letztes Exemplar

A CONTRIBUTION TO THE SEPARABILITY OF NATURAL AND SYNTHETIC EMERALDS

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There are various features to be used as a means of discriminating between natural and synthetic emeralds. In general, refractive indices and birefringence are lower in synthetic stones. Also the specific gravity is lower in synthetic stones in comparison with natural. But again there are exceptions, like Linde and Lechleitner hydrothermal synthetics (Webster, 1975). Another diagnostic feature is fluorescence. It cannot be used exclusively but has its diagnostic value only in connexion with other observations. A very important criterion is the internal aspect, i.e. the inclusions and growth marks. In many cases observation of these allows a rapid and secure diagnosis (Gübelin, 1969). But too often inclusions are lacking or undiagnostic, being difficult to interpret or never having been seen before. At the same time, the physical constants may be found to be in the overlapping region between natural and synthetic stones. In such troublesome cases the ingenious gemmologist has to look for new methods and sometimes is well advised to borrow techniques from neighbouring sciences. I have in mind, for instance, the method of x-ray topography (Schubnel and Zarka, 1971), which reveals characteristic growth defects in crystalline matter.

We know emeralds as a variety of beryl. Its green colour derives from a small admixture of Cr, but V and Fe may contribute to this colour too. Besides these visible impurities in originally colourless beryl there may be invisible impurities as well. These are elements which do not lead to absorptions in the visible part of the spectrum and thus do not cause colour. This contamination in the atomic dimension is best seen from chemical analyses of different beryls (Bakakin and Belov, 1962). In Table 1 chemical analyses of two emeralds (one synthetic, one natural) are presented in comparison with the theoretical concentrations calculated from the beryl formula. Gilson synthetic emerald is still very close to the ideal composition, containing a small proportion of Cr which

ISSN: 0022-1252 XVIII (2) 138 (1982)

replaces some Al in the crystal lattice. The natural emerald from Sandawana, however, is far away from the ideal beryl composition. It has considerable amounts of Na_2O and MgO and a certain content of FeO, MnO and, of course, Cr_2O_3.

TABLE 1

Theoretic and real compositions of beryl and emeralds in comparison

	$Be_3Al_2Si_6O_{18}$	Gilson synth. emerald	Sandawana, Zimbabwe
SiO_2	67.0	67.0	64.2
Al_2O_3	18.9	17.8	15.1
TiO_2	—	—	0.0
FeO	—	—	0.2
MgO	—	0.1	2.4
MnO	—	—	0.2
K_2O	—	—	0.0
Na_2O	—	0.1	2.4
Cr_2O_3	—	0.6	0.3
V_2O_3	—	—	0.0
BeO	14.1*	14.0*	13.9*
H_2O	—	—	2.0**
	'pure'	⟶	'impure'

* Stoichiometric content of BeO. Be is not detectable by microprobe.

** This value is put from experience and gives only the range of H_2O concentrations expected in natural emerald (Hänni, 1980).

It would therefore appear that this difference in purity could be a basic diagnostic feature in distinguishing between natural and synthetic emerald. To test this, 45 cut stones of different origins and manufacturers were examined. They were analysed chemically by electron microprobe (see Appendix, p.144); on every sample four point analyses were carried out. The purpose of this investigation was to check whether the result found would be characteristic and to a certain extent safe. Obviously 45 stones cannot represent the whole range of emerald compositions found today. Nevertheless the diagrams (Fig. 1) give persuasive evidence of useful and characteristic differences between natural and synthetic emeralds, capable of being used as a means of discrimination.

