Reports

Hexagonal Diamonds in Meteorites: Implications

Abstract. *A new polymorph of carbon, hexagonal diamond, has been discovered in the Canyon Diablo and Goalpara meteorites. This phase had been synthesized recently under specific high-pressure conditions in the laboratory. Our results provide strong evidence that diamonds found in these meteorites were produced by intense shock pressures acting on crystalline graphite inclusions present within the meteorite before impact, rather than by disintegration of larger, statically grown diamonds, as some theories propose.*

Recently a previously unknown polymorph of carbon, referred to by us as hexagonal diamond, was prepared in both static and shock high-pressure experiments (*1–4*). The temperature-pressure conditions under which these diamonds formed suggested that this phase might be present in diamond-bearing meteorites. Our primary purpose is to report the discovery and characterization of hexagonal diamonds in the Canyon Diablo and Goalpara meteorites, and to show how these findings have important implications concerning the origin of meteoritic diamonds.

Identification and synthesis in the laboratory of hexagonal diamond by static pressure methods have been described (*1, 2*). This new phase has also been made in the laboratory by shocking a dispersion of fine graphite in a metal matrix (*4*). Basically, this polymorph of carbon has a hexagonal lattice with four atoms per unit cell at 000,00 3/8, 1/3 2/3 1/2, 1/3 2/3 7/8. The lattice parameters are $a = 2.52$ Å and $c = 4.12$ Å. The corresponding x-ray density is 3.51 g/cm^3—equivalent to that of cubic diamond. The hexagonal diamond has a wurtzite-like structure except that every atom is carbon. Figure 1 shows schematically the calculated relative intensities and positions of the x-ray lines, with nonzero structure factors, in the pure hexagonal and cubic phases; the corresponding *d*-spaces appear in Table 1. It is particularly interesting that all cubic lines coincide with hexagonal lines.

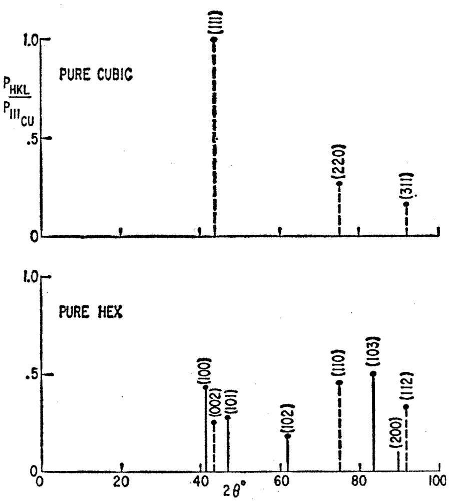

Fig. 1. Calculated relative positions and intensities of the x-ray lines, with nonzero structure factors, in pure cubic and pure hexagonal diamond phases (Cu*K*α).

The approximate range of pressure-temperature conditions under which hexagonal diamonds can be formed in the laboratory is shown in a carbon-phase diagram (Fig. 2). Cubic diamonds can also be formed in the laboratory by three other types of methods: (i) the catalytic or indirect process, which utilizes certain liquid metals or alloys and static pressures (*5*); (ii) the direct static transition (*6*); and (iii) the direct shock transition (*7*). The pressure-temperature conditions required for success with each of these methods are also shown in Fig. 2.

We obtained three diamond-bearing samples of the Canyon Diablo meteorite and diamond samples of the Goalpara and Dyalpur meteorites (*8*); all were in the form of small, black, fine-grained agglomerates, a few tenths of 1 mm in size. Metallographic examination of the metallic regions immediately surrounding the Canyon Diablo diamond agglomerates revealed clear evidence of the ε-iron transition (*9*); thus the specimens must have been shocked above 130 kb.

