TRAPICHE EMERALDS FROM CHIVOR AND MUZO, COLOMBIA

K. Nassau and K. A. Jackson, *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974*

Abstract

Emerald beryl from Chivor, Colombia, having a clear central region and a sectored outer area has been termed "trapiche" emerald. Examination of a large number of specimens shows a considerable variation of the internal structure; nevertheless all are single crystals.

Two distinct growth regimes separated by a transition region are indicated: during the first, the central hexagonal, slightly tapered, clear emerald prism grew; the second involved the simultaneous growth of emerald and albite from a fluid dose to saturation with respect to both phases. The outer sectored emerald regions are separated from each other by emerald intermixed with large amounts of albite. The transition region between the inner prism and the outer sectored region also contains large amounts of albite.

A somewhat similar emerald, with a dark inner core and clear, sectored outer region, occurs at Muzo, Colombia, and can also be explained by two separate growth regimes.

Introduction

Among the emeralds found in the Chivor, Colombia, emerald mine is an unusual type known as "Trapiche" (trah-pee'-chay), after the Spanish word for the sugar cane crushing gear it resembles (McKague 1964). If large enough, such crystals are cut up for the usable gem-grade emerald they may contain, if too small, they are generally discarded at the mine, so that only small quantities of recognizable form are ever seen.

Descriptions based on examinations of a few crystals each have been given by McKague (1964), Leiper (1967), and Schiffman (1968). None of these has given any suggestions of the growth process producing the unusual morphology, other than noting an apparent twinning. A similar emerald from the Muzo Mines, Colombia has been reported (Muñoz, 1948), again without any explanation.

We have examined over a thousand very small Chivor trapiche emeralds and fragments courtesy of A. Fitzgerald Co., New York City, as well as smaller quantities of larger crystals courtesy of Dr. F. H. Pough of Santa Barbara, California, Mr. F. P. Yeager of New York City, and Mr. R. Crowningshield of the Gemological Institute of America, New York City. Mr. Crowningshield also permitted us to examine two rare crystals from the Muzo district which will be discussed separately at the end of this report. None of these specimens was in matrix.

The Chivor Emerald Occurrence

The Chivor Mine, previously also known as the Somondoco Mine after the nearest town, is located in central Colombia, about 90 km

northeast of Bogota. The area consists of sedimentary clay and shale of Cretaceous origin which was highly folded and faulted, containing lenses of carbonaceous shale. There are several iron-containing bands with pyrite changing to geothite to hematite. There is also some limestone in the area. Fissures and pockets in the clay and shale contain quartz and pyrite, followed later by emerald and albite. This mineralization is viewed as originating from deep-seated hydrothermal solutions. The detailed geology has been given by Mentzel (in Rainier, 1940) and Johnson (1961).

The term "morralla" is used for a low grade opaque emerald which is mostly poly-crystalline. The most common inclusions in these Chivor emeralds are quartz, albite, pyrite, goethite, and, in three-phase inclusions, halite, a liquid, and a gas (Schiffman, 1968; Johnson, 1961). A spectrographic analysis given by Johnson (1961) for a pale green crystal indicated in addition to the expected Be, Al, and Si, MgO 0.1 to 0.01 percent, Fe_2O_3 0.001 to 0.0001 percent, and Cr_2O_3, $V_2\acute{O}_5$, and Na_2O all less than 0.0001 percent. The water content does not appear to have been checked.

EXAMINATION

As shown in Figure 1, the Chivor trapiche emeralds are generally elongated prisms of roughly hexagonal cross-section. Sizes of specimens available to us ranged up to $\frac{1}{2}$ inch long and up to $\frac{3}{8}$ inch in diameter, although a specimen $1\frac{1}{2}$ inch diameter and 3 inches long has been seen by R. Crowningshield (this contained gem grade material and was scheduled to be cut up).

