ON THE ORIGIN OF NATURAL DIAMONDS

R. N. WENTORF, JR., AND H. P. BOVENKERK
General Electric Research Laboratory

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ABSTRACT

So far, not all the different kinds of diamonds found in nature can be duplicated by men, but enough laboratory experience in diamond formation has been accumulated to make possible the comparison of several kinds of natural and man-made diamonds In this way some tentative hypothesis can be made about the origin of natural diamonds, both meteoritic and terrestrial. It is proposed that most natural diamonds were formed at high pressures and temperatures in the presence of an iron-alloy catalyst. The black polycrystalline meteoritic diamonds could have been formed at low temperatures (1200° C) and high pressures (above 55000 bars). The larger terrestrial crystals could have formed at somewhat higher temperatures and pressures by a falling-temperature and/or increasing-pressure process.

I. INTRODUCTION

Now that it has been discovered how to make diamond, it would be interesting to compare natural diamonds with those made by men, perhaps to shed some light on the genesis of diamonds in nature. To begin with, we note that we cannot ever hope to compare natural and human diamond-making processes directly; the inaccessibility of proposed natural diamond-forming regions, both deep in the earth and far out in space, precludes direct experimental determinations of the pertinent quantities, even if diamonds were being formed at this moment. The best that we can hope to do is to compare the diamonds of men and the diamonds of nature and, from our knowledge of men's processes attempt to infer something about the processes of nature. It follows, then, that we cannot here describe with certainty the processes by which natural diamonds formed; we can only surmise that certain processes could have, or were likely to have, occurred in nature. Indeed, the extreme complexity of the natural systems in which diamonds are found makes the duplication in the laboratory of natural diamond-growing processes impossible for all practical purposes. Moreover, it is not yet possible for men to duplicate all the different kinds of natural diamonds. Nevertheless, the comparison between man-made and natural diamonds should permit us to discard some hypotheses about the genesis of natural diamonds and concentrate on the more plausible ones.

Natural diamonds at present can be classified into two groups: meteoritic and terrestrial. Although relatively few meteorites have so far been found to contain diamonds and the total weight of all diamond extracted from meteorites up to now is probably about 10 gm (50 carats), these diamonds resemble each other far more than they resemble any kind of terrestrial diamond. Meteoritic diamonds are found as friable black lumps composed of many tiny diamond crystals, each perhaps 0.01 mm or less in average diameter. The crystal size of terrestrial diamonds, on the other hand, is usually considerably larger; it is rarely below 0.02 mm, even in carbonado, and is often 5 or 10 mm.

The conditions of pressure, temperature, chemical environment, and time used to form diamonds are now tolerably well known, and it is natural to attempt to relate the various conditions of formation to the kind of diamond produced. F. P. Bundy, H. T. Hall, H. M. Strong, and the authors, among others, have been making such observations for the past several years, and the following rough rules have been established (Bovenkerk *et al.* 1959; Hall 1960).

1. No diamond forms unless the pressure is high enough for diamond to be stable at

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the particular temperature employed. With the catalyst systems now known, the minimum pressure seems to be around 45000 bars.

2. Diamond forms from non-diamond carbon in the presence of a molten metal (or molten metal-carbon mixture) which acts as a catalyst for the transformation by mechanisms that mainly resemble the solution and deposition of carbon. The best catalytic metals are Cr, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt. The direction of the temperature gradient seems to be unimportant.

3. The habit of a diamond crystal depends principally upon the pressure and temperature at the instant of its formation. Once formed, a diamond crystal is loath to change in type, size, or crystal habit, except to graphite.

4. The higher the temperature of formation for a given system, the more colorless are the resulting diamonds, although the chemical environment may have secondary influences. At the very lowest temperatures so far found effective (about 1200° C), the diamonds are usually black.