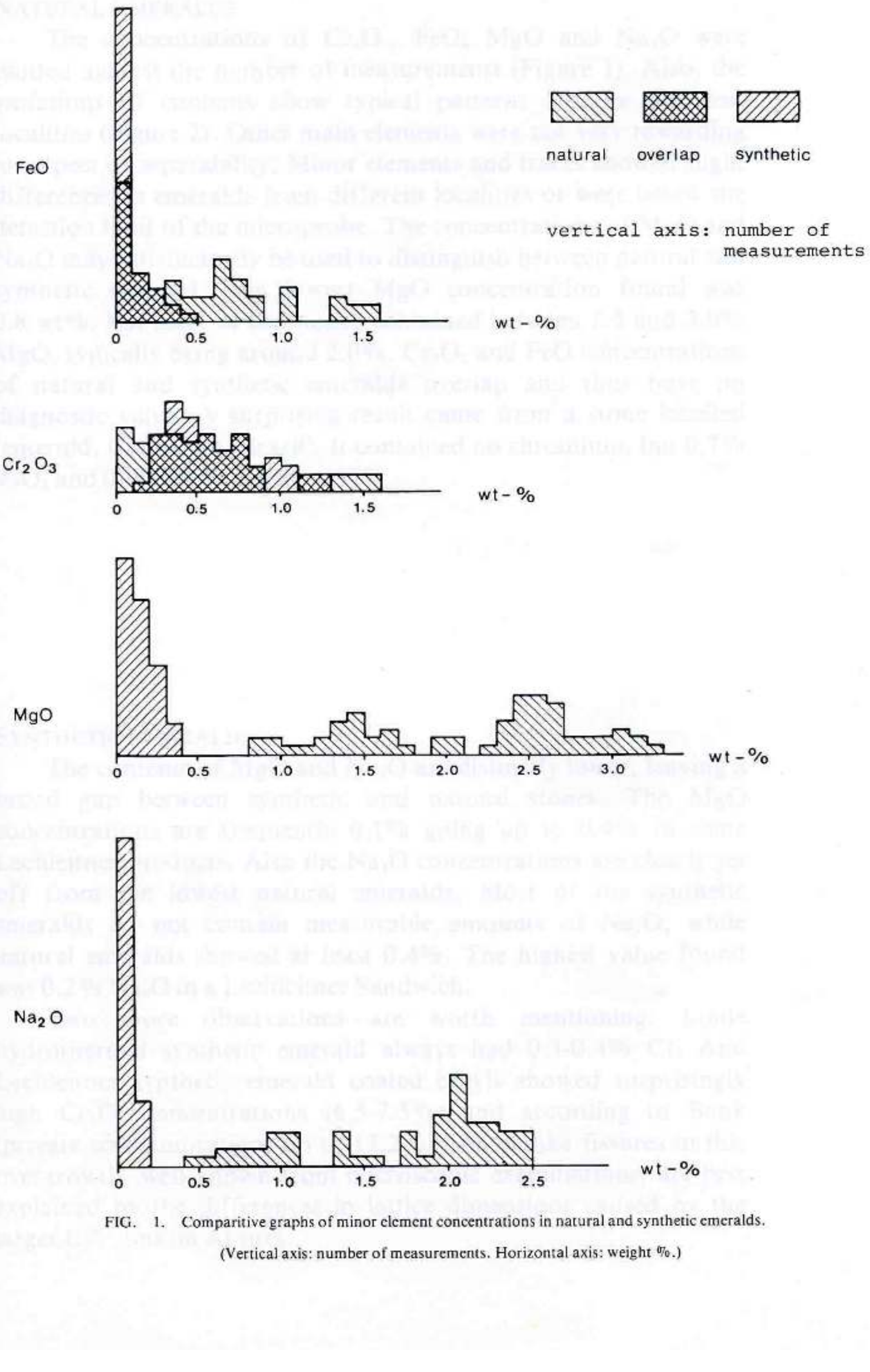

FIG. 1. Comparitive graphs of minor element concentrations in natural and synthetic emeralds.

(Vertical axis: number of measurements. Horizontal axis: weight %.)

NATURAL EMERALDS

The concentrations of Cr_2O_3, FeO, MgO and Na_2O were plotted against the number of measurements (Figure 1). Also, the variations of contents show typical patterns for the different localities (Figure 2). Other main elements were not very rewarding in respect of separability. Minor elements and traces showed slight differences in emeralds from different localities or were below the detection limit of the microprobe. The concentrations of MgO and Na_2O may satisfactorily be used to distinguish between natural and synthetic emerald. The lowest MgO concentration found was 0.8 wt%, but most of the stones contained between 1.5 and 3.0% MgO, typically being around 2.0%. Cr_2O_3 and FeO concentrations of natural and synthetic emeralds overlap and thus have no diagnostic value. A surprising result came from a stone labelled 'emerald, Conquista, Brazil'. It contained no chromium, but 0.7% V_2O_3 and 0.9% FeO (Taylor, 1977).