There is considerable variation in the cross-sectional appearance, and the photograph of Figure 2 and the schematic drawings of Figure 3 illustrate the range observed. In addition, many intermediate types were seen. As previously noted (McKague, 1964), the central core usually has a taper. We have observed crystals which at one end may have the appearance of Figure 3 B, and the other end may show no central core at all, as in Figure 3 C. The interior lines and shaded regions in Figure 3 indicate white to gray opaque material appreciably softer than the emerald and may be stained brown to red by iron on the surface; clear regions represent more or less transparent emerald. The white material may be quite thick or may form a very thin dividing plane between core and arms only. There are often feathery extensions into the arms, as shown in Figures 1 to 3. The central core usually contains better gem quality emerald than the outer regions. The outer clear regions, which we term arms, have been previously described as trapezohedral (McKague, 1964) or trapezoidal (Schiffman, 1968) prisms, or rays (Leiper, 1967).
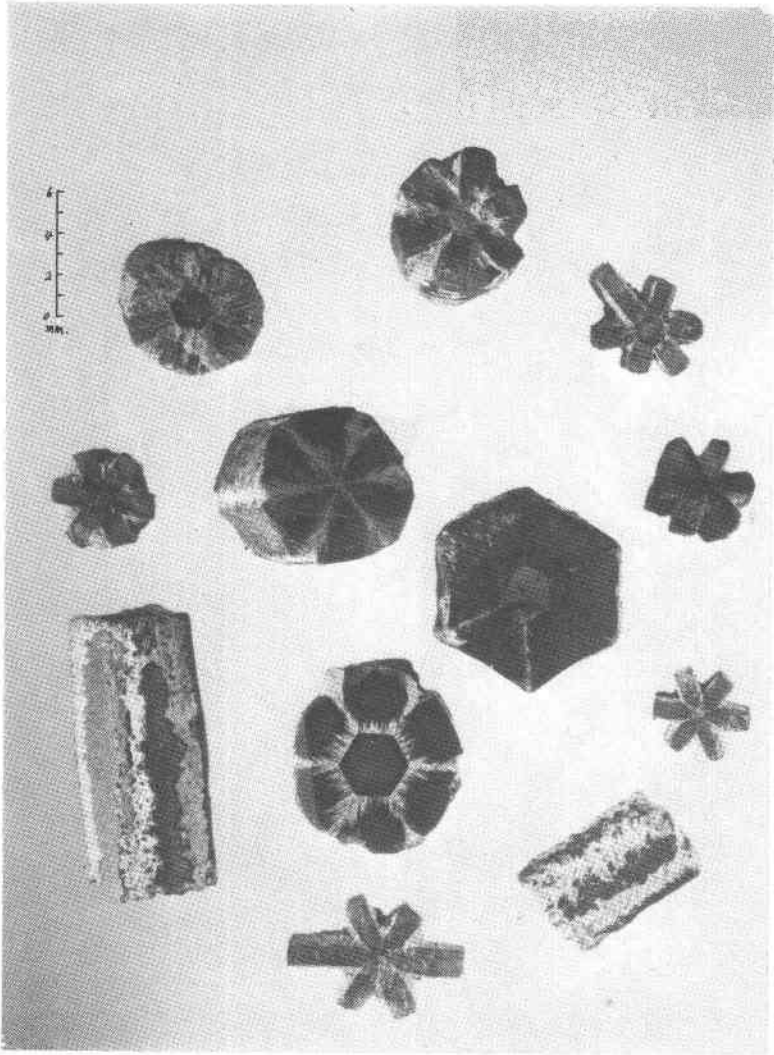
Fig. 1. Chivor trapiche emeralds.

These reports have shown illustrations of types A, B and E of Figure 3 only. The development shown by the trapiche emeralds conforms to the six-fold symmetry except for two specimens which had one or two arms appreciably longer than the others. These are included in Figure 1, and one is illustrated in Figure 3 F.