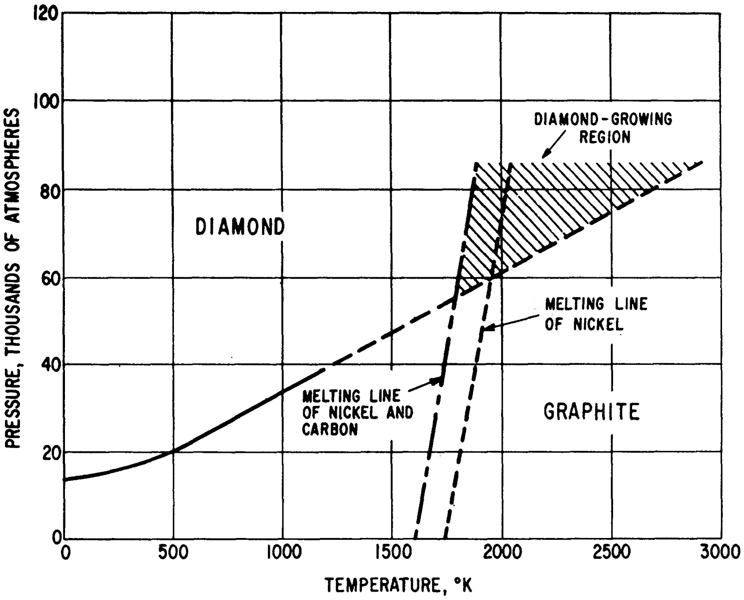

FIG 1.—Phase diagram with diamond-growing region

5. At a given temperature, the more the pressure exceeds that necessary for equilibrium, the greater the rate of nucleation and growth of diamond crystals, and the smaller and more imperfect they are, regardless of the time taken for their formation.

6. At pressures below about 50000 bars the cube habit predominates; at higher pressures the octahedral habit is more common. This "low-pressure" cube habit does not resemble that of natural diamond (Bovenkerk 1961; Tolansky 1960). The man-made cube faces tend to be smooth or show terraces; natural cube faces tend to be rough, made up of tiny octahedral faces.

Rules 1 and 2 are conveniently expressed in the phase diagram shown in Figure 1, in which the diamond-growing region is indicated for a particular catalyst system (Bovenkerk *et al.* 1959). The pressures quoted here are based on the abrupt electrical resistance changes in bismuth metal at 25000 bars and in barium metal at 60000 bars.

From time to time the hypothesis is raised that diamonds may form metastably, i.e., at relatively low pressures, from Fe_3C or some iron-carbon mixture. So far, laboratory experience has shown that at pressures of 43000 bars or below, graphite is formed

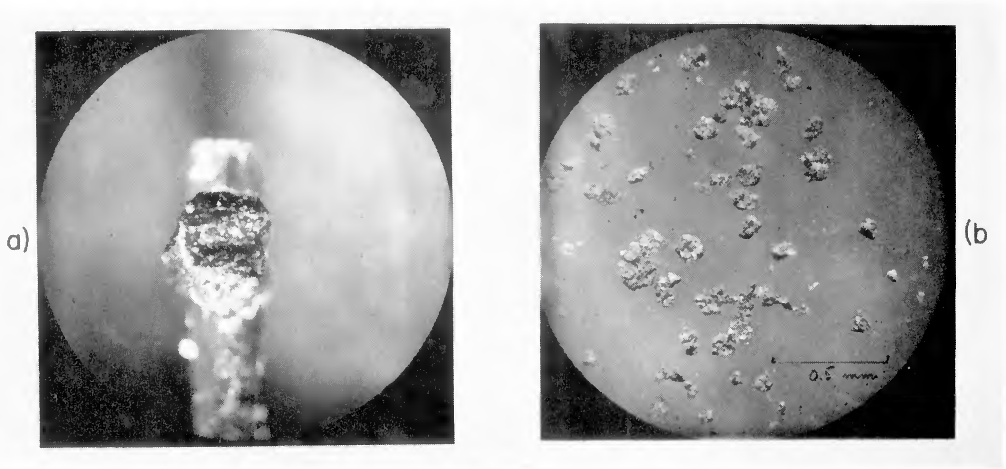

FIG. 2.—*a*, Canyon Diablo meteorite diamond; *b*, Novo Urei meteorite diamond

from such mixtures whether they be quenched or cooled slowly. In spite of the obvious commercial advantages of a low-pressure process for producing diamond and in spite of much labor on the problem, no reproducible process has yet been found by which diamond can be formed at pressures where graphite is stable. Until someone reproducibly succeeds in making diamonds metastably, this hypothesis of diamond formation deserves to be regarded as extremely tentative.

Some graphitization studies in this laboratory at temperatures ranging from 1700 to 2250° C showed that, at 2000° C in a near-vacuum, natural diamond chips became entirely graphite in about 100 seconds, on the average. The apparent activation energy of the process is about 170 kcal/gm atom. The rate of graphitization decreased about tenfold, and the activation energy increased to about 250 kcal/gm atom at 20000 atm. Diamonds containing more impurities graphitize at higher rates. In the presence of molten catalyst alloys, the change to graphite is quite rapid (limited, at most, by diffusion) at any pressure below equilibrium for diamond.

The above graphitization-rate measurements do not agree well with the results of Phinney (1954). Phinney found 1–2 per cent graphitization of well-formed natural diamond crystals in 48 hours at 1400° C, the highest temperature reported. The studies in this laboratory were done at higher temperatures, where the graphitization was rapid and usually over 25 per cent complete. It is possible that a different mechanism operates at the lower temperatures, whereby graphitization proceeds slowly and mainly on the surface. It is known that, on account of percussion or subterranean chemical action, the outer portions of natural diamond crystals are frequently different from the interior portions and might be expected to graphitize differently, in view of the sensitivity of the rate of graphitization to crystal imperfections or chemical purity.