Debye-Scherrer x-ray powder-pattern films were obtained from each of the specimens by use of Co*K*α and Cu*K*α radiations. Quantitative intensity-versus-θ data were then obtained from microdensitometer traces of the films by use of a calibrated instrument. Figure 3 shows the intensity-versus-θ plot (corrected for background) obtained from one of the Canyon Diablo specimens. On the basis of the known crystal structure of hexagonal diamonds, determined during our earlier laboratory studies (*1, 2*), the individual hexagonal and cubic peaks were reconstructed by standard analytical techniques. These reconstructed peaks obey the criteria that: (i) their maxima fall at the positions coinciding with those of the hexagonal phase made earlier; (ii) the relative intensities of the 100, 002, and 101 lines are in the calculated ratios, which were confirmed experimentally from the synthesized phase; and (iii) the half-breadths of the 100, 002, and 101 peaks are approximately equal. Similar peaks were obtained for all other Canyon Diablo and Goalpara specimens; the Dyalpur specimens were too small to yield adequate patterns.

The volume fractions of hexagonal and cubic diamond coexisting in the meteorites were determined from the experimental integrated x-ray intensities of both phases by use of expressions derived from established x-ray theory (*10*). Our experimental results reveal that the three Canyon Diablo specimens comprise about 30 percent

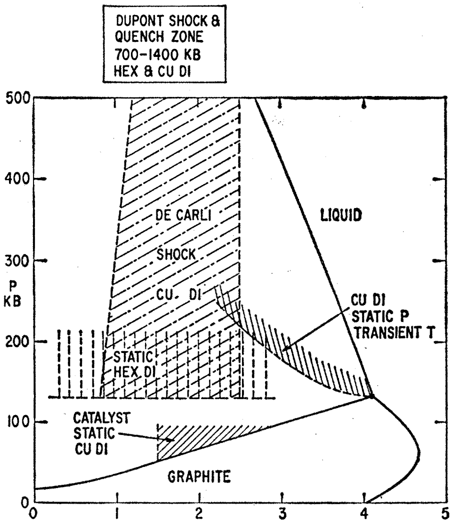

Fig. 2. *P, T* carbon-phase diagrams showing *P, T* areas where different diamond-synthesis reactions occur.

hexagonal phase and 70 percent cubic phase. The Goalpara diamonds are mainly cubic, with less than 10 percent hexagonal.

The approximate crystallite sizes of the meteoritic diamonds were determined by x-ray line-broadening and electron microscopy. The broadening established a lower limit of the crystallite size, since other contributions such as strain-broadening may be present. Electron microscopy established the upper size limit, since the diamond particles seen under the microscope could be composed of one or more individual crystallites. The x-ray crystallite size was determined from the familiar broadening equation, $D = K\lambda/\beta_p \cos \theta$, by use of established procedures to relate the particle-size broadening β_p to the measured half-breadths (Fig. 3). Average crystallite sizes of hexagonal and cubic diamonds in the Canyon Diablo meteorite proved to be about 50 and 90 Å, respectively. Electron microscopy of the Canyon Diablo specimens at × 25,000 and × 100,000 indicated a maximum limit of the crystallite size of less than 200 Å.

The origin of meteoritic diamonds has recently excited considerable interest and controversy (*11–13*); two types of theories have evolved to explain their existence. According to the static pressure–type theories, the diamonds were made at high gravitational pressures inside parent bodies of lunar size or larger. On the other hand, the shock-type theories suggest that they were formed from graphite preexisting within a much smaller original body; the diamond-producing shock could have been generated by either impact with Earth or collision in space.

The following facts, established by experimental studies of diamond synthesis in the laboratory, are relevant to consideration of formation of meteoritic diamonds (Fig. 2):

1) The static catalyst–molten metal process yields only the cubic type of diamond, with crystal sizes ranging from microns to millimeters.

2) The static direct-transition process for formation of cubic-type diamond from randomly oriented polycrystalline graphites requires very high threshold temperatures ranging from 3500°K at 130 kb to 2500°K at 230 kb; it yields crystallite sizes of many hundreds of angstroms.

3) The static direct-transition process for forming hexagonal diamond requires well-crystallized graphite, with the *c*-axes of the crystallites parallel with the direction of compression, and with "setting" temperatures (*2*) exceeding about 1300°K. The yield may approach 100 percent hexagonal diamond, with crystallite sizes of a few hundred angstroms.