Powder X-ray diffraction patterns show only emerald (beryl) in the clear side-arms and central core. The whitish substance in between the
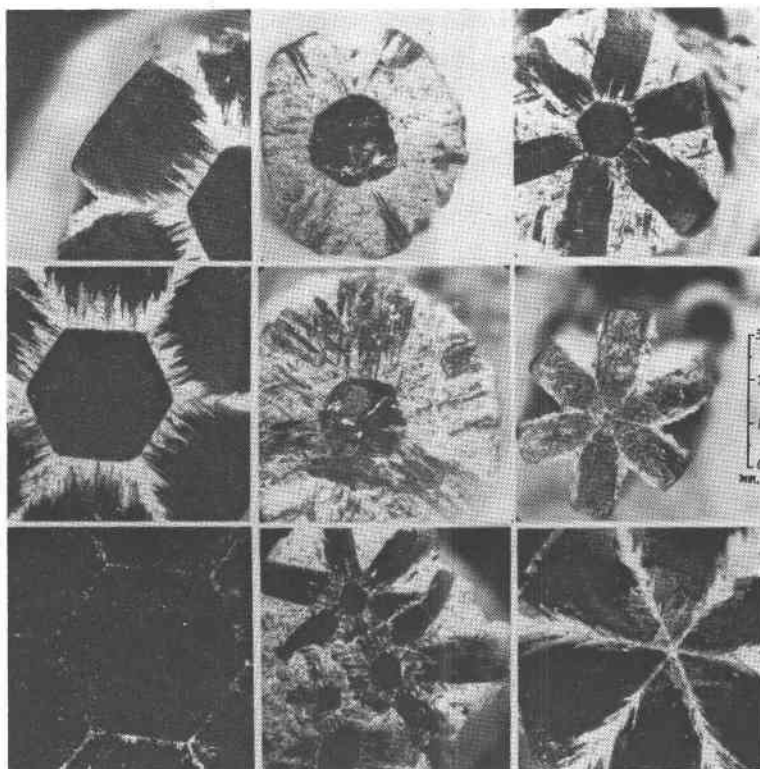
Fig. 2. Cross-sections of Chivor trapiche emeralds.

side arms of a crystal of type E, of Figure 3 is a mixture of emerald and albite. A Laue back-reflection diffraction pattern on the central core and on the six side arms shows the single crystal emerald to have the same orientation, the *c*-axis being along the hexagonal symmetry axis of the crystal as expected.

Most surprising, however, is the observation that the white filling between the arms also gives a single-crystal emerald pattern, with the same orientation as the rest of the trapiche, a result which was confirmed on two other crystals. Accordingly, the trapiche emerald as a whole is a single crystal of emerald, with light to massive inclusions of albite. The relative softness of the white material and the apparent parting (McKague, 1964) are now seen as originating from a weakening of the emerald by the large amount of included albite. Twinning of the emerald does not seem to be involved. Single crystal diffraction of X rays was not obtained from the albite, presumbaly because it is polycrystalline.

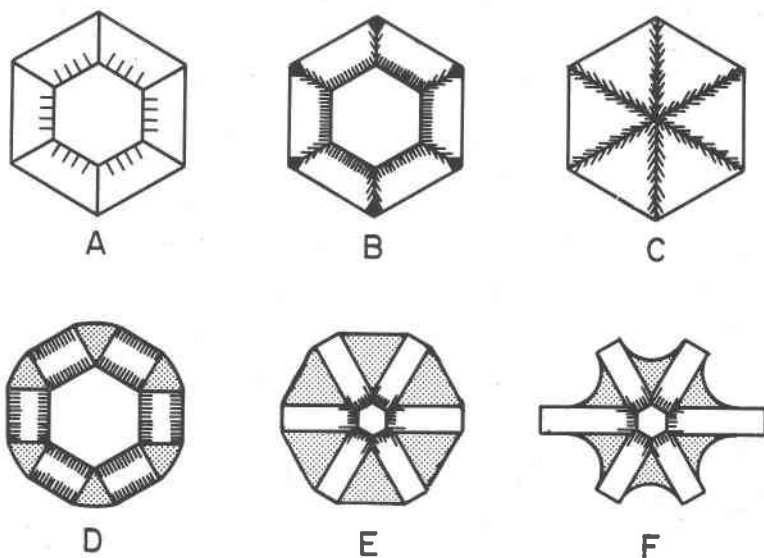Polarized infrared absorption spectroscopic examination using the

Fɪɢ. 3. Schematic cross-sections of Chivor trapiche emeralds.

technique described by Wood and Nassau (1968) shows the presence of appreciable amounts (of the order of 1%) of types I and II water, the latter implying an appreciable alkali content. There is about 10 percent more water in the outer arms than in the central core of the specimen examined.

