

DIAMOND AND ITS ORIGIN - NEW APPROACHES

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by

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Summary

The properties of the diamond which make it a unique mineral are reviewed and its meteoritic and terrestrial origins are described. The formation conditions for synthetic diamond are considered; they are related to the temperature and pressure conditions postulated for the Earth's upper mantle and to the global distribution of diamond production.

Introduction

The diamond, since it was first recognised as a distinct material, has never failed to attract the attention of observers. Its hardness and brilliance are the properties which are best known, but it has many others which combine to make it a unique material. The solid state may be subdivided on the basis of the type of chemical bonding, and Grimm (1929) has suggested that the four extremes, molecular, metallic, ionic, and covalent, may be represented by solid argon, sodium, halite, and diamond respectively at the apices of a tetrahedron. These, and some intermediate bond type materials, are shown in Text-fig. 1.

Properties

The diamond, then, is to be noted for its extreme covalency. This type of bonding between the atoms creates a mechanically strong material, and one manifestation of this strength is the hardness of the diamond. This is a difficult property to measure, or even to define. Indentation with a hard pyramidal or ball point, as in the Vickers or Brinell hardness tests, is scarcely practicable with diamond, as only a diamond point can be used. This deforms as the indent is made, and so reduces the accuracy of the subsequent measurements. Abrasion hardness tests using either a grinding wheel (Wilks 1961) or an air blast armed with corundum (Grodzinski 1952) have both been used to estimate the hardness of diamond, and widely varying results have been achieved, both because of the directional variations in the diamond but also because of the inherent errors in the methods used. Compressibility can also be used as an index of strength or hardness, and diamond gives a value about $1/20$ that of quartz, and about $1/3$ that of corundum. Mohs' scale is a very rough indication of relative hardness, and merely indicates that diamond (10) is harder than corundum (9), but the figures have no quantitative significance.

Very high refractive index and dispersion, giving the renowned 'fire' of the diamond, also indicate the great rigidity of the atomic lattice. The refractive index is the highest known for a colourless solid. Similarly the high thermal conductivity ($1/3$ that of silver), and the low coefficient of expansion ($2/3$ that of Invar) are other indications of the lattice properties. The diamond has a very wide transparency both in the infra red and in the near ultraviolet. A less known property which merits further examination is its low coefficient of friction, which is the same as that of polytetrafluoroethylene, and half that of the other carbon allotrope, graphite.

The diamond is again remarkable in that it has two totally different natural origins, for it is found as a rare accessory mineral in igneous rock and also as a rare component in both stony and iron meteorites. The study of the diamond has been handicapped in the past by the failure of reproducible synthesis, if indeed it had been achieved at all, but in 1956 the synthesis was accomplished by Bovenkerk, Bundy, Hall, Strong, and Wentorf, and is now the basis of a flourishing industry. Lastly, the diamond has been regarded with awe because of the difficulties of working it, although the methods used are in fact extraordinarily unsophisticated.

The diamond lattice of tetrahedrally linked carbon atoms having a constant spacing of 1.54 \AA is the key to the methods of diamond working, as well as to the common crystal forms. It is cubic, of high symmetry, although slight doubt still exists as to its holohedral nature (Eppler and Rose 1925). The commonest form seen is the octahedron, but rhombic dodecahedra, cubes, trisoctahedra, and combinations of these are known, and are illustrated fully by Fersmann and Goldschmidt (1911). Polycrystalline diamond in the form of ballas bort, carbonado, and framesite are known and are valued for their toughness.

In the working of single crystal diamond, the lattice directions are all-important. The principal cleavage is octahedral, and an examination of a lattice model shows why this should be so. The crystal can also be divided by sawing with a bronze disc armed with diamond powder, but only in a direction parallel with either the cube or dodecahedron faces, and 'cutting' or grinding on a cast iron wheel or scaife is only possible in certain lattice directions. Bruting, a crude turning operation, is used to produce round shapes in the production of brilliants. Grodzinski (1952) has described the manufacturing processes of the diamond industry exhaustively, and Tolansky (1962) has given an account of the history of these processes. Other methods of working are possible but have not been used extensively. These include flame cutting, graphitizing by heating in vacuo to about 900°C ., etching in oxidising agents, and neutron irradiation, after which the diamond may be cut in any direction, and annealing, which partially restores its directional properties (Wilks 1963).