Table 1. Interplanar spacings for hexagonal and cubic diamond phases.

hkl		*d*
Hexagonal	Cubic	(Å)
100		2.18
002	111	2.06
101		1.93
102		1.50
110	220	1.26
103		1.16
200		1.09
112	311	1.076

4) When liquid carbon freezes at pressures higher than that of the graphite-diamond-liquid triple point (about 130 kb), large crystallites of cubic-type diamond and graphite are formed.

5) The DeCarli shock-pressure process uses blocks of polycrystalline graphite of subtheoretical density and yields only cubic-type diamond of crystallite sizes around 100 Å.

6) The du Pont shock-pressure process uses graphite particles, of theoretical density, dispersed in a massive metal matrix that serves as the shock plate and as a thermal-quenching medium. It yields a mixture of cubic and hexagonal diamond, with crystallite sizes ranging from 50 to 100 Å; the hexagonal fraction ranges downward from about 40 percent—generally less than 10 percent (*4*).

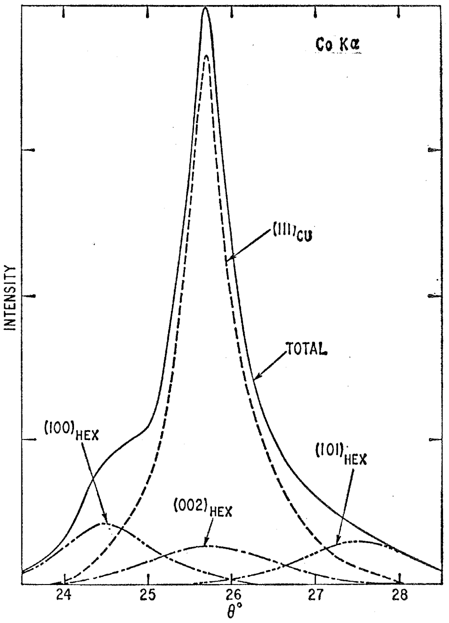

Fig. 3. Intensity-versus-θ plot obtained from one of the Canyon Diablo meteoritic-diamond specimens, with resolution into component lines (Co$K\alpha$).

7) Quantitative x-ray intensity profiles obtained from powder patterns on the du Pont shock diamonds were virtually identical with a Canyon Diablo profile (Fig. 3; *15*).

8) Our evidence indicates that cubic diamond cannot be transformed, even partially, into hexagonal diamond by application of static or shock pressure combined with temperature.

9) There is no evidence of hexagonal diamond in any diamonds of terrestrial origin.

These findings lead to the conclusion that the diamonds present in the Canyon Diablo and Goalpara meteorites were formed by impact shock from well-crystallized graphite existing within the meteorites before impact.

This diamond-producing impact of the Goalpara meteorite was almost certainly a collision in space, whereas the Canyon Diablo diamonds appear to have been produced by collision of this meteorite with Earth (*13*). The theories (*12, 14*) that meteoritic diamonds were formed, upon shock, from "large" parent diamonds existing in the meteorites before impact are ruled out by the presence of hexagonal diamond. In principle, it is possible that the hexagonal x-ray pattern found in the meteoritic samples could be due to a chemical compound; but this possibility is extremely improbable since the line positions, relative intensities, and breadths of this meteoritic phase are identical with those of the hexagonal-diamond pure-carbon polymorph synthesized in the laboratory.

Although the results of our study indicate that crystalline graphite was the immediate source of the observed meteoritic diamonds, the origin of the graphite is not specified. One cannot rule out the possibility that the graphite came from graphitization of diamonds formed during the earlier histories of the bodies involved (*15*). Goldstein and Ogilvie (*16*) have shown that the Canyon Diablo and other metallic meteorites must have cooled from temperatures exceeding 1000°K at low pressures for periods of the order of 10^8 to 10^9 years. Their results do not a priori exclude the possibility that the conditions for static catalyst growth of large cubic diamonds out of molten iron-nickel existed before this cooling cycle. Such conditions could conceivably explain the cubic morphology of reported (*17*) cliftonite (graphite) particles; yet other postulates may explain the formation of cliftonite (*11, 12*).