MODE OF GROWTH

The evidence indicates that growth began with the clear, tapered, central beryl prism in a normal fashion. After a transition stage which produced the albite-containing outline of the central core, growth of the outer sectored region is interpreted as the basis of a eutectic type growth with both beryl and albite growing simultaneously. The beryl grew parallel to the faces of the original prism and a two phase beryl-albite structure grew at the corners.

In the regions of clear beryl outside the central prism there are striations parallel to and perpendicular to the faces of the prisms. These markings indicate that the lateral faces of the trapiche emeralds grew with a plane interface. This plane interface moved out parallel to the original faces of the prism. Because of these markings we have discarded the possibility that the two-phase region of growth from the corners of the prism occurred first, followed by a filling-in of the material at the prism faces. If this had occurred, there would be growth markings out

from the corners, rather than parallel to the original prism faces. The growth markings indicate clearly that the two-phase growth at the corners did not precede the single phase beryl growth of the flat faces but that the two occurred simultaneously.

During two-phase growth the two phases usually, but not always, originate from a single pair of nuclei. In the case where a crystal of one of the phases was pre-existing, one would expect, as indeed happened in this case, that the growth of the beryl phase maintains the orientation of the original crystal. This kind of structure commonly occurs in metal eutectic systems where it has been studied extensively (Kraft, 1963; Liebmann and Miller, 1963). One of the phases of the eutectic will grow from a single crystal of that material. The other phase forms either from a single nucleus which subdivides extensively or from many nuclei, and grows in an intimately mixed fashion with the starting phase. Thus the observation that all of the beryl present in a single trapiche emerald has the same orientation can be readily accounted for in terms of the eutectic growth. Multiple nucleation of the ablite probably occurred since it does not appear to be all one single crystal. The suggestion of McKague (1964) that there was a transformation which occurred after the growth of the crystal to produce fine grain beryl is inconsistent with the fact that the beryl is all of the same orientation.

One of the problems in the morphology of these emeralds is to understand why the two phase growth occurred at the corners of the prism. During the growth of a polyhedron, the corners and edges are in a more favorable position for diffusion than the centers of the faces. The concentration of rejected species should therefore be highest near the center of the faces. This effect leads to the well-known hopper growth of crystals where the corners and edges of the crystal grow more rapidly, the centers of the faces becoming hollow and depressed. This diffusion effect also leads to dendritic types of growth. In the present instance, however, the precipitation of the second phase occurred preferentially at the edges of the crystal. This growth form has been termed "sectored layerite" (Smith, 1963). The observed morphology is probably due to the anisotropic growth rate of the crystal. The rapid lateral growth of new layers which form on the side faces of the prisms suppressed the growth of the second phase at these places. At the corners, however, where the new layers must nucleate, the difficulty of initiating new layers permitted the continued presence of the second phase.

A similar phenomenon is observed, infrequently, in snow flakes as illustrated in Figure 4 (Bentley and Humphries, 1962). The outline of the growth form indicated by arrow *A* is the usual mode of growth. The bumps at the corner of the figure are incipient dendritic growth. The

stage labelled B indicates the growth of a hexagonal figure with the entrapment of gas at the corners. The instability which occurred at the corner is similar to the growth of two phases in the trapiche emerald. In this snow flake a third stage of growth occurred with spikes, C, growing at the corners and subsequent filling-in between the spikes. Here the growth returned to the more usual growth form, dominated by diffusion from the corners. The outline of the shape at B, however, and the presence of the gas bubbles at the corner of the figure indicates clearly that here too is a case where a second phase has nucleated at the corners.