II. METEORITIC DIAMONDS—GENERAL

Meteoritic diamonds have a black color and are usually found as irregular lumps of tiny crystals in a few meteorites, including Canyon Diablo, Goalpara, and Novo Urei. The first is a nickel-iron meteorite, whereas the latter two are predominantly stone.

The diamond lumps in the Canyon Diablo meteorite may be as large as $1 \times 1 \times 1.5$ mm and are usually found in a black, non-metallic matrix which occurs in the form of pockets in the metal. The matrix generally consists of troilite (iron-rich FeS), with smaller amounts of graphite, iron-nickel phosphides, and magnetite (Moissan 1904; Nininger 1952, 1956; Lipschutz and Anders 1961).

Some of the diamond lumps were pried out of the black matrix of a fragment of this meteorite. Their Debye-Scherrer patterns showed diffuse lines of diamond, FeS, magnetite, and traces of graphite. The fragments were strongly ferromagnetic and easily scratched a boron carbide test plate.

One of the lumps, about 0.1 mm in diameter, was heated in boiling mixtures of sulfuric, nitric, and hydrochloric acids in order to remove superficial FeS, graphite, etc. Its Debye-Scherrer pattern showed it to consist of tiny diamond crystals mixed with a small amount of iron and FeS. After acid treatment it was weakly ferromagnetic and appeared as shown in Figure 2, *a*. Only a few tiny octahedral crystal faces about 0.01 mm on edge are visible here and there on this fragment. However, the X-ray pattern of the lump is not so sharp as would be expected from 0.01-mm crystallites.

A number of tiny diamond fragments from the Novo Urei meteorite are shown in Figure 2, *b*. These fragments were isolated, together with some graphite, from a part of this stony-iron ureilite meteorite by G.O.S. Arrhenius. They were sent to the authors through the courtesy of Dr. H. C. Urey, and the graphite was removed by a few minutes' oxidation in a hot mixture of H_2SO_4 and KNO_3. (This treatment has not been found to affect diamond.) An X-ray diffraction pattern of these diamonds showed them to be made of tiny crystals, and through a microscope one can see occasional portions of octahedral faces about 0.01 mm long.

The diamonds extracted from the Goalpara meteorite by Urey and co-workers (Urey *et al.* 1957) are reported to be small and mixed with graphite. Their average crystallite size was estimated to be about 100 A from their X-ray diffraction patterns.

Diamonds similar to these meteoritic diamonds in size, color, and X-ray diffraction patterns are formed in the laboratory under conditions of low temperature (to produce the black color) and moderately high pressure (to produce a high nucleation rate and many tiny crystals). A high-pressure, high-temperature apparatus similar to the one described by H. T. Hall (1960) was used. By taking special care to operate at the minimum required temperature at 67000 bars with nickel-metal catalyst and spectroscopic carbon, in a reaction cell as shown in Figure 3, the diamond shown in Figure 4, *a*, was obtained. The diamond is the thin, black deposit of tiny black crystals on the nickel metal. In Figure 4, *b*, is shown a similar kind of diamond which was produced on iron-metal catalyst under similar conditions. Both these deposits were formed in about half a minute. If the reaction is allowed to continue, i.e., if the reaction zone is kept hot for about 10 minutes, diamond lumps, such as those shown in Figure 4, *c*, are obtained from iron and carbon. If the synthesis pressure is reduced below 50000 bars or so, the nucleation rate for diamond crystals is reduced so that significantly larger crystal sizes begin to appear. Moreover, diamond cubes are formed instead of octahedra. Thus the product loses its resemblance to meteoritic diamond. If the temperature is permitted to increase slightly, the rate of growth and the crystal size increase, and the diamonds become more or less transparent instead of black.