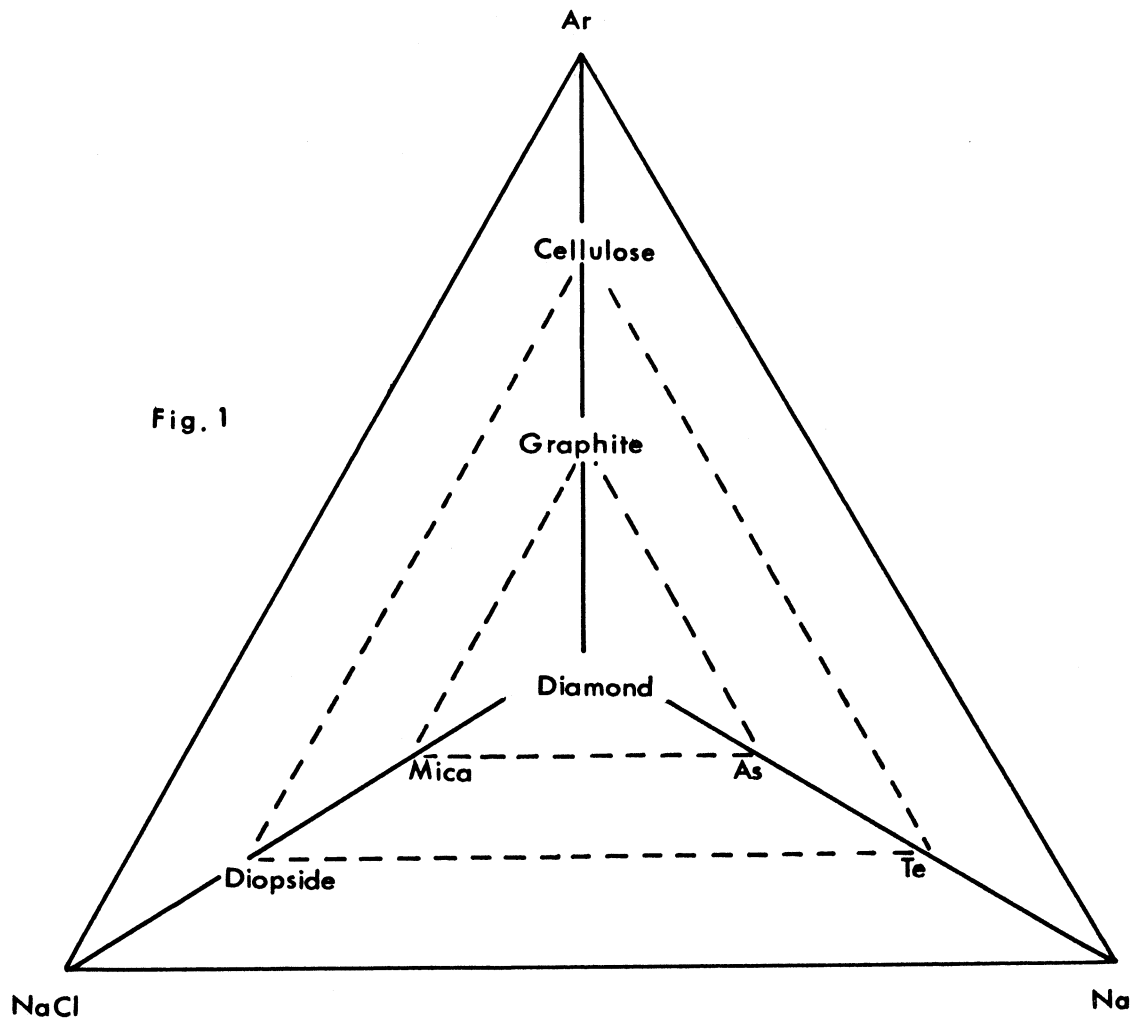


Fig. 1

after Grimm

In addition to its use as a gem, the unique combination of properties of the diamond make it useful in other fields. Its transparency enables it to be used for instrument windows, while owing to its low atomic weight, its relative transparency to x-rays combined with its strength makes it ideal as a pressure vessel material in high pressure x-ray diffraction work. Its high refractive index enables it to extend the range of refractometers, and it has been used as a lens. For solids of normal hardness, diamond indenters are ideal, and its anti-frictional and anti-abrasion properties make it suitable for watch and instrument bearings and as a stylus. Industrially the diamond tool is an essential for working other hard materials and for dressing abrasive wheels, while suitably shaped crystals, after drilling, find application as wire dies of incomparable longevity and accuracy. The polycrystalline, misshapen, and impure diamonds are set in drilling bits, and in powder form the diamond is the hardest and fastest cutting abrasive.

The Occurrence of Natural Diamonds

The terrestrial diamond occurs most commonly as monocrystals, and more rarely as polycrystals. It is found associated, as about 1 part in 10^6 , with one or two kimberlites in a hundred. These are brecciated, hydrothermally altered mica peridotites containing (besides diamond) corundum, chrome-diopside, pyrope garnet, and boulders of eclogite. (Williams 1932). Unaltered shales, lava blocks, limestones, plant remains, and granite boulders have all been reported from kimberlites. Within the diamond may be included pyrope, diopside, graphite, quartz, olivine, and liquid CO_2 . The true matrix of the terrestrial diamond has not been established, but it seems clear that the kimberlite is not a candidate as it is obviously a low-temperature rock, acting merely as a vehicle. Eclogite seems a more likely material as its constituents are included in the diamond. The kimberlite 'pipes' are often elongated in plan, may be arranged in lines, and may be more in the nature of fissures. Terrestrial diamonds are mined, or produced from alluvial sources, at the rate of about 25 million carats (5 million grams) annually.

