An unusual emerald

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An Unusual Emerald

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With 6 figures in the text

Abstract

The paper describes unusual gear shaped emeralds. These emeralds are composite crystals consisting of a central hexagonal core of poor quality emerald and an overgrowth of good quality emerald on the prism faces of the core. This overgrowth has a slightly longer a axis and greater ω than the core. The c axis of the overgrowth, however, is slightly smaller. It is concluded that these variations are due to higher content of Cr_2O_3 in the later overgrowth. The growth history of these composite crystals is discussed.

Sometime back I obtained from one of my friends and former pupil Shri N. K. Agrawal some pieces of unusual emeralds reportedly from Columbia. The present paper describes the preliminary work carried out on them.

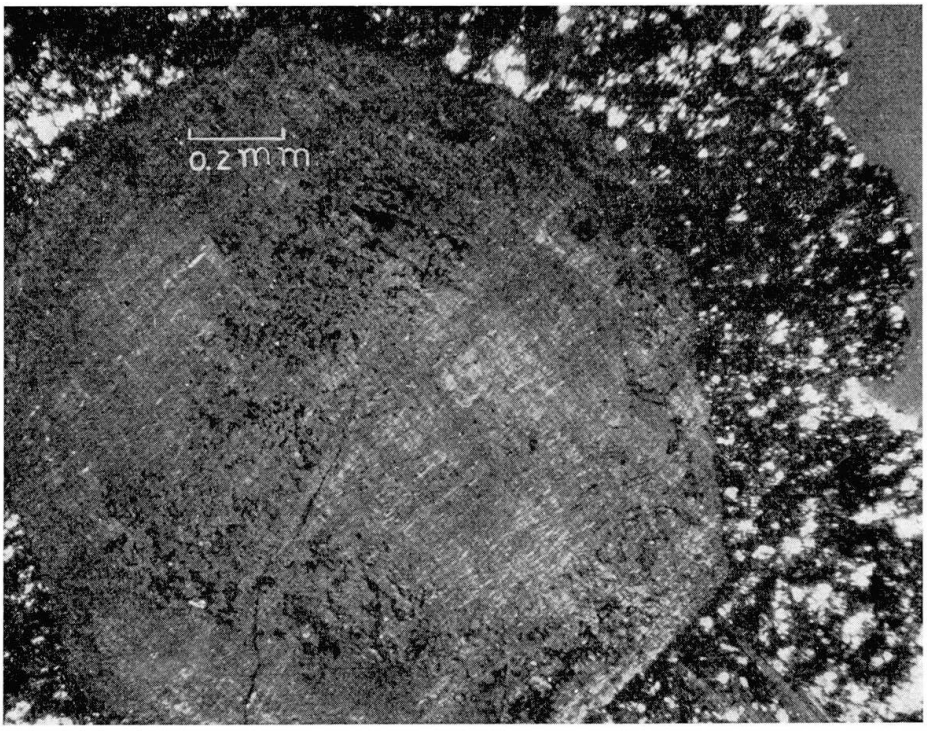

Fig. 1. Basal section of emerald. Nicols x.

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These emeralds occur as small crystals on the average 8 mm long and 4 mm wide. The most unusual thing about them is their shape which resembles the gears of a cane crusher (Figs. 1, 2). The core of these crystals is almost invariably of hexagonal shape (a in Fig. 2). Only in one solitary case a departure from this was observed. The diameter of the central core is not necessarily uniform throughout the length of the crystal. In some cases it tapers at one end. The core has a very pale green colour, is non-pleochroic and even if it is classified as emerald it is decidedly of poor quality. Dark green, pleochroic, good quality emerald occurs as an overgrowth on the prism faces of the core (b in Fig. 2). It has a saw-tooth contact with the core with the intervening spaces filled by a very fine-grained clay-like matrix (c in Fig. 2). Quartz is one of the important constituents of the matrix. It is, however, very difficult to identify the minerals of the matrix by usual optical methods.