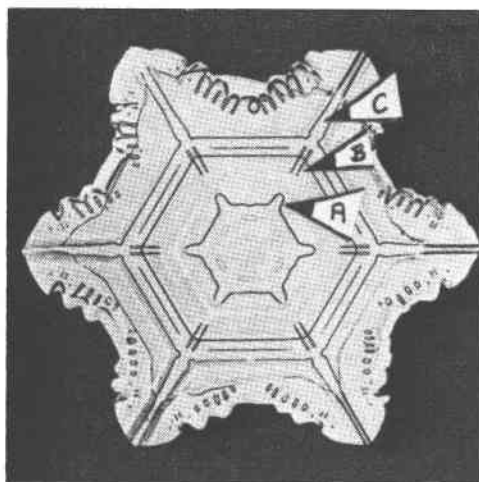There are several other phases present in very small amounts as micro-

FIG. 4. Snow flake showing several stages of growth (after Bentley and Humphries, 1962).

scopic crystals in the two-phase region of the emeralds, that is, at the corners where the albite and beryl are growing simultaneously. The inclusion of the other phases indicates the complexity of the solution from which the emeralds were growing. We have made no attempt to identify any of these other phases.

The other problem in the morphology of these emeralds is the nature of the transition between the inner and outer growth regions. This region is up to 1 mm thick and contains both beryl and albite. It is possible that this region was formed as the composition of the growth solution became depleted in the components of beryl and reached the two-phase beryl-albite line to produce two-phase growth on the surface of the prism; a subsequent change then led to the sectored growth.

Another possibility which could explain both the initiation and the

termination of the transition region in one mechanism, would be an abrupt increase in the growth rate. Such a mechanism is well known in the laboratory (Tiller *et al.* 1953; Müller and Wilhelm, 1964) and has been described in detail mathematically (Smith *et al.*, 1955). This process is usually responsible for compositional zoning in crystals grown from multi-component melts. Briefly, it occurs because the foreign species (in this case the components of albite) is able to diffuse away from the growing crystal at slow growth rates. When the growth rate is increased abruptly, the distance over which diffusion can occur, *i.e.*, the width of the boundary layer around the crystal, decreases. Immediately after the increase in growth rate, the pre-existing boundary layer cannot diffuse away rapidly enough and so the composition of the rejected species, increases at the interface. For a short period the excess will be incorporated as a separate phase within the growing crystal until the boundary layer around the crystal is reduced to the thickness characteristic of the new growth rate, which then yields the sectored growth in the case under discussion. The transition layer would then be produced during the brief interval when the boundary layer is becoming thinner by diffusion, a period estimated to last no more than a few minutes if one uses diffusion coefficients appropriate for normal hydrothermal systems. The more viscous the system, the longer a transition period could be involved.

In the absence of detailed knowledge of the local conditions at Chivor it is not possible to suggest detailed parameters involved in the various stages of the growth of trapiche emeralds. It is likely that the transition occurred at the same time throughout the relatively restricted area in which this type of emerald is found. This is consistent with the fact that the transition from the central prism occurs at different stages during the growth of various trapiche crystals. If the transition were due to some growth property of the beryl then we would expect them all to grow to some particular size before the transition occurred, but this is not the case. Furthermore, none of the emeralds exhibit more than one discontinuity in the growth characteristics, except, of course, for the initiation and termination of growth. It seems likely that these emeralds were all growing at the same time in the same or similar environments in a relatively small region, possibly only a part of the Chivor mine.

Muzo Trapiche Emeralds

The zoning arrangement of Muzo trapiche emeralds is quite different from the Chivor samples, yet a somewhat similar situation does exist. We have examined two specimens of this rather rare material, and have found only one reference to it (Muñoz, 1948).