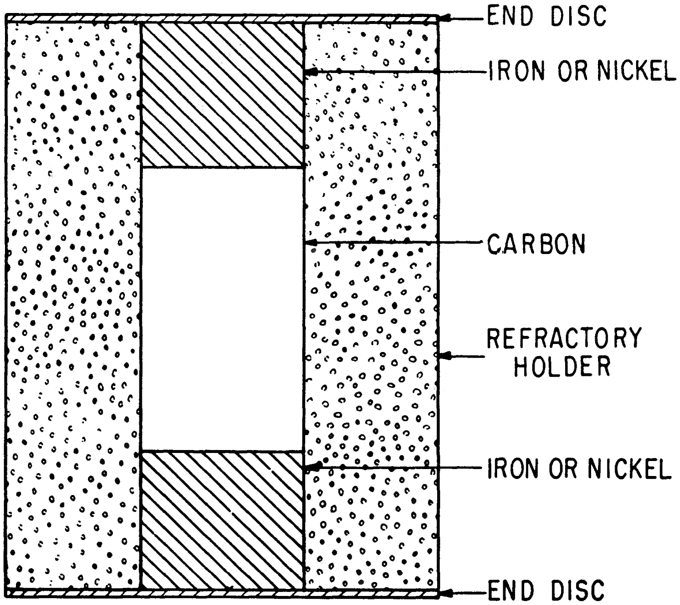

FIG. 3.—Diamond synthesis cell

If the reaction conditions of high pressure and low temperature are approached by some other path essentially different from increasing the temperature at high pressures, the black polycrystalline diamond does not form. Some other kind of diamond forms and persists, according to the rough rules. There are only two other essentially different paths of approach to these conditions.

a) Increasing the Pressure at Constant Temperature

If the temperature is below the melting temperature of the catalyst-carbon system, then no diamond forms. If the temperature is above the appropriate melting tempera-

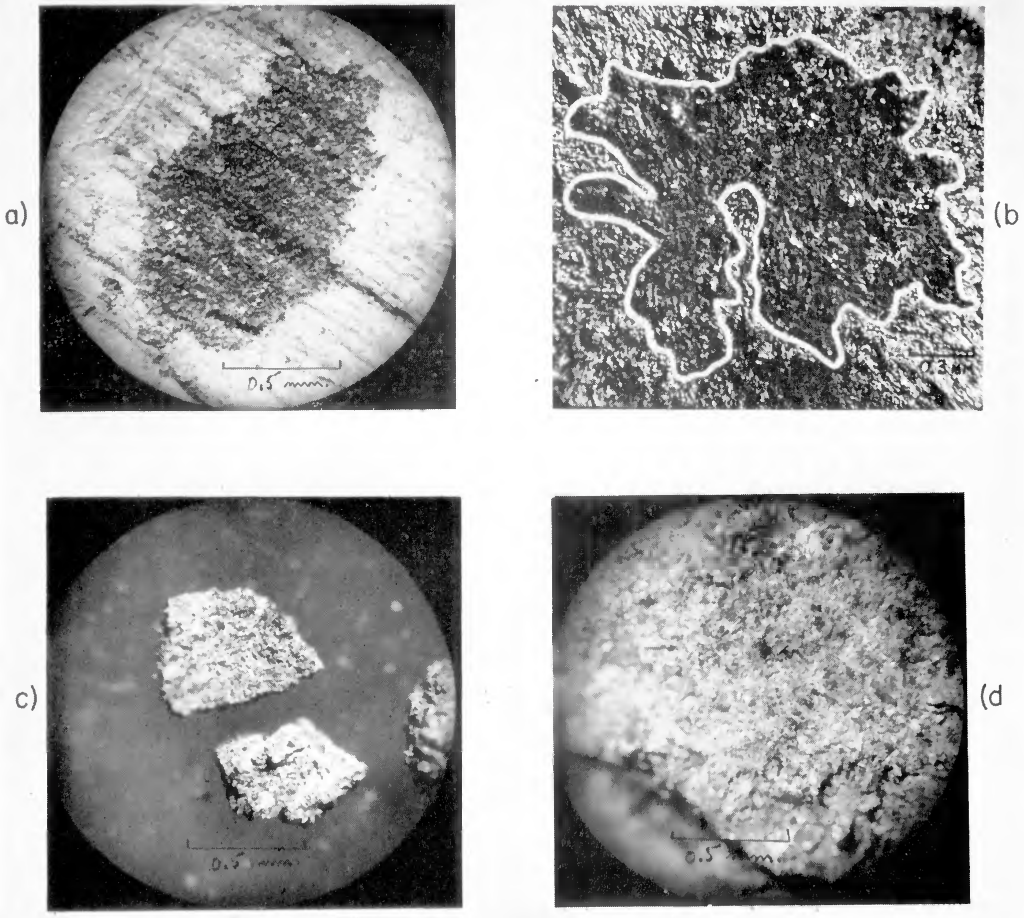

FIG. 4.—*a*, Diamond layer on nickel; *b*, diamond layer on iron (inside white boundary); *c*, black diamond lumps grown with iron; *d*, white polycrystalline diamond mass.

ture, either of two things will occur, depending on the temperature. If the temperature is in the narrow interval suitable for production of black diamond, then black diamond will form, but the crystals will be large (0.1 mm) and have the cube habit. If the temperature is higher than this, green, yellow, or colorless diamond crystals will form.

b) Decreasing the Temperature at Constant Pressure

If the pressure is high enough for octahedra to form, the temperature at which they first form is thereby high enough to produce green, yellow, or colorless crystals. Of course, the temperature and pressure may follow a wide variety of paths before the diamonds form, but the actual entry into the diamond-forming region should be at conditions of high pressure and low temperature to produce small, black octahedra.

