

CARBONADO: A MICROSTRUCTURAL STUDY

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ABSTRACT

Brazilian carbonados consist of mostly anhedral, randomly oriented diamond crystallites with a size ranging from a fraction of a micron to over 20 μm . These crystallites are aggregated and interlocked into porous polycrystalline masses with a microstructure reminiscent of that of ceramics. Variable amounts of inclusions consisting mainly of crystallites of an aluminum silicate are present both on the surface and inside the stones.

INTRODUCTION

Natural terrestrial and statically synthesized diamonds occur predominantly as single crystals and have been extensively studied. Polycrystalline diamonds on the other hand have generated relatively little interest for many years. This situation has changed only recently, mainly because of several detailed studies on meteoritic diamond which is black and microscopically polycrystalline (Wentorf *et al.*, 1961; Lipschutz *et al.*, 1961; Lipschutz, 1962; Lipschutz, 1964; Sciacca *et al.*, 1964; Kalashnikov *et al.*, 1966; De Carli, 1967; Kennedy, 1967). Meteoritic diamond is thought to have been generated from graphite in a very fast diffusionless solid-state phase transformation under the effect of the shock wave set up when the meteorites hit the earth or possibly extraterrestrial bodies before impacting on the earth (Anders *et al.* (1966)). Another recent development is the explosive shock synthesis of diamond which was first reported by De Carli *et al.* (1961). Such diamonds are also polycrystalline and have significant microstructural similarities with the meteoritic variety, such as very small crystallite size and preferred orientation of the crystallites (Trueb, 1968).

To our knowledge, no detailed work on the microstructure of natural terrestrial polycrystalline diamond has been published recently. Among the several known varieties, the Brazilian carbonado is the most important one; other types such as ballas, framesite and "stewartite" have been found in Brazil, South Africa (Moissan, 1893; McDonald, 1914; and the Soviet Union (Kravtsov, 1960). These minerals are known to be much tougher than monocrystalline diamond and are therefore attractive both from a scientific and technological point of view. Polycrystalline diamonds appearing to be similar to carbonado (Wentorf *et al.*, 1961), and ballas (Kalashnikov *et al.*, 1966) have also been synthesized statically in recent years.

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The term "carbonado" was originally coined by Brazilian miners to designate the opaque, black or gray polycrystalline diamond which is found mainly in the highlands of Bahia and in smaller amounts in Venezuela and British Guiana (Fettke *et al.*, 1933; Kerr *et al.*, 1948). Both meteoritic and shock-synthesized diamond have a grayish color and are occasionally called carbonado or carbonado-like. While this designation tends to be used indiscriminately for all kinds of dark diamond, it is not justified in the case of explosively shock-synthesized and meteoritic material owing to differences in the conditions of formation and of microstructure.

Carbonado is used industrially, particularly in drill bits designed to pierce very hard rocks where the extraordinary toughness of these diamonds, which exceeds that of monocrystalline diamond, is advantageous. Some carbonado is also crushed for use as loose abrasive. The total production of carbonado is relatively small (30,000 carat/year) compared to the world production of industrial diamond (over 30 million carat/year), which may have contributed to the relative lack of interest it has generated in the past.

According to Kerr *et al.* (1948), carbonado has been known as a distinct form of diamond since at least 1843. Early investigators, such as Roth *et al.* (1926) noticed that the density of carbonado is lower than that of monocrystalline diamond and concluded that carbonado is a mixture of diamond and amorphous carbon, which would also explain its color. Gerlach (1924) postulated the presence of amorphous carbon or graphite as a binding agent between diamond crystals, but Brandenberger (1930), using monochromatic X rays, found no such evidence. The latter author concluded from the fact that the Debye-Scherrer rings were split up into small discrete reflections that carbonados are a mass of small crystallites resembling the aggregates of single crystals found in metals. Fettke and Sturgis (1933) examined a cut and polished sample of carbonado and found it to be a porous aggregate of very small irregularly shaped interlocking units with a diameter varying between 63 and 95 μm . Some of these crystallites were recognized to be octahedra. Kerr *et al.* (1948) examining a specimen from Venezuela, found that it was composed of light brown individual crystallites the size of which was estimated to be 20 μm . The dark gray color of the stone was attributed to the presence of amorphous carbon or graphite and various metallic oxides and minerals; the main impurities were found to be Si, Al, and Ti with traces of Fe, Ni, Cu, Mg, and Be. The presence of Si was explained by a white crust, thought to be chalcedony, filling minute cracks of the specimen.