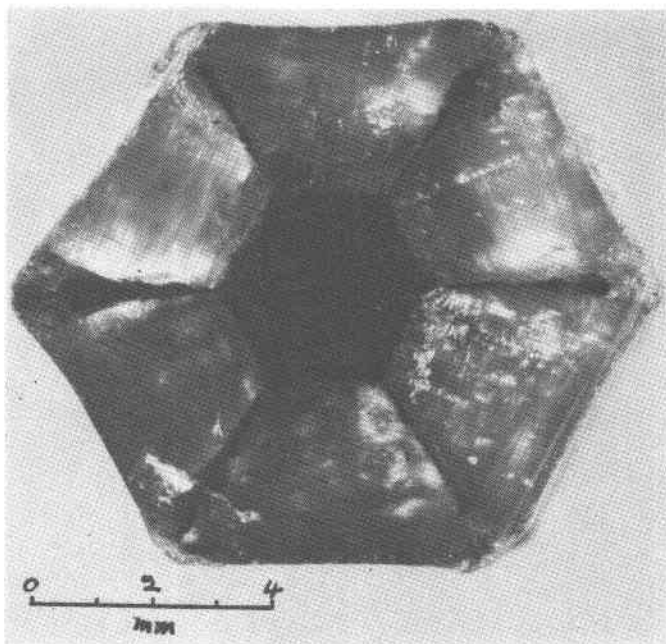The Muzo, Colombia, mining district is about 40 km NW of Chivor.

FIG. 5. Muzo trapiche emerald.

The geological environment is somewhat similar to that of Chivor, except that essentially all the shale is black with a high carbon content; there is also much calcite, dolomitic limestone, and pegmatitic bodies in the Villeta formation (Oppenheim, 1948). Emerald occurs in the shale or calcite layers in the Viletta formation associated with calcite, dolomite, pyrite, parisite, quartz, barite, fluorite, and apatite. Inclusions of carbonaceous matter are well known in Muzo emeralds (Muñoz, 1948).

The fragments from two crystals, one of which is shown in Figure 5, which we have examined, came from the same type of crystals as were briefly described by Muñoz (1948). Figure 6, combining elements from Muñoz (1948) and our own observations, shows a shematic cross-sectional drawing. In this case the central tapered hexagonal region is black and not appreciably softer than the clear emerald in the six outer sections. These are separated by sheets of dark material closely resembling the Chivor structures of Figure 2B where the sheets are, however, white from albite inclusions. The maximum dimensions were $\frac{1}{2}$ inch long and $\frac{3}{8}$ inch diameter. We have not seen any terminations which we can recognize as such.

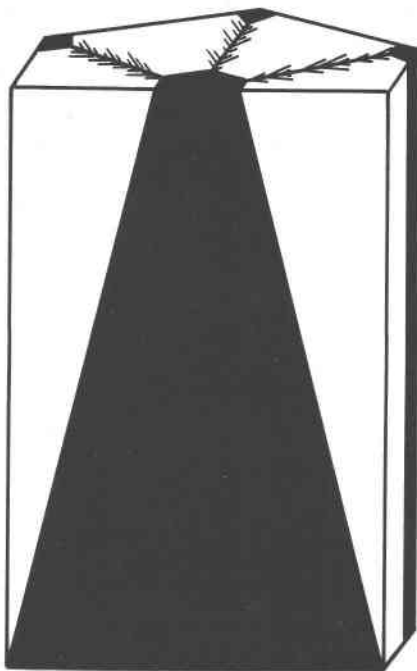Powder X-ray diffraction shows only emerald in both central core and

Fig. 6. Schematic cross-section of a Muzo trapiche emerald
(in part after Muñoz, 1948).

outer arms. Back reflection Laue patterns again demonstrate that one single crystal is involved with none of the twinning suggested by Muñoz (1948). The spectrochemical analysis results of Table I indicate an appreciably higher Fe, Ti, and Ca content in the central core. On heating this black material to red-heat in air the color changes to green with traces of orange-brown, presumably due to loss of the carbanaceous content. Unfortunately, not enough material was available for further testing.