As for the time variable, the laboratory experience is that the diamond-formation rate is a very steep function of the temperature near the melting temperature of the catalyst. i.e., either the reaction occurs in a few seconds or it fails to occur in a few hours. Higher pressures tend to accelerate the linear rate of transformation of graphite to diamond by virtue of an increased rate of nucleation, but ultimately the rate of transformation is limited by diffusion of carbon or catalyst. The fastest growth rates for diamond lumps so far observed in laboratory syntheses do not exceed 1 mm per second. If the meteoritic diamonds of Canyon Diablo formed by processes now known to exist, one would accordingly place a lower limit of about 1 second on their formation time, since some of the lumps are at least 1 mm in diameter. The smaller sizes of the diamonds found in Goalpara and Novo Urei imply that shorter times would have sufficed for the formation of these diamonds. So far, laboratory studies on diamond alone do not permit an accurate estimate of the upper limit for the formation-time interval. Perhaps other studies of meteorites or the discovery of new diamond-making processes will help to establish the formation-time intervals more exactly.

Perhaps not all meteoritic diamonds, despite their similar appearances, were formed by the same single process. So far, of all the components of meteorites, only the iron- (and nickel-) rich phases are known to catalyze diamond formation, and, so far, diamonds have been found only in meteorites which contain some iron. The necessary high pressures and temperatures could have been produced either deep inside a large body or by collision processes. There are certain obstacles in the way of adopting either of these views, which will be discussed later.

III. METEORITIC DIAMONDS—GOALPARA AND NOVO UREI

The relatively intact appearances of the stony Novo Urei and Goalpara meteorites, as well as the fact that they are not associated with large terrestrial craters, suggest that relatively low pressures were developed in them upon collision with the earth. Hence it appears that their diamonds were synthesized extra-terrestrially, either by impact processes or deep inside a large body. Goalpara appears to have been well annealed since its last collision. These meteorites also contain some graphite. It is possible that very little of the matter now making up these meteorites is the actual mother matrix of the diamonds.

The laboratory experiments on diamond formation indicate that it is possible that these diamonds formed in a matrix similar to that in which they are now found, under conditions of pressure exceeding about 55000 bars and slowly increasing temperatures in the neighborhood of 1200°–1300° C. Such conditions are likely to occur deep inside a large body. Temperatures just high enough to produce such black diamonds would not have permitted fusion of the silicate components of the meteorite, particularly since the melting temperatures of such silicates increase with pressure more rapidly than those or iron, nickel, etc. (Boyd and England 1959; Strong and Bundy 1959). The fact that metal is dispersed throughout the fragments of the meteorites would help preserve from solution in metal any diamonds which were formed. A relatively small amount of iron-nickel next to a lump of carbon would have sufficed to transform the carbon into diamond.

These meteorites deserve further study to determine just how their diamonds are distributed in them and with what phases they are now in contact.

IV. METEORITIC DIAMONDS—CANYON DIABLO

The diamondiferous fragments of this meteorite have been studied carefully by many investigators (Moissan 1904; Nininger 1952, 1956; Lipschutz and Anders 1961). The diamonds in these fragments are usually found embedded in masses of troilite (FeS) and are often associated with schreibersite (Fe, Co, Ni phosphides). The bulk of the fragments consists of iron-nickel with some cohenite (impure Fe_3 C). Usually the diamondiferous meteorite fragments have only traces of Widmanstätten structure; these fragments appear to have been heated (Lipschutz and Anders 1961) and have always been found near the crater rim. On the plain surrounding the crater are found fragments which have well developed Widmanstätten structures; many tiny metallic spheres, which were probably condensed from vapor, are also found there. A few fragments are found which are unlike the main mass (Nininger 1952, 1956). Both the heated and the unheated fragments of this meteorite contain some graphite. However, only rarely do the diamonds lie in contact with graphite; most often they are embedded in troilite or schreibersite.

Usually the troilite which surrounds the diamonds contains some excess iron. Laboratory experiments at high pressures with iron–iron sulfide mixtures indicate that the main features of the 1 atm. iron-sulfur equilibrium diagram exist also at about 65000 bars. Thus the iron now dispersed in the meteoritic troilite probably separated as the melt froze. Evidently the melt cooled rapidly enough that there was not much reaction between the diamond and the iron, nor was there much gross separation of the phases of the solidifying melt.

