trace level did not appear at all in the natural specimens. In conjunction with the

data on minor-element composition, these data enable us to distinguish between natural and synthetic emeralds of the localities and types analyzed, since every natural specimen in the study collection contains at least one trace element not found in any of the synthetics and/or at least one minor element found at levels appreciably greater than in the synthetic samples.

Table 3 summarizes the earlier data published by Schrader (1983) and Hänni (1982). Schrader's data were originally presented in atomic-percent units, but have been converted to weight-percent oxides for comparison with the other data presented here. A comparison with table 2 shows that the data reported by Schrader generally agree with the results obtained in the present study. The only notable exception among his data are two synthetic emeralds that have appreciably more iron than has otherwise been found: a Gilson with about 0.25 wt.% FeO and an Inamori with approximately 0.52 wt.% FeO. The greater range of vanadium (V₂O₃) reported in table 2 is largely due to the new Biron hydrothermal synthetics that are included in the present study but are not yet available on the gem market (and, in all probability, were not available to Schrader at the time of his study). Other minor but nonsignificant differences between the two sets of data probably reflect differences in test samples: The present study includes stones from six localities and three manufacturers not sampled by Schrader, whereas he reported on samples from two localities and one manufacturer not analyzed here (see table 1).

The data published by Hänni (1982) agree for the most part with those obtained here and by Schrader, except that the figures reported for TiO₂ and MnO appear to be considerably higher than otherwise found. Of greater concern, however, Hänni reported the presence of MgO in amounts greater than 0.1 wt.% in synthetic emeralds. This is a significant departure, given the almost total agreement between the latest data (table 2) and Schrader's findings. However, about half of the elements reported by Hänni, including MgO, MnO, and TiO₂, were measured by means of an energy-dispersive X-ray (EDX) detector (Hänni, pers. comm.), which is considerably less sensitive and less accurate than the wavelength-dispersive spectrometers usually used for quantitative microprobe analyses (as in the present study). The inconsistencies reported by Hänni fall below the detection limits of the EDX detector (around

TABLE 2. Chemical data (in wt.%) for the study collection of natural and synthetic (hydrothermally grown and flux-grown) emeralds.^a

Components	Natural (38 stones)	Hydrothermal (6 stones)	Flux (5 stones)
Oxides			
Na ₂ O	≤ 2.3	nd	< 0.1
MgO	≤ 3.1	nd	nd
FeO	tr - 2.0	nd	≤ 0.1
Al ₂ O ₃	11.7-18.2	18.1-18.8	18.1-20.1
V ₂ O ₃	tr- 2.0	≤ 0.7	≤ 0.1
Cr ₂ O ₃	tr- 1.2	0.3- 0.8	0.2- 0.9
SiO ₂	63.3-66.5	65.8-66.6	65.7-67.4
Cl	nd	tr- 0.3	nd
Trace Elements			
K	*	-	-
Ca	**	-	-
Sc	**	-	-
Ti	*	-	-
Mn	*	-	-
Ni	**	*	-
Zn	**	*	-
Ga	*	*	*
Rb	**	-	-
Zr	*	-	-
Mo	*	-	**
Rh	-	**	**
Cs	**	*	-
Ba	**	-	*
La	**	*	-

^aSymbols:

nd = not detected

tr = traces detected by EDXRF

** = traces detected in 50% or more of the specimens examined

* = traces detected in fewer than 50% of the specimens examined

- = not detected at trace levels

TABLE 3. Chemical data for natural and synthetic (flux-grown and hydrothermally grown) emeralds from the Schrader (1983) and Hänni (1982) studies.^a

Components	Schrader		Hänni		
	Natural (44 stones)	Flux (13 stones)	Natural	Hydrothermal (43 stones total)	Flux
Oxides					
Na ₂ O	~0.04–2.29	0.002–0.04	0.6– 2.3	nd	≤ 0.1
MgO	tr–0.83	nd	1.0– 3.1	≤ 0.2	≤ 0.4
FeO	0.06–0.64	*≤0.52	≤ 1.3	nd	nd
Al ₂ O ₃	nr	nr	13.4–17.7	18.6–18.8	18.1–19.9
V ₂ O ₃	tr–0.22	≤0.19	≤ 0.9	nd	≤ 0.1
Cr ₂ O ₃	≤2.06	0.57–2.19	≤ 1.4	0.5– 0.8	0.3– 1.9
SiO ₂	nr	nr	63.0–65.9	66.1–66.2	66.0–67.6
Cl	nr	nr	nd	0.3– 0.4	nd
Also Reported					
K ₂ O	0.02–0.04	tr–0.013	nr	nr	nr
MnO	tr–0.005	≤0.0003	≤ 0.1	nd	≤ 0.2
TiO ₂	tr	tr	≤ 0.1	nd	nd
Also Detected					
	Sc, Ni, Rb, Ga, Y, Cu, Zr, Cs	Ga, Mo, Rh, Ni, Y, Cu, Zr, Cs, Rb, W, Pt			

^aSymbols:

nr = not reported

nd = not detected

tr = traces detected

* = usually 0.04 wt. %

0.5–1.0 wt.%) and can thus be accountably superseded by the more recent data reported here and by Schrader.

Additional chemical data on natural emeralds from a number of researchers (Gübelin, 1958; Bank, 1974; Metson and Taylor, 1977; Graziani and Lucchesi, 1979; Hänni and Kerez, 1983; see also Sinkankas, 1981, pages 376, 400, 419, 535, and 607) show no significant differences from the analyses of the natural emeralds in the current study collection, although only the most recent reports include information on vanadium content.

CONCLUSIONS

The information provided by this study verifies and supplements the existing body of chemical data on natural and synthetic emeralds so that clear distinctions can now be made. Natural emeralds invariably include at least one and usually more chemical components that are not found in any of the synthetic emeralds currently being manufactured. Moreover, the ability to determine these characteristic components by nondestructive analytical techniques renders such chemical distinction a viable gemological test, although the expense and limited availability of good microprobe and XRF analyses, as well as the expertise required, essentially restrict use of these methods

to important cases in which all other gemological tests have been exhausted.

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