Some insight into the conditions of formation of carbonado can be gained from the work of Wentorf and Bovenkerk (1961); these authors

found that lumps of black polycrystalline diamond are formed at relatively high pressures (130 kbar) and moderately high temperatures (2000°K) in the presence of a nickel-iron catalyst. Under these conditions, substantially above the equilibrium line between diamond and graphite in the phase diagram of carbon, the nucleation rate is high, which results in the growth of a great many small and imperfect crystallites. These "artificial carbonados" were found to occlude small amounts of metal catalyst and graphite. From these observations, Wentorf and Bovenkerk concluded that carbonado might form under the effect of rapid cooling-off processes at high pressures, or by a sudden increase in pressure at moderately high temperatures in a suitable plutonic environment.

EXPERIMENTAL RESULTS AND DISCUSSION

The remarkable properties of polycrystalline diamond and the unfortunate confusion between its terrestrial, meteoritic, and shock-synthesized varieties prompted us to undertake a detailed characterization of the Brazilian carbonado in the hope of demonstrating therewith some of the unique features of the most important terrestrial variety of polycrystalline diamond. In view of the considerable spread of data found in the literature concerning the density of carbonados, the size and shape of the crystallites, their aggregation, the presence or absence of binders between crystallites and the nature of impurities, it was decided to investigate specifically these points. For this purpose about fifty small carbonados, believed to be typical samples of Brazilian material, were purchased in the state of Bahia from local claim-holders who wash them out of diamond-bearing gravel and clay of old stream beds in the Sincora/Morro de Chapeo area. Our specimens were anhedral, measured 3–5 mm in their longest axis, and weighed up to 0.6 carat. Under reflected light they had a dark gray metallic luster; fractured surfaces were of a lighter gray reminiscent of cast iron. Examination with a light microscope showed that the outer surfaces exhibited a highly variable number of pores having a diameter of up to approximately 200 μm : the presence of very small crystallites, some of which had highly reflective facets, could also be recognized, as shown in Figure 1. Small lumps of a yellowish crust adhered to most of the stones, usually filling pores; this material was not affected by concentrated hydrochloric acid but could be dissolved in hydrofluoric acid. It was thus assumed that this crust consisted of silica or a silicate stained with iron oxides. Similar inclusions were also observed on fractured surfaces.

Electron probe microanalysis showed that most inclusions had essentially the same composition and appeared to be an aluminum silicate. Figure 2 shows X-ray area scans clearly outlining the inclusions mentioned above. Aluminum occurred in the yellowish-white crystallites

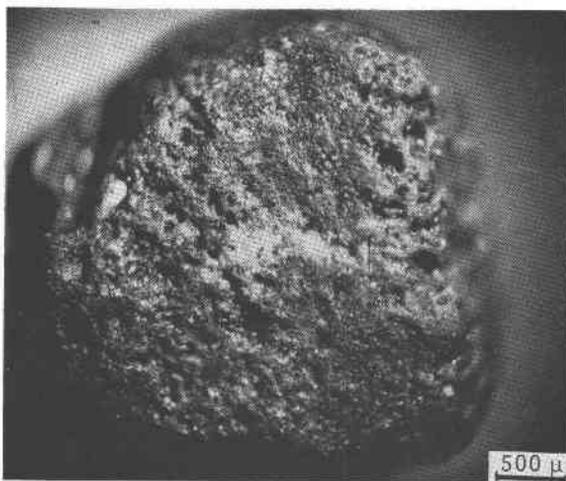


FIG. 1. Carbonado after removal of silicate inclusions in the pores (photomicrograph).

together with Si, K, and Fe. The low-level general distribution in the Al- K_{α} scan was presumably caused by the 300 Å aluminum coating applied by vapor deposition to make the examined surface electrically conductive. Silicon appeared to be the major contaminant in the examined carbonados and was concentrated in the crystalline inclusions. Calcium occurred mainly in the whitest particles, some of which also contained potassium and silicon, while others were relatively free of both of the latter elements. In most instances potassium was associated with aluminum and silicon. Only the brighter areas in the K- K_{α} micrograph in Figure 2 represent potassium, the rest being background noise. Iron occurred mainly in red-brown crystallites present as inclusions in the aluminum silicate, as shown in the Fe- K_{α} area scan. Titanium was randomly distributed; this impurity can thus be presumed to be incorporated in the diamond lattice. Chromium was also present as a minor impurity associated with iron. Copper was identified as a trace impurity at the limit of detectability (0.05–0.1%) and could not be located specifically.