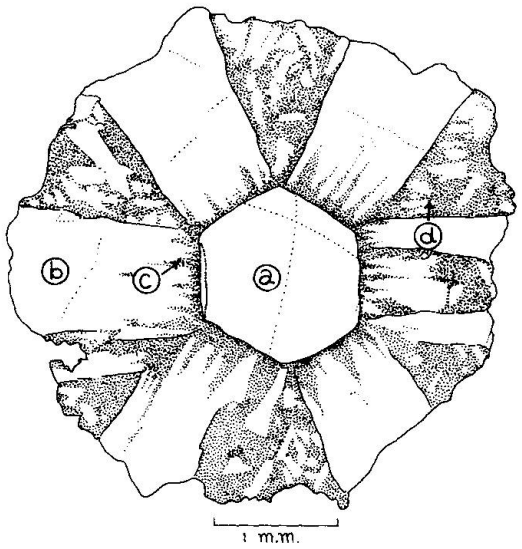

Fig. 2. Schematic diagram of the complete basal section of emerald.

The rapid growth of emerald on the prism faces of the core has left some gaps, in between their prism faces (d in Fig. 2). These gaps are now occupied by the clay-like matrix. The formation of stringers of emeralds at 60° to each other can occasionally be observed in the matrix occupying these gaps. But on the whole they are comparatively free of the later growth of emerald. The peculiar shape of these crystals is, therefore, due to the uneven growth of emerald in a horizontal direction. The finer details of their growth are still more interesting, and particularly manifest under crossed nicols. The core, in these conditions, shows a sort of grating structure. Such a structure has been described in beryls (CHAUDHARI, 1956) but it is rather unusual in aquamarine-like cores. It might be due to thermal strain. Both the core and the overgrowth of emerald show distinct biaxiality which is more pronounced in the

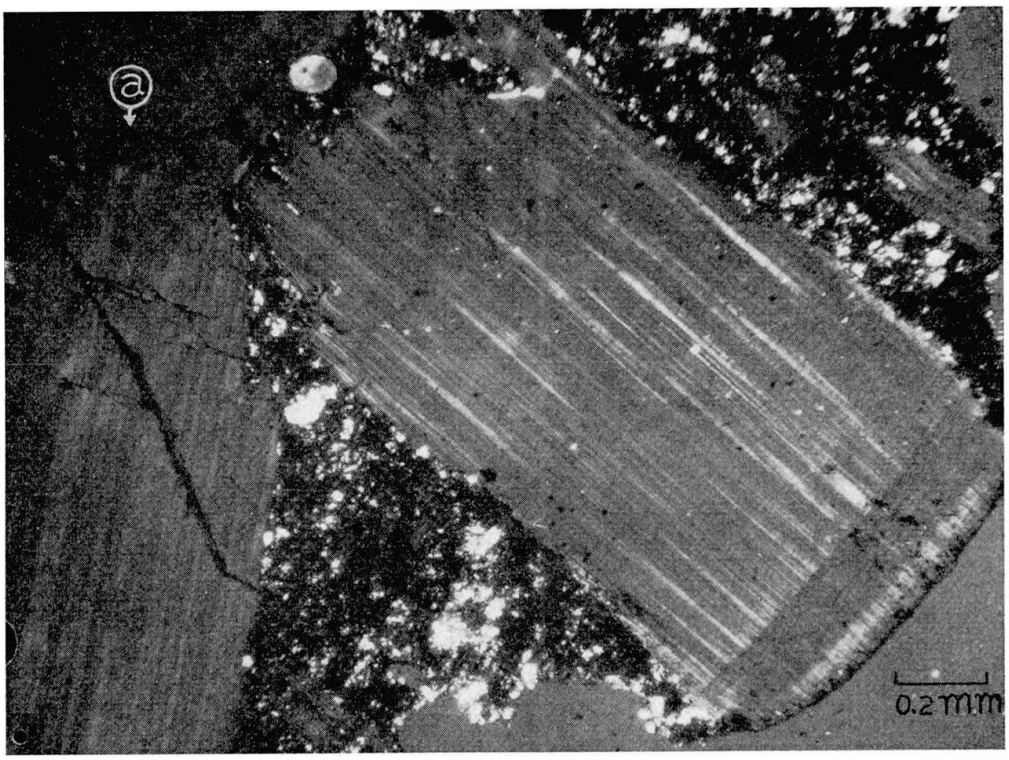

Fig. 3. Basal section.