TABLE 1. SPECTROCHEMICAL ANALYSIS OF TRAPICHE EMERALD FROM MUZO, COLOMBIA

Range	Outer Arms (green)	Inner Core (black)
>5%	Be, Al, Si	Be, Al, Si
~1	—	Ti, Fe
0.1–0.9	Cr, Fe, V, Mg	Cr, V, Mg, Ca
0.001–0.009	Ti, Mn	Mn, B, Zr, Na, Li
0.0001–0.001	Ca, Na, Li, Cu	Cu, K

Absorption spectroscopy (Wood and Nassau, 1968) on the clear outer arms again indicates the presence of water types I and II and alkali. Also observed was a noticeable vanadium absorption in addition to the chromium absorption, as expected from the analytical data: an X-ray fluorescence analysis on the clear material gave 0.10 percent Cr and 0.12 percent V. Both chromium and vanadium thus contribute to the green color. The presence of both chromium and vanadium in Muzo emerald was noted by Goldschmidt (1958).

The growth mechanism is in most respects similar to that deduced for the Chivor trapiche emeralds, except that at Muzo the change in composition and color probably resulted from an abrupt reduction in the growth rate. In the black tapered inner hexagonal core growth was very rapid, resulting in the trapping of the carbonous material as well as appreciable amounts of Ti, Fe, and other impurity elements. With the abrupt deceleration of growth, the clear emerald of the arms resulted. The impurities were now able to diffuse away from the flat faces and were trapped only at the corners as in the second stage of the Chivor trapiches. An alternative explanation of the transition would be an abrupt change in the growth medium composition to a much lower carbonaceous material concentration.

REFERENCES

BENTLEY, W. A., AND W. J. HUMPHRIES (1962) Snow Crystals. Dover Publications, New York, p. 76.

GOLDSCHMIDT, V. M. (1958) Geochemistry. Clarendon Press, Oxford, p. 212.

JOHNSON, P. W. (1961) The Chivor emerald mine. J. Gemmology 8, 126-152.

KRAFT, R. W. (1963) The structure of the Mg-Mg₂Sn eutectic. Trans. Met. Soc. AIME 227, 393.

LEIPER, H. (1967) Rare trapiche emerald crystals show unique twinning evidence. Lapidary J. 21, 565.

LIEBMANN, W. K., AND E. A. MILLER (1963) Preparation, phase-boundary energies, and thermoelectric properties of InSb eutectic alloys with ordered microstructures. J. Appl. Phys. 44, 2653.

McKAGUE, H. L. (1964) Trapiche emeralds from Colombia. Gems and Gemmology 11, 210–213 and 223.

MÜLLER, A., AND WILHELM, M. (1964) On periodic changes of temperature in liquid InSb causing stratified inclusions of Te in crystallizing InSb. Z. Naturforsch., A, 19, 254.

MUÑOZ, G. OTERO (1948) Emeralda di Colombia. Bank of the Republic of Colombia, Bogota, Colombia, pp. 122–123.

RAINIER, P. W. (1930) The Chivor—Somondoco emerald mines of Colombia. AIME Trans. 90, 204–221.

OPPENHEIM, V. (1948) The Muzo emerald zone, Colombia, S. A. Econ. Geol. 44, 31–38.

SCHIFFMAN, C. A. (1968) Unusual emeralds. *J. Gemmology*, 11, 105–114.

SMITH, F. GORDON (1963) *Physical Geochemistry*. Addison-Wesley, p. 60.

SMITH, V. G., W. A. TILLER AND J. W. RUTTER (1955), A mathematical analysis of solute redistribution during solidification. *Can. J. Phys.* 33, 723.

TILLER, W. A., K. A. JACKSON, J. W. RUTTER, AND B. CHALMERS (1953) The redistribution of solute atoms during the solidification of metals. *Acta Met.* 1, 428.

WOOD, D. L., AND NASSAU, K. (1968) The characterization of beryl and emerald by visible and infrared absorption spectroscopy. *Amer. Mineral.* 54, 777–800.