Some of the particles extracted with replicas gave electron diffraction diagrams which could be identified as α -hematite. Attempts to obtain more information on the potassium-aluminum silicate inclusions were not successful. Powder X-ray diagrams from crushed carbonados gave several weak lines characteristic for quartz and many silicates. After heating crushed carbonados in oxygen at 800°C for several hours in order to burn the diamond away, a residue was obtained which represented 2.6 percent of the weight of carbonado. This yellowish-white residue was in the form of the original crystalline inclusions, but even light handling made them

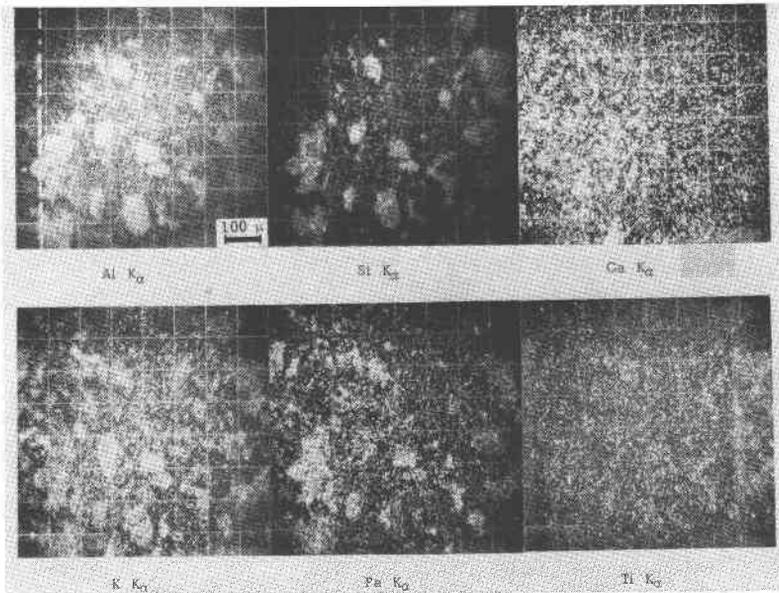


FIG. 2. X-ray area scans showing the distribution of impurities in carbonado.

collapse into a fine powder. X-ray diffraction diagrams from the calcined material gave an astonishingly good fit with the monazite structure, but the impurities in carbonado form no known compounds having this type of crystal structure. Traces of rutile were also identified by X-ray diffraction; this compound is assumed to have formed during the oxidation process.

The carbonados were divided into several groups according to their porosity and crystallite size as judged from their outer appearance. Density determinations were made on six representative stones after the outer siliceous crust has been dissolved in concentrated hydrofluoric acid. Table 1 gives a list of these densities which were determined by

TABLE 1. DENSITIES OF SELECTED CARBONADOS MEASURED TO $\pm 0.001 \text{ g-cm}^{-3}$

Designation	ρ Uncoated	% Theory	ρ Coated	% Theory
13	3.326	94.62	3.101	88.56
20	3.355	95.47	—	—
17	3.372	95.95	3.289	93.59
7	3.373	95.98	—	—
4	3.391	96.49	—	—
11	3.434	97.72	3.392	96.52

the liquid displacement method in bromoform. For several of the specimens, measurements were also made with the stones encapsulated in wax

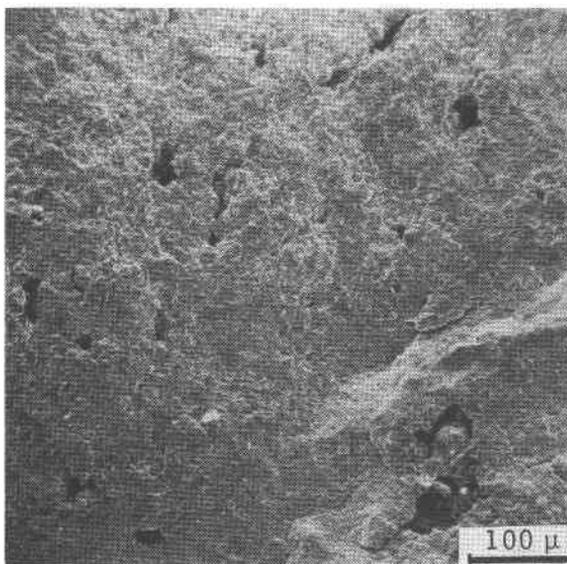


FIG. 3. Scanning electron micrograph of fractured carbonado surface.