It has been observed in laboratory tests that, at high temperatures and pressures suitable for diamond formation, graphite may absorb enough catalyst iron, nickel, etc. from nearby masses containing these elements (alloys or certain compounds of these elements, such as sulfides, oxides, etc.) to catalyze the formation of diamond in the graphite. In fact, several of the earliest preparations of diamond in our laboratory used graphite which extracted the necessary iron catalyst from some nearby iron sulfide (Bovenkerk *et al.* 1959). Only a relatively small amount of catalyst, perhaps 5 per cent, may suffice to transform a relatively large amount of graphite carbon into diamond.

It has also been found that carbon is not very soluble in iron sulfide at diamond-forming conditions. Thus a lump of graphite enclosed by FeS may be converted to diamond while a nearby mass of iron does not become saturated with carbon. The iron sulfide can permit enough iron to reach the carbon to "saturate" the carbon with iron and allow diamond formation but would not necessarily permit the carbon or diamond to diffuse very rapidly into the iron. A similar occurrence in the Canyon Diablo meteorite does not seem impossible; in fact, this might almost be necessary to permit diamond to exist in this meteorite, whose average carbon content is below that required to saturate the iron-nickel alloy of the meteorite, particularly if the temperature of the fragment were ever appreciably above the carburizing temperature or melting temperature of the iron-nickel-carbon eutectic for more than a few minutes.

There is thus ample evidence that the diamonds found in some Canyon Diablo fragments could have been produced from graphite at high pressures in the presence of small amounts of iron and troilite. The evidence is not good that they were formed by decomposition of Fe_3C at high pressures because in laboratory tests Fe_3C is usually found in contact with growing diamond crystals after quenching at high pressures or even after several hours of slow cooling at high pressure (65000 bars) in the iron-carbon eutectoid region. Thus Fe_3C is stable under these conditions. This is not too surprising because the decomposition of cementite to graphite or diamond and iron involves an increase in volume. Furthermore, the Canyon Diablo diamonds are lumps as large as 1.0 mm in which the diamond crystals are bonded to each other. One would expect the products of the decomposition of a lump of Fe_3C to consist of many tiny diamond grains, more or less separate from each other, embedded in a mass of iron, for the volume ratio of iron to diamond would be about 7.

It is not yet possible to say with certainty how the pressures and temperatures necessary for the formation of the Canyon Diablo diamonds were produced, whether by impact with the earth or deep inside a large body. Both hypotheses will be discussed in more detail in a future paper. A brief summary of the two alternatives is given below.

An impact hypothesis certainly does not seem implausible on the basis of energy or momentum considerations. The crater is about 170 meters deep and about 1.3 km in diameter. The meteorite probably struck with a velocity not much below 11 km/sec, the earth's escape velocity. Öpik (1958) estimated that the meteorite weighed about 2×10 tons (diameter 60 meters, if iron) and had a velocity of 15 km/sec. The calculations of Gilvarry and Hill (1956) on the impact of large meteorites indicate that relatively high pressures, well over several hundred thousand atmospheres, would be produced in the meteorite for a small fraction of a second during impact. Shoemaker (1960) has considered many of the details of the impact.

Similar high pressures and concomitant high temperatures would be expected in the rock under the colliding body. This view is reinforced by the discovery of coesite, a dense form of silica, in some of the sheared and partially melted sandstone in the crater (Chao *et al.* 1960). Evidently the rock reached temperatures of the order of 1500°–2000° C; to form coesite at such temperatures requires static pressures of the order of 35000 bars or higher. Static pressures of the order of 25000 bars at 600° C are normally necessary to produce this form of silica (Coes 1953). Dachille and Roy (1960) have found that added shearing stresses may greatly accelerate the approach to equilibrium in silicate systems. The combination of impact compression, heating, and shearing would be favorable for producing some coesite, even though such conditions would not be expected to last for more than about 0.1 second.

An impact hypothesis is also favored by some authors because it would not then be necessary to postulate the existence of meteoritic parent bodies large enough to produce diamond-forming pressures in their interiors. The gravitational pressure, p, at the center of a body of uniform density ρ and radius R is given by

$$p = 6.67 \times 10^{-14} \times \tfrac{2}{3} \pi \rho^2 R^2 ,$$

where p is in bars, ρ is in grams/cc, and R is in centimeters.