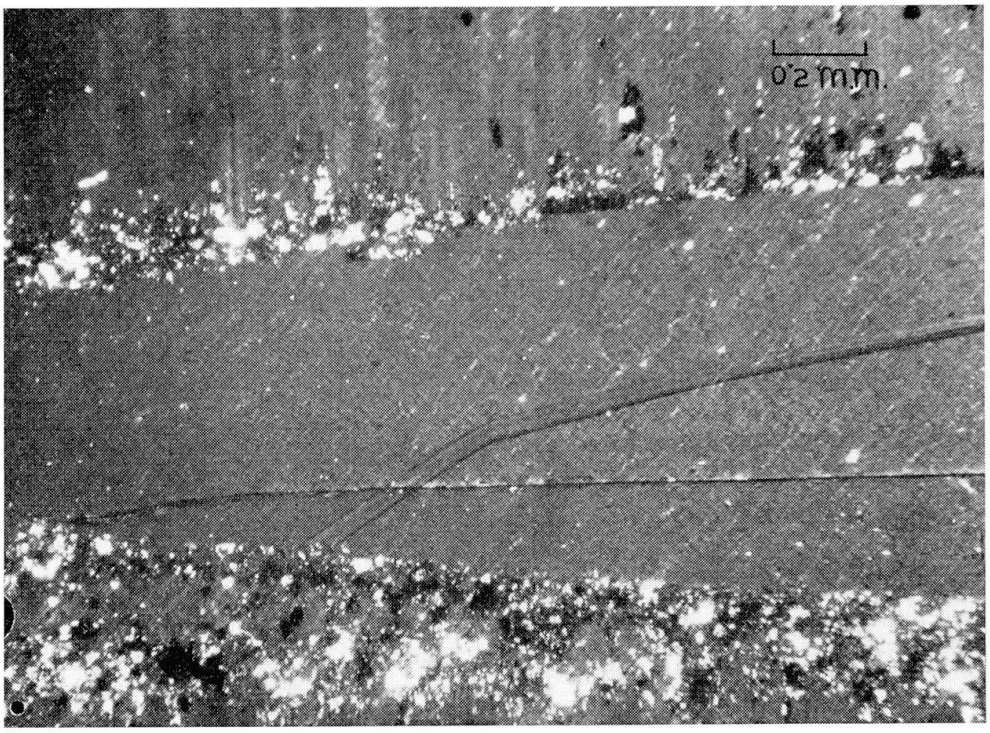

Fig. 4. Prismatic section. Nicols x.

Fig. 3 and 4. Growth striae in emerald.

overgrowth. Under crossed nicols the overgrowth shows fine growth striae (Fig. 3) which are very narrow on the (0001) face and comparatively broad perpendicular to it (Fig. 4). In one case the growth striae are seen to penetrate deep into the core. This new boundary with the core is again parallel to the older one (a in Fig. 3). Indeed at first sight no penetration of the core by the later growth is observed. It is only on close scrutiny that it becomes noticeable. The corrosion of the core, parallel to the prism face, by the later emeraldine growth is thus evident.

EXAMINATION OF THE EMERALD

Small samples from a and b (Fig. 2) were taken from the crystal for X-ray and optical studies. The paucity of material precluded chemical analysis. The cell dimensions of these samples were determined from their diffractograms, using quartz as internal standard. Two different smear mounts of each sample were run in the diffractometer under identical operating conditions. The averaged measurements of these charts were used to calculate the a and c lengths. The refractive indices were determined for sodium light (Table 1). There is an increase in a and slight decrease in c in the emerald as compared to the core. The R. I. ω also shows slight increase in the overgrowth. The entry of larger trivalent ions in $R^{3+}O_6$ sites increases both ω and a and causes slight decrease in c (FRONDEL and ITO, 1968; SCHALLER et al., 1962). Since

Table 1. *Data of Emerald*

Sample	Colour	a (Å)	c (Å)	ω
Outer overgrowth.	Deep Green	9.209	9.189	1.583
Core	Very Pale Green	9.199	9.194	1.580

the overgrowth of emerald has a deeper green colour than the core we may attribute the increase in these parameters to higher Cr_2O_3 content in the overgrowth.