SYNTHETIC EMERALDS

The contents of MgO and Na_2O are distinctly lower, leaving a broad gap between synthetic and natural stones. The MgO concentrations are frequently 0.1% going up to 0.4% in some Lechleitner products. Also the Na_2O concentrations are clearly set off from the lowest natural emeralds. Most of the synthetic emeralds do not contain measurable amounts of Na_2O, while natural emeralds showed at least 0.4%. The highest value found was 0.2% Na_2O in a Lechleitner Sandwich.

Two more observations are worth mentioning: Linde hydrothermal synthetic emerald always had 0.3-0.4% Cl. And Lechleitner synthetic emerald coated beryls showed surprisingly high Cr_2O_3 concentrations (6.5-7.5%) and according to Bank (private communication) up to 13.2%. The netlike fissures in this overgrowth, well known from microscopic examinations, are best explained by the differences in lattice dimensions caused by the larger Cr^{+3} ions on Al sites.

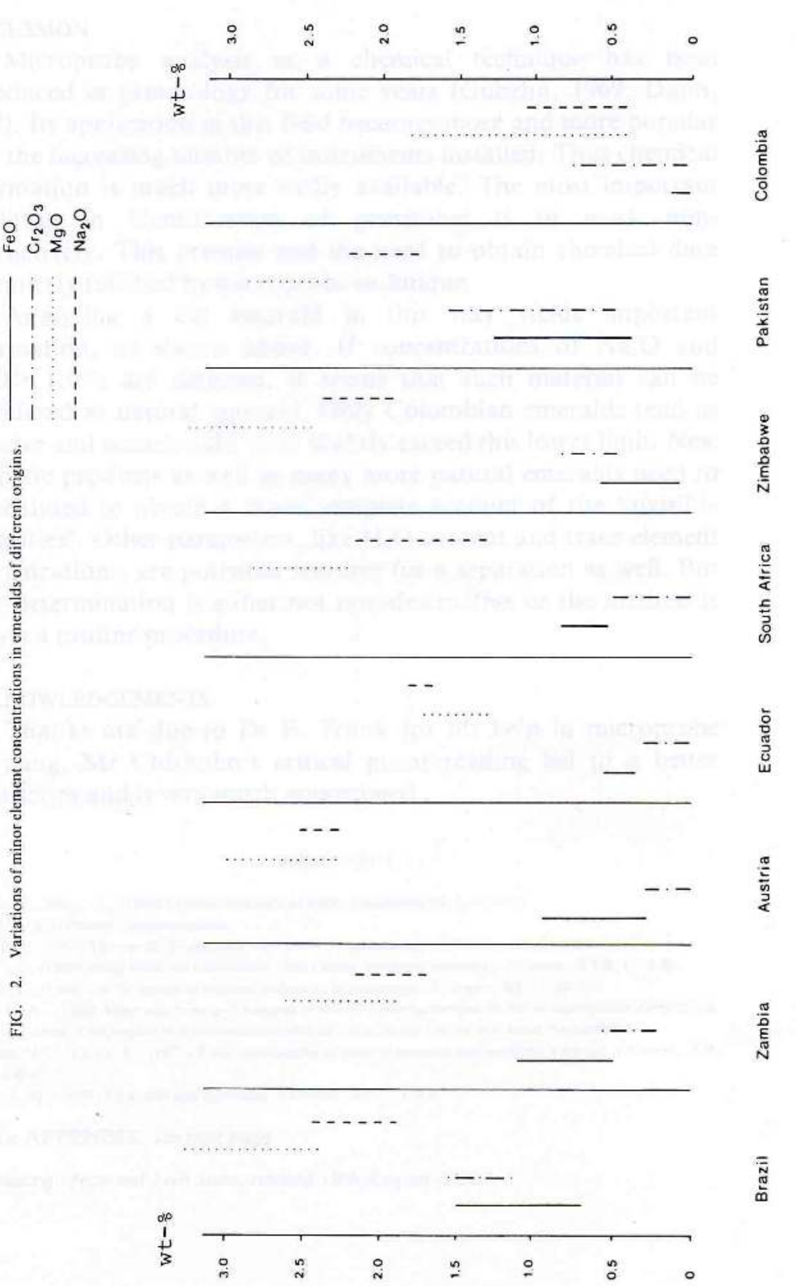

FIG. 2. Variations of minor element concentrations in emeralds of different origins.