in order to determine the bulk density. The data in Table 1 show that a significant fraction of the pores were open. Both density values would be influenced by the presence of closed pores and inclusions; microscopic examination of freshly fractured surfaces demonstrated the presence of both of the above features. Figure 3, a low-power scanning electron micrograph, shows a typical specimen with irregularly shaped, often elongated holes ranging from $10\ \mu\text{m}$ to over $100\ \mu\text{m}$. The inclusions of silicate impurities are readily visible in the light microscope, due to their yellowish-white color, which contrasts rather well with the dark gray diamond background. Figure 4 shows the edge of a fractured particle which contains a large number of crystallites of silicate in the form of platelets with a diameter of $10\ \mu\text{m}$ to over $100\ \mu\text{m}$. The central feature in Figure 4, a $120\ \mu\text{m}$ cavity partly filled with whitish, well-formed $20\text{--}50\ \mu\text{m}$ silicate crystallites, has the appearance of a small geode. Figure 5 shows the same feature at a higher magnification, as photographed with the scanning electron microscope.

The examination of outer surfaces and fractured surfaces of carbonados yields only very limited information as to the location of the silicate impurities. Contact radiography was used to obtain the distribution of these impurities in the whole carbonados or in large fragments thereof. The specimens were placed on the emulsion of a Kodak high-resolution plate and held in place by means of a thin rubber membrane stretched over a metal frame and pressed down onto the plate. The whole assembly

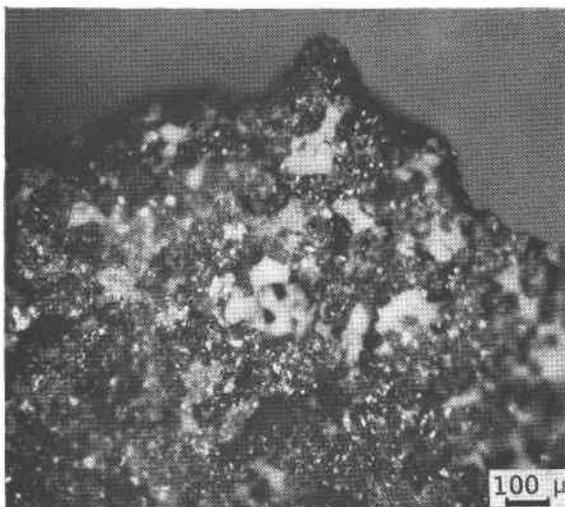


FIG. 4. Fracture surface of carbonado. The white particles are silicate inclusions (photomicrograph).

was contained in a sealed cardboard box which was exposed for 1 hour to nickel-filtered Cu-K_α X-ray radiation, the tube being operated at 35 kV and 20 mA. The radiographs were examined on a Reichert metallo-

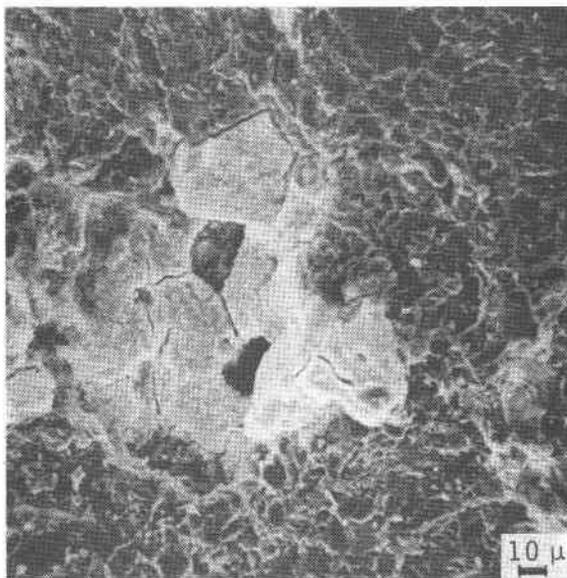


FIG. 5. Scanning electron micrograph showing details of Figure 4. Notice the silicate crystallites filling a small cavity.