It is generally regarded that the deep green colour of emerald is due to its Cr_2O_3 content which in some specimens attains 2.0% (FLANIGEN et al., 1967). It seems, however, that Cr_2O_3 *alone* may not be responsible for its colour. A basal plate of emerald heated to 900° C for 9 hours showed interesting changes. There was no noticeable change in the central core. Considerable decolouration took place in the overgrowth. It developed moreover an overtone of yellowish tinge. An examination of the microsection of the heated specimen shows numerous extremely small yellow particles which are difficult to identify because of their size. They appear to be of V_2O_5. The decolouration of emerald, therefore, appears to be due to the change in the valency state

of one or more chromophoric ions of the transition metals. The important chromophoric ions in emerald are Cr^{3+}, V^{3+} and $Fe^{2+} + Fe^{3+}$. The change of Fe^{2+} to Fe^{3+} is known to cause decolouration in beryl (DEER et al., 1962). But since the green colour in emerald is not due to Fe^{2+} its role in the decolouration of emerald must be insignificant. Chromium oxides in glass impart colours ranging from green, yellow green to orange depending on the proportion of Cr_2O_3 to chromate. Pure chromate glass is formed under high oxygen pressures (MOREY, 1954). Since some colour is still retained after heat treatment and high oxygen pressure is required for the conversion of Cr^{3+} to chromate the decolouration in emerald does not seem to be due to the conversion of Cr^{3+} to the high valency state, although it may have played a contributory part towards it. Vanadium is almost always present in emeralds. V^{3+} gives green colour whereas V^{5+} imparts yellow colour (MOREY, ibid.). Beryls grown with a V_2O_5 flux are colourless (LINARES, 1967). The change of V_2O_3 to V_2O_5 therefore appears to be responsible for the decolouration of emerald. The participation of V^{3+} in giving green colour to emerald has been suggested on the basis of infrared spectroscopic studies (WOOD and NASSAU, 1968).

THE GROWTH HISTORY

These emerald crystals are composite crystals made of two distinct entities. The core is clearly different from the overgrowth in chemical composition, cell dimensions, optical properties and its growth history. The emerald was deposited over it much later under greatly changed physical and chemical conditions, with a significant increase in the Cr_2O_3 content. The evidence at hand indicates that the overgrowth took place at the expense of the fine-grained matrix which shows interlaminations and a saw-tooth contact with the emerald particularly in the early stages of growth near its contact with the core. It seems that the rate of reaction in the early stages was not fast enough to assimilate the fine-grained matrix into emerald. In the later stages of growth, some distance away from the core, a faster rate of reaction is indicated by more uniform and homogeneous growth of emerald. This uniform

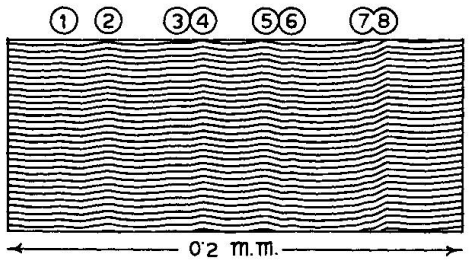

Fig. 5. Schematic diagram showing twists in growth striae.

linear growth of emerald continued for the major part of its crystallogenic history. Its culmination, however, again witnessed, in some crystals, as many as eight changes in growth. Each such fluctuation is registered by a sudden twist in the linear growth striae (Fig. 5).

Since the overgrowth of emerald is of a uniform deep green colour without any apparent heterogeneity, the chemical potential seems to have remained nearly constant throughout its growth. Thus, the growth history of this emerald is, in principle, comparatively simple in spite of the complexity of finer details. Starting from the core, the seed on which the subsequent nucleation took place, only one major change in chemical environment took place. It is marked by the first epitaxial growth of emerald on the prism face of the core. After this event the chemical environment remained nearly uniform and constant. However, the physical conditions underwent a number of fluctuations enumerated above (Fig. 6).

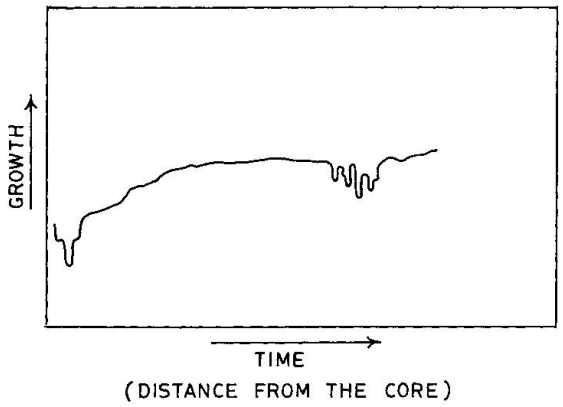

Fig. 6. Diagrammatic representation of the growth history of emerald.

It is difficult to visualise the causes of such a varied growth history. Natural emeralds do not normally show so complex features. All these peculiarities are indeed more compatible with synthetic growth. However, it is not possible, on the basis of available data, to draw any definite conclusions about its origin.

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