Meteoritic diamond is a comparative rarity. Only about 50 carats (10 grams) has been recovered, and this from five meteorites. The Cañon Diablo iron and the Novo Urei and Goalpara achondrites have particularly been studied (Carter and Kennedy 1964). The diamond is associated with iron, nickel-iron alloy, graphite, olivine, troilite, and magnetite.

Analyses of diamond impurities are few. Chesley (1942) has reported on the elements found by spectrographic analysis in 33 stones, and shows that Al, Si, Ca, and Mg are always present, while Cu, Ba, Fe, Sr, Na, Ag, Ti, Cr, and Pb are sometimes seen. Raal (1957), reporting on another group of stones, comes to a rather similar result, but reports an absence of Ag, Ni, Na, and Sr. Kaiser and Bond (1959) have shown by electron spin resonance measurements that nitrogen can occupy substitutional positions in the diamond lattice up to 0.15%. Evans and Phaal (1962) in a particularly elegant study have shown that the nitrogen occurs as platelets, and these produce dislocation loops which can be seen in the electron microscope.

The variations of crystal habit and of impurity are therefore known, and it may be surmised that these are indicative of growth under a range of conditions. The surfaces of natural and synthetic diamonds have been closely studied by Tolansky and his school (see for instance Tolansky 1960 and Patel and Tolansky 1957), and they and Seal (1962) have shown that by sectioning the diamond and then etching the cut surface, growth layers constituting a stratigraphic history of the growth are revealed. It is seen that the habit of the stone may change during growth, that growth may be interrupted by periods of dissolution, and that impurities may be incorporated in the stone at certain stages. Coated stones are well known to the trade and often contain a clear core.