Since the moon suffers many highly energetic impacts, unattended by atmospheric friction, one may expect to find shock-formed hexagonal and cubic diamonds on its surface.

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5 December 1966

Molecular Beams with Energies above One Electron Volt

Abstract. *By using as sources supersonic jets of hydrogen or helium containing small concentrations of heavier molecules we have been able to obtain molecular beams with kinetic energies of the heavy molecules well into the range above 1 electron volt. A variety of molecules have been successfully accelerated. Intensities of 10^{16} to 10^{17} heavy molecules per steradian-second have been achieved at these high energies.*

In the usual molecular-beam apparatus, gas effuses from a source cavity or "oven" through a small hole into a chamber maintained at high vacuum by continuous pumping. The gas in the oven is maintained at a density sufficiently low that the molecules undergo no collisions in passing through the hole. Once in the evacuated chamber they travel in straight-line continuations of their original trajectories until they strike a surface and lose their identity in the background gas. If one or more collimating orifices are placed coaxially with the source hole, those molecules having trajectories within the solid angle defined by the source and collimating apertures emerge from the last collimator in the form of a beam or ray. This collision-free beam of molecules may be subjected to deflection by various kinds of fields. Or these molecules may be directed at various kinds of targets (such as surfaces and intersecting beams of electrons, ions, photons, or other molecules) resulting in collisions under highly specified and controlled conditions. Both deflection and collision experiments have been a source of information about the structure and properties of atoms and molecules (*1*) and have led to such important technological developments as the atomic clock, the maser, and the laser.

In collision experiments relating to chemical reactions and structure, molecular beams play a role analogous to the more familiar one performed by particle beams from high-energy accelerators in the study of nuclear reactions and structure. Molecular beams have suffered from limitations in energy and intensity which are analogous to the limitations encountered by their more famous high-energy cousins (*2*). Effusive sources of the type we have described are very often incapable of providing beam intensity sufficient to give useful signal-to-noise ratios in experiments involving collisional events that have small cross sections or probabilities of occurrence. Perhaps even more important has been the energy limitation. With the refractory materials now available, source ovens have a maximum operating temperature of about 3000°K which corresponds to an upper limit in mean kinetic energy of the beam of about 12 kcal per mole or 0.5 ev per molecule. Beams formed by charge-exchange neutralization of electrostatically accelerated ions have essentially no upper limit to their energy but because of space-charge effects cannot provide the intensities necessary for many experiments at energies below 10 ev. Consequently, the range from 0.5 to 10 ev has been virtually inaccessible to molecular-beam experiments. In just this range occur the gas-phase collision processes important in many chemical reactions and in high temperature transport phenomena.

Kantrowitz and Grey in 1951 suggested that very large increases in useful beam intensity might be obtained if the quiescent gas in the usual oven source were replaced by a low-density supersonic jet (*3*). They reasoned that if the gas at the entrance to the source orifice or "skimmer" had a streaming velocity that was large relative to the random thermal velocity of the molecules, that is, if it had a high Mach number or speed ratio, the molecules passing through the skimmer would be "focused" on the beam axis by the high component of velocity in the beam direction. Since Becker and Bier reported the experimental substantiation of this idea (*4*), a number of groups have confirmed the effectiveness of the Kantrowitz-Grey technique for providing useful intensities thousands of times greater than those possible with effusive sources (*5*). We now report that the use of a supersonic jet as the source gas for a molecular beam permits increasing the beam energy into the hitherto inaccessible range above 0.5 ev.

If a pure gas expands isentropically in a free jet, the average kinetic energy of the molecules in laboratory coordinates due to their streaming motion is:

$$\tfrac{1}{2}\, mV^2 = \int_{T}^{T_0} c_p\, dT \qquad (1)$$

where V is the flow velocity, m is the molecular mass, c_p is the molecular specific heat at constant pressure, T_0 is the stagnation or source temperature, and T is the static temperature in the jet. At Mach numbers above 5 the static temperature becomes effectively zero and the average kinetic energy of the molecules rapidly approaches a limiting value which is slightly larger than the average kinetic energy in an effusive beam having the same source temperature. In the case of a binary