To produce 55000 bars in a predominantly stony material of density 4 requires the body to have a radius of about 1540 km, about the radius of our moon. According to the calculations of Allan and Jacobs (1956), such a body would be expected to be too large to cool off sufficiently in 4×10^9 years to produce the Widmanstätten figures, which are believed to have formed at temperatures between 350° and 700° C (Uhlig 1954; Urey 1956). (Potassium-argon dating methods indicate that many meteorites are as old as 4×10^9 years; such an age is comparable with the ages of older terrestrial rocks.) Lastly, there would remain the problem of breaking up such a large body into meteorite-sized fragments. Many of the observed properties of meteorites may be more easily explained if their parent bodies are assumed to have been only tens or hundreds of kilometers in diameter (Anders and Goles 1961).

Some arguments can be made against an impact origin of the diamonds. The strongest of these is that the diamond lumps are sometimes larger than 1 mm, which, on the basis of laboratory experience, calls for growth times of at least 1 second. However, the duration of high impact pressures could not have exceeded 0.1 second. (The ratio of crater depth to probable impact velocity is about 0.01 second.) The catalyzed growth rate of diamond is limited ultimately by diffusion of carbon or metal, and one would not expect the compressions during impact to affect this rate materially. If the extremely high transient pressures of the initial stages of impact had been, by themselves, sufficient to produce diamond from graphite, without benefit of catalyst action, then one would expect nearly all diamond and very little graphite in most of the fragments of the meteorite. However, much graphite is found in them, which indicates that strong shock compression is not always sufficient for diamond production and that the formation of the diamonds was dependent on catalytic action.

It is possible that an impact might create complex high stresses inside a body and that the relief of these stresses might be slow enough to maintain diamond-forming pressures for as long as several seconds inside bodies more than several meters in diameter. However, the probability of such an event would seem to be low because of the mechanically weak structures of most meteorites, which would permit their easy fragmentation, and because of the weakness of meteoritic materials at diamond-forming temperatures.

A large-body origin of the pressures necessary for diamond synthesis is quite compatible with the laboratory experience on diamond formation. It is also compatible with the observation that much cohenite (impure Fe_3C) is found in the meteorite fragments. The decomposition of Fe_3C to iron and graphite involves an over-all decrease in density, so that pressure should enhance the stability of Fe_3C. Presently available thermodynamic data evidently do not permit an accurate estimate of the equilibrium pressures required to preserve Fe_3C at various temperatures. For example, Lipschutz and Anders (1961) estimated that the equilibrium pressure at 800° K was about 0.7 kb, while Ringwood (1960), using different but presumably equally reliable data, estimated the pressure to be about 18 kb at 800° K. Both calculations unfortunately indicate that Fe_3C should be stable at 1100° K and 1 atm., where it is observed experimentally to decompose, and illustrate the need for more accurate thermodynamic data for this system. Laboratory tests at high pressure have indicated that Fe_3C is stable with respect to diamond or graphite at pressures of about 50000 bars in the temperature range 500°–1700° K. By comparison, at 1 atm., Fe_3C commonly decomposes to graphite and iron at about 900°–1100°K in the manufacture of malleable iron. These processing temperatures are comparable to those believed to be involved in the formation of the Widmanstätten patterns (Uhlig 1954). However, the pressures required for stability of Fe_3C are apparently not so high as those required for diamond formation, and there is the possibility that certain impurities in the cohenite may serve to stabilize it at low pressures.

It is not the presence of diamonds or cohenite but rather other aspects of meteorites that presently make the large-body hypothesis difficult. Chief among these is the problem of cooling a large body so as to produce the Widmanstätten figures in 4×10^9 years or so. Higher pressures would tend to reduce the temperature at which the γ–α transition (believed to be the basis for the formation of the Widmanstätten patterns) occurs and thus prolong or block the process (Kaufmann *et al.* 1961). On the other hand, Vogel (1951) has suggested that the presence of phosphorous in meteorites might permit the formation of the Widmanstätten patterns at higher temperatures than are observed for pure nickel-iron alloys.

It is generally agreed that the meteorites were derived from more than one parent body. Urey (1956) has proposed that several generations of parent bodies may have existed.

As an extreme case, one might consider a body quite rich in iron. Diamond-forming pressures would be produced in such a body if it had a radius of perhaps 900 km. Such a body might cool rapidly enough to form Widmanstätten figures in 4×10^9 years, for it would have a small size, a high thermal diffusivity, and a radioactivity lower than average. The probability of forming such bodies would appear to be low, since special segregative effects would be necessary. Possible effects would include the greater toughness and density of iron compared with rock, so that the fragments dispersed from a collision would tend to be more stony, and the possible presence of appreciable magnetic fields, which would have enhanced the attraction of iron particles for each other.

At the moment there appear to be drawbacks to either hypothesis of meteoritic diamond formation. It is intended that a future paper will examine the impact and large-body hypotheses in greater detail, paying special attention to the impact processes, the environment of the diamonds, and the behavior of possible parent bodies.