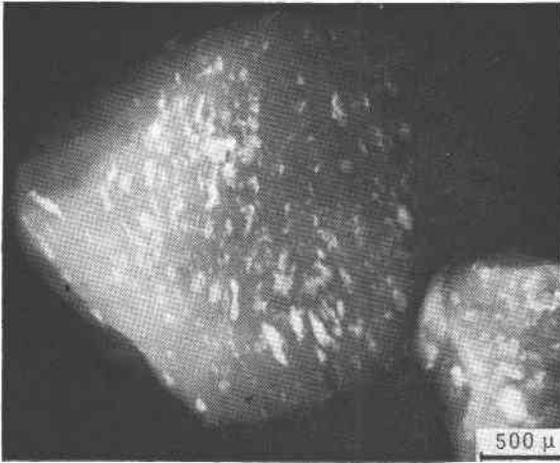


FIG. 6. Carbonados with low concentration of silicate inclusions (contact radiograph).

graph, pertinent sections being photographed on Polaroid PN film from the negatives of which the final enlargements were made. Some of the stones had a rather low impurity content as shown in Figure 6, which shows inclusions with a size varying between 10 and 200 μm . In other specimens the number of inclusions was much higher, as shown in Figure 7. Approximately 20 percent of the examined stones showed a clear longitudinal alignment of the silicate crystals; this feature is visible in

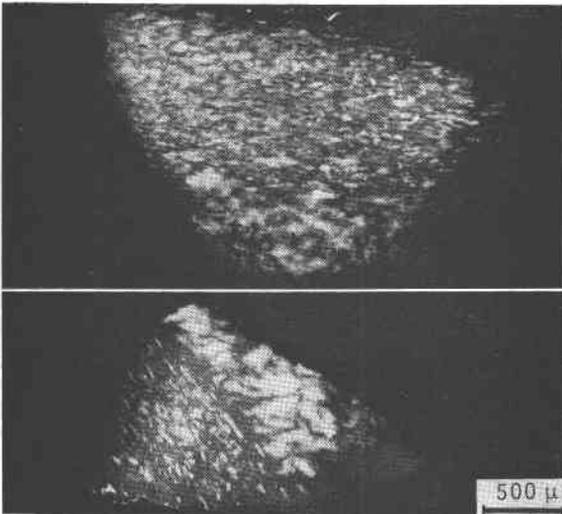


FIG. 7. Carbonados with high concentration of silicate inclusions, mostly in parallel orientation (contact radiograph).

both stones shown in Figure 7. Apparently these platelets are seen edge-on in the left part of the bottom stone in Figure 7 and head-on in the right part. It is not known whether this peculiar alignment is the result of a preferred orientation of the pores in the carbonados, but some of the stones did show a parallel alignment of elongated pores on their outside surfaces.

The size and distribution of diamond crystallites in the examined carbonados were determined from fractured surfaces by scanning electron microscopy and electron microscopy of two-stage cellulose acetate/carbon replicas shadowed with platinum-palladium. The first replicas were discarded and the third or fourth was used for preparing the final carbon replica. Several hundred particles were measured in each of the examined carbonados. In most instances the crystallite size was found to vary between 0.5 and 12 μm , with a flat maximum of the distribution curve between 1 and 4 μm . Some of the carbonados, however, contained an appreciable proportion of much larger crystallites, up to 20 μm , with a very flat distribution throughout the 1–15 μm range. The considerable variation of the crystallite size within similar stones of the same origin is in line with the wide disparity of crystallite sizes in carbonado that are cited in the literature.

The overall appearance of fractured surfaces can be judged from high magnification scanning electron micrographs. Figure 8 is a typical ex-