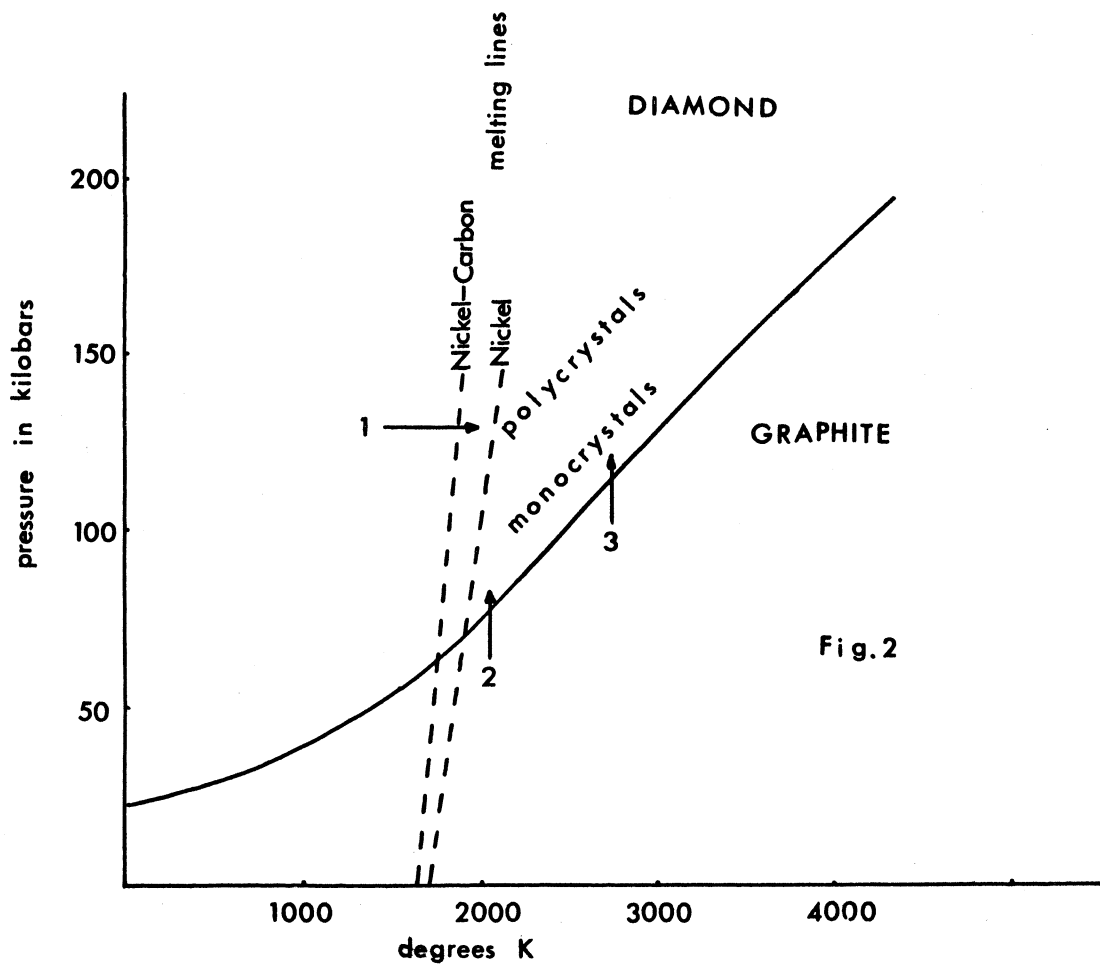


Fig.2

The Synthesis of Diamond

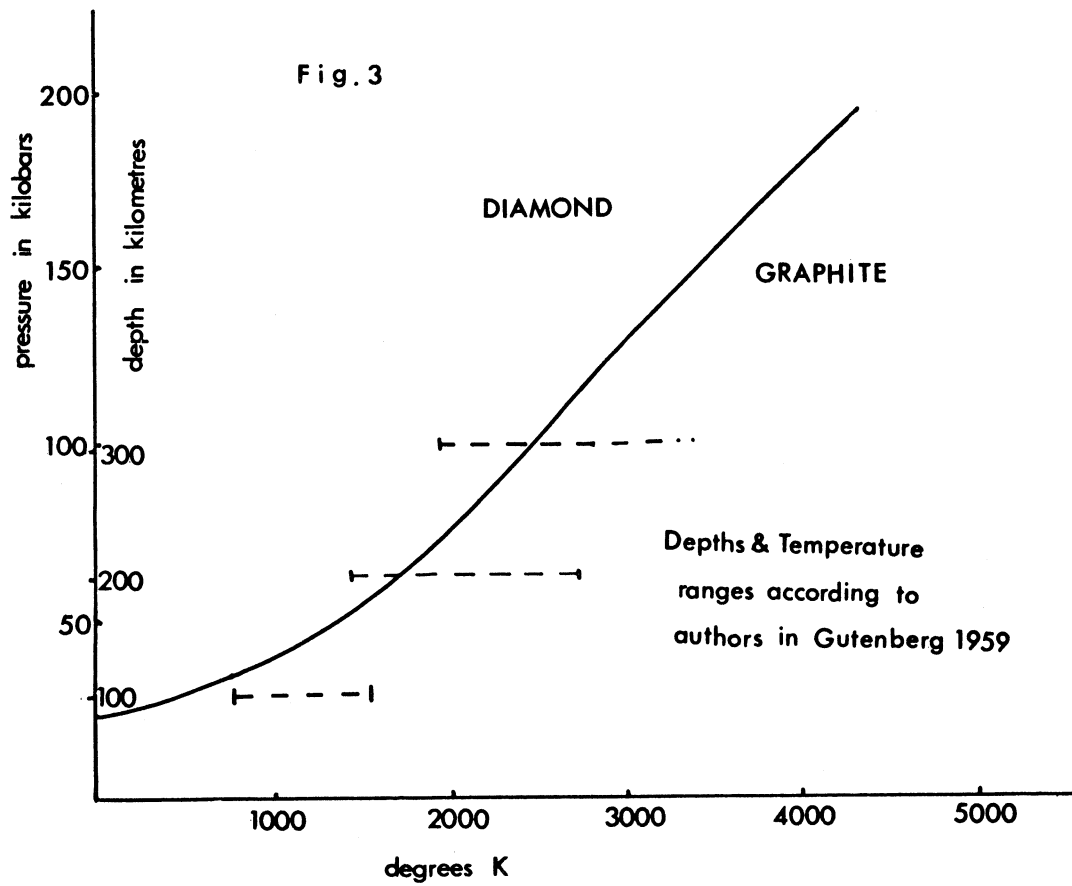
Berman and Simon (1955) postulated an equilibrium diagram for the graphite-diamond system, and the subsequent synthesis confirmed their views. Below 1500°C. the transition is very slow, but above this temperature and at a pressure above about 55 kilobars, it takes place rapidly. At this pressure and temperature the presence of a solvent which may also act as a catalyst is required, and although nickel is commonly used, many metals and salts will serve (Giardini and Tydings 1962). In the absence of a catalyst, the transition has been brought about around 213 Kb and 4000°C. The pressures required are generated in a tetrahedral anvil or 'belt' apparatus (Hall 1960) and the heat applied by passing a current through the reaction cell. De Carli and Jamieson (1962) have described a more spectacular method of producing simultaneous high pressures and temperatures by an explosive charge.

The crystal habit may be controlled during the transition by the manipulation of pressure and temperature. The effects of changes along different paths, according to Wentorf and Dovenkerk (1961) together with the Simon-Berman line and the nickel and nickel-carbon melting lines are shown in Text-fig. 2. Path 1 produces black polycrystals, path 2 black cubes and path 3 green or colourless octahedra. These effects may not be analogous to the changes taking place during the growth of natural diamond, but at least they offer some suggestions. The speed of transition is quite rapid, requiring but a few minutes, and this may mislead us into thinking that the natural growth is equally rapid. If it is not, then it may take place at a lower temperature and pressure, but still somewhere along the Simon-Berman line.