V. TERRESTRIAL DIAMONDS

In contrast to meteoritic diamonds, many forms of terrestial diamonds have been found (Grodzinski 1944). They can be put into two main classes: (1) small crystals, e.g., carbonado, framesite, ballas, and other polycrystalline forms, and (2) large crystals, e.g., the bulk of natural diamond stones, which usually consist of one crystal, or perhaps two, three, or four crystals grown together. Considering small diamonds first, one finds that such diamonds form at pressures substantially above those required for equilibrium, so that nucleation is rapid. Many tiny crystals form. Some are shown in Figure 4, *d*. Such a cluster contains only a relatively small amount of catalyst metal and graphite in the interstices between crystals. The color of the mass becomes substantially white at moderate synthesis temperatures, 1700° C or so.

It is possible that natural polycrystalline diamond lumps were formed at conditions of relatively high pressures and moderate temperatures. The various subsequent plutonic mineral environments to which such lumps were exposed could have produced the various forms of carbonado, framesite, etc. that are found today. Surely, millions of years were available for such processes, and no great stretch of the imagination is required to suppose them. There is yet no experimental evidence to contradict a view that natural polycrystalline diamonds were formed by a rapid heating-up or cooling-off process at high pressures or by a sudden increase in pressure at moderately high temperature.

We turn, at last, to a problem which has fascinated men, and ladies too, for a long time: the genesis of large diamond crystals.

All laboratory experience so far indicates that the most perfect diamond crystals are formed at pressures and temperatures not far removed from the equilibrium line between graphite and diamond. The higher the temperature, the more nearly colorless the diamond, although the chemical environment may have secondary effects.

These findings suggest that large, pale, natural diamond crystals could have formed out of a mixture of graphite and catalyst, which was originally at high temperatures and pressures suitable for the stability of graphite, via either or both of two processes: (*a*) a slow pressure increase into the diamond-forming pressure-temperature region or (*b*) a slow temperature decrease into the growing region (Neuhaus 1954, 1957). In either case the slowness of the changes would have permitted the system to remain close to the graphite-diamond equilibrium at a temperature of at least 1600° C for several days. The existence of many stones in which a second crystal has grown around a first suggests that the growth process may have been interrupted (Williams 1932).

The high formation temperature implied by the pale color of these diamonds also implies that they were formed under pressures thermodynamically required for diamond stability. For the rate of change of diamond to graphite is too rapid at 1600° C and higher to permit any diamond to persist for long at a low, graphite-stable pressure, even if it could be formed there. The octahedral habit of many diamond crystals also implies a high formation pressure. Taken together, the laboratory experience suggests that large natural diamond crystals formed at pressures of at least 60000 bars with 70000–80000 bars more likely. Of course, the higher the pressure, the deeper the diamonds were in the earth, and the greater the difficulty would have been for the diamonds to reach the surface.

Many natural diamonds contain mineral inclusions, such as garnet, olivine, diopside, etc. Most such minerals are found in the laboratory to be stable in the presence of molten iron, nickel, and growing diamond. The inclusion of pyrope-almandine garnet in a diamond implies, in addition, that the diamond was formed at a pressure at least high enough for this garnet to be stable, about 20000–25000 bars (Boyd and England 1959; Wentorf 1959).

There is, so far, no experimental evidence to support the view that the "blue ground" of South Africa was the solvent or medium in which diamonds formed. It is true that this material will dissolve carbon, even at high pressures and temperature. But, so far, laboratory tests show that only graphite, never diamond, seems to precipitate from this solution. It is more likely that the blue ground served merely as a vehicle to carry the diamonds from great depths (over 100 miles) to the earth's surface. The medium in which the diamonds formed was probably an iron alloy (saturated with carbon) because iron is such an abundant element; diamonds would float on such an alloy and be more easily caught up and carried away. Obviously, there are any number of subterranean processes which could be expected to produce the various changes in local temperature or pressure suitable for growing diamond.

VI. SUMMARY

Laboratory tests indicate that the most likely conditions of formation of meteoritic diamond may have been high pressure (above about 55000 bars) and low temperature (about 1200° C), with graphite as the source of carbon and iron or an iron alloy as the catalyst. In this way black polycrystalline diamond lumps would be formed.

On the other hand, terrestrial diamonds, for the most part, could have been formed at somewhat higher temperatures, probably at least 1600°C, and pressures of 60000 bars or higher, by processes of pressure increase and/or temperature decrease. When these processes occurred rapidly, polycrystalline diamonds would have formed; when they occurred slowly, the larger, more perfect diamond crystals could have formed.

Not all the types of terrestrial diamond have yet been duplicated in the laboratory. As time goes by, we hope that our increasing knowledge of diamond synthesis will help us to understand more about our world.

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