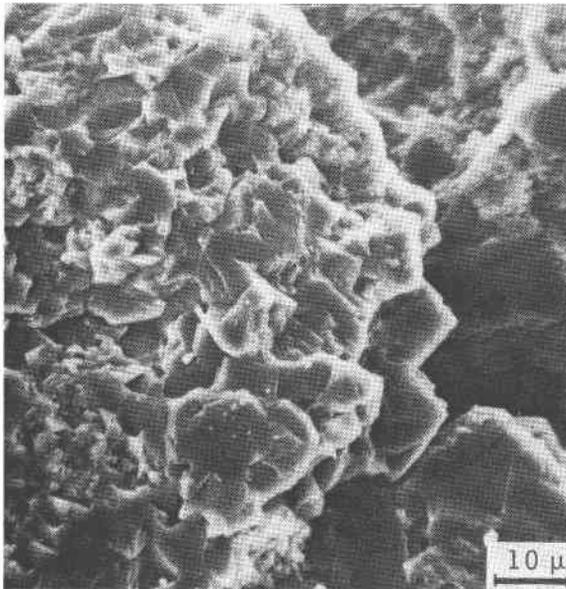


FIG. 8. Scanning electron micrograph of fractured carbonado surface.



FIG. 9. Electron micrograph of fractured carbonado surface. The arrow points to a small, near-perfect octahedron. (Replica)

ample, showing the random but very dense arrangement of diamond crystallites which is somewhat reminiscent of fractographs obtained from many ceramics. A more detailed view of a typical fracture surface can be obtained from electron micrographs of replicas, such as Figure 9. The cleavage steps show that fracture occurred mainly in a transgranular way; the smooth surfaces are assumed to be octahedral planes, *i.e.*, planes of easy cleavage in diamond. The crystallites generally have irregular shapes and are strongly interlocked; interstices are often filled with very small, sometimes well-formed crystallites, such as those seen in the center of Figure 9. The arrow points out a 0.5- μm , near-perfect octahedron. The black dots in Figure 9 are fragments of diamond particles that were extracted from the examined surface by the replicating medium. Many of the fragments had sufficiently thin edges to allow electron transmission: the corresponding selected area electron diffraction diagrams confirmed that these particles were indeed monocrystalline diamonds.

Figure 10 is an example of a characteristic fracture interface of carbonado with a larger average crystallite size than that seen in Figure 9. The boundaries between crystallites are usually clearly outlined by black lines resulting from the penetration of replicating medium into cracks which were presumably formed during the fracture of the carbonado.

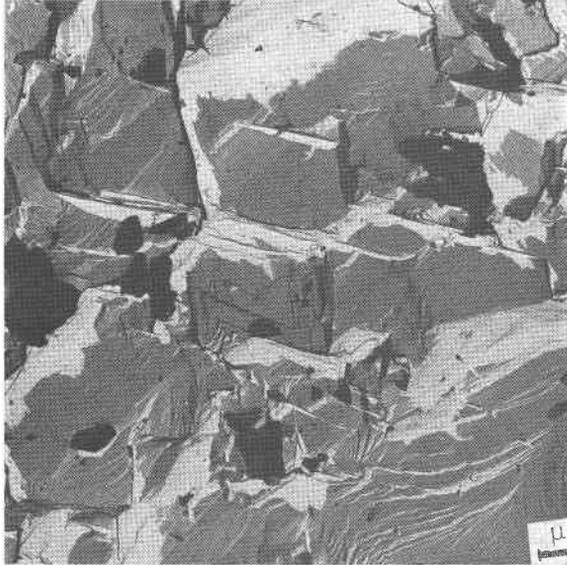


FIG. 10. Electron micrograph of fractured carbonado surface showing mainly transgranular fracture. (Replica)

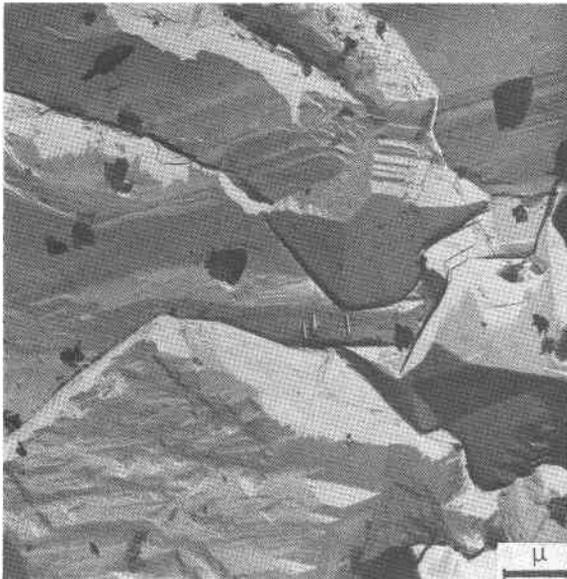


FIG. 11. Electron micrograph of fractured carbonado surface showing evidence of intergranular fracture and minute pores on crystallite boundaries. (Replica)

Perfectly continuous boundaries between crystallites were also often observed, and there did not seem to be any foreign phase at the crystallite boundaries. While most of the crystallites appear to undergo transgranular fracture, intergranular fracture also occurs, as shown in Figure 11. The pyramidal shapes on the right side of Figure 11 presumably belong to 3- μm octahedra intercalated between larger, anhedral crystallites. Some of the surfaces in Figure 11 exhibit a pattern of 500 Å pores which are presumed to be gas bubbles trapped along crystallite boundaries.