Turning again to natural diamond, more is known of the origin of meteoritic than of terrestrial diamond. The true matrix of the meteoritic diamond is accessible, and although infinitely less material is available, this is in some respects an advantage. Even here a major difference of opinion obtrudes. The pressures and temperatures required to bring about a transition from graphite to diamond may be produced either by gravitational forces in the interior of a planet (which must subsequently fragment and fall on the Earth) or they may be produced by impact. The planet theory requires a body about the size of the Moon, but the requirements of the impact theory are more modest. Lipschutz and Anders (1961) indicate that a sphere of nickel-iron 60 m. in diameter travelling at 15Kms./sec. would provide ample energy, and the known situation at Cañon Diabolo lends credence to the idea, although both ideas are tenable.

Growth Depths of Natural Diamond

In the problem of terrestrial diamond, it is of interest to add to the graphite-diamond equilibrium diagram, the pressure-temperature and depth values quoted by Gutenberg (1959) for the mantle of the Earth (Text-fig. 3.) Giardini and Tydings (1962) have pointed out that natural and synthetic diamond formation are not at all comparable, in that natural diamond is but a trace presumably in a silicate system, while synthetic diamond forms a large proportion of the reacting carbon-nickel system. Nevertheless, the equilibrium diagram is quite general, and so the P-T relations indicated by it must apply; and it seems likely that natural growth takes place from solution. The control of crystal habit in nature is not clearly indicated by the synthetic conditions, for even small amounts of impurity can affect the habit of crystal growth. Wentorf and Bovenkerk (1961) point out that natural diamonds occur either as large monocrystals or as small aggregated polycrystals, and suggest that the latter were produced well above equilibrium, giving rapid nucleation, whereas the former grew near equilibrium. The interruptions of growth in monocrystals described above seem to confirm this.



It seems reasonable to suppose that diamond growth in nature may take place at temperatures and pressures approaching those required in the laboratory, and the known stability of its associated minerals in these conditions tends to confirm this. We may therefore see that the depths at which formation is likely are in the order of 200 Kms.

Distributional Considerations

Bardet (1964), following a line mapped out by Brock (1957) and independently by Russian workers, has shown that 99% of all diamond production comes directly or indirectly by way of alluvial deposits from shield or platform areas. The latter are distinguished from the former by a thin cover of more or less unfolded younger sediments. They are together the areas which tend to behave as unitary blocks of the crust, and which tend to maintain their individuality through all the vicissitudes of diastrophism. Conversely, almost no diamonds are found in areas of folded sediments. The argument runs, then, that any fractures found in the shield or platform areas, and they are generally large, must of necessity be deep-seated, even to the extent of being an expression of stresses in the upper mantle. The apparently deep-seated source of some components of the kimberlites, the linear arrangements of pipes, the suggested depth of origin of the diamond, and the restriction of diamond production to the rigid areas where fractures may penetrate more deeply, all appear to agree together. The practice of drawing fractures on a small scale map of Africa causes doubt in the minds of some, but in fact if the fractures are real they will be large, and so realistically represented. Fielder's (1963) work on the tectonics of the Moon has shown that large fractures may exist and appear to have a near planet-wide distribution, and it would be no surprise to find that the lunar fractures are deep-seated also.

The present time is very propitious for a further investigation of the origin of natural diamond. The synthesis of diamond has provided a firm base from which advances can be made, and at the same time solid-state physics and particularly the study of crystal growth and imperfections can offer new assistance. The geologist, who for too long has neglected the diamond, has started to work on problems of the lower crust and upper mantle, and can evaluate and use the laboratory results. Out of such work could come not only the true origin of the diamond but also an increased knowledge of sub-crustal geology.

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