DISCUSSION

Microprobe analysis as a chemical technique has been introduced in gemmology for some years (Gübelin, 1969; Dunn, 1977). Its application in this field becomes more and more popular with the increasing number of instruments installed. Thus chemical information is much more easily available. The most important condition in identification of gemstones is to work non-destructively. This premise and the need to obtain chemical data are entirely fulfilled by microprobe technique.

Analysing a cut emerald in this way yields important information, as shown above. If concentrations of Na_2O and $MgO > 1.0\%$ are detected, it seems that such material can be considered as natural emerald. Only Colombian emeralds tend to be purer and occasionally only slightly exceed this lower limit. New synthetic products as well as many more natural emeralds need to be analysed to obtain a more complete account of the 'invisible impurities'. Other parameters, like H_2O content and trace element concentrations, are potential features for a separation as well. But their determination is either not non-destructive or the method is not yet a routine procedure.

ACKNOWLEDGEMENTS

Thanks are due to Dr E. Frank for his help in microprobe analysing. Mr Chisholm's critical proof reading led to a better manuscript and is very much appreciated.

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For the APPENDIX, see next page.

[*Manuscript received 11th June, revised 19th August 1981.*]

APPENDIX: Microprobe partial analyses of natural and synthetic emeralds (see p.139 above).

Natural Emeralds

	Brazil		Zambia		Ecuador		South Africa		Zimbabwe		Pakistan		Colombia		Trapiche		Austria		
SiO_2	64.7	63.6	63.7	63.9	65.6	65.9	64.9	65.4	63.7	63.2	64.2	63.7	66.4	66.6	65.2	64.6	63.0	63.4	SiO_2
Al_2O_3	16.1	13.4	14.2	14.9	16.9	16.4	14.8	16.6	14.3	14.1	14.8	13.7	16.9	17.7	16.3	16.3	14.3	14.5	Al_2O_3
TiO_2	.0	.0	.0	.1	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.1	.0	.0	TiO_2
FeO	.6	.8	.7	1.1	.7	.8	.8	.7	.4	.6	.4	1.3	.0	.0	.0	.0	.7	.5	FeO
MgO	1.8	3.0	2.4	2.1	1.4	1.7	2.6	1.6	3.1	2.6	2.7	2.4	1.4	1.0	1.0	1.2	2.4	2.6	MgO
MnO	.0	.0	.0	.0	.0	.0	.1	.0	.0	.0	.0	.1	.0	.0	.0	.0	.0	.0	MnO
Cr_2O_3	.4	.0	.4	.3	.2	.2	.2	.2	.5	.6	.8	1.4	.2	.3	.2	.2	.1	.2	Cr_2O_3
V_2O_3	.0	.9	.0	.0	.1	.0	.1	.0	.0	.0	.1	.0	.3	.4	.8	.6	.0	.0	V_2O_3
Na_2O	1.6	2.3	2.0	1.7	1.4	1.5	2.1	1.3	2.3	2.1	2.1	1.9	1.0	0.6	.8	.8	2.0	2.0	Na_2O

Synthetic Emeralds

	Lechleitner								Japan								
	Emerita Sandwich				Linde		Chatham		Crescent vert		Gilson			Zerfass	Lennix		
SiO_2	64.7	64.6	65.2	65.9	66.1	66.2	66.8	68.0	67.1	66.8	67.6	66.3	66.9	66.7	66.4	66.0	SiO_2
Al_2O_3	13.9	18.0	18.2	17.7	18.6	18.8	19.5	19.1	19.8	19.9	19.3	19.3	19.4	19.4	18.1	18.7	Al_2O_3
TiO_2	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	TiO_2
FeO	.0	.0	.2	1.1	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	FeO
MgO	.3	.0	.2	.1	.0	.2	.2	.2	.3	.3	.0	.4	.0	.2	.0	.0	MgO
MnO	.1	.0	.0	.0	.0	.0	.0	.0	.0	.1	.0	.2	.0	.0	.0	.0	MnO
Cr_2O_3	7.0	.6	.5	.5	.8	.5	.4	.8	1.0	.9	.3	.6	.8	1.0	1.4	1.9	Cr_2O_3
V_2O_3	.0	.0	.0	.0	.0	.0	.1	.0	.1	.0	.0	.1	.0	.1	.0	.0	V_2O_3
Na_2O	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.1	.0	.0	.0	Na_2O
Cl	.0	.0	.0	.0	.3	.4	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	Cl

for analytical details see Hänni (1980)