The continuous and inclusion-free nature of the crystallite boundaries in carbonado was further confirmed by transmission electron microscopy. For that purpose, fragments of carbonado obtained by crushing larger stones in a cast iron mortar were treated in hot hydrofluoric acid and heated in a quartz boat to 700°C for 1 hour while a steady stream of pure oxygen was allowed to flow over the sample. Many of the fragments were thus sufficiently thinned for electron transmission at 100 kV. Figure 12 shows a transmission micrograph of a typical aggregate of $0.25 \times 1\text{-}\mu\text{m}$

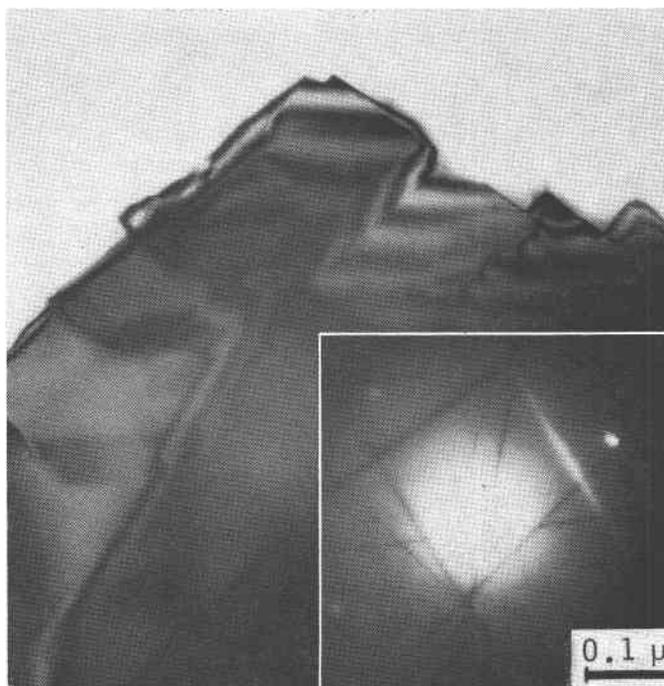


FIG. 12. Transmission electron micrograph of oxygen-thinned fragment of carbonado. Insert: Selected area diffraction diagram showing Kikuchi lines and $\{220\}$ reflections.

crystallites which are firmly interlocked and have perfectly straight boundaries. The latter are accentuated by the broad fringes which are extinction contours resulting from a slight bending of the particle; they outline the change of orientation at the crystallite boundaries. The insert shows the corresponding selected area diffraction diagram with Kikuchi lines and $\{220\}$ reflections.

CONCLUSIONS

The present study of carbonados from the State of Bahia, Brazil, showed that the microstructure of this material resembles that of ceramics. It is in good agreement with the model proposed by Brandenberger (1930) who postulated that carbonado is an aggregate of randomly oriented diamond crystallites. These crystallites do not show any evidence of a coating or cementing agent such as amorphous carbon or silica, and are presumably bonded by interatomic forces as is usually the case in polycrystalline materials. With the possible exception of titanium, all the impurities in carbonado appear to be due to the presence of variable amounts of a potassium-aluminum silicate and α -hematite. These inclusions are not expected to contribute to the strength of carbonado, and may even weaken it; fracture was often observed to occur on planes containing large concentrations of silicate particles and pores. The silicate inclusions are single crystals and not crypto-crystalline masses as has sometimes been assumed. The fact that they are decomposed by calcining in oxygen would indicate that these inclusions are not remnants of the mineral environment in which the carbonados were formed, but are probably due to subsequent infiltration. The examined carbonados exhibit a widely varying porosity and some of the pores are certainly connected to the outside as shown by the difference between the coated and uncoated density values.

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