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The Origin of Diamonds in the Ureilites

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ABSTRACT

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The previously suggested shock origin of diamonds in stony meteorites has been verified by the finding of a pronounced preferred crystallographic orientation in diamonds from two of the three ureilites. In agreement with theory the only other diamonds which show such structures were produced by anisotropic processes such as shock.

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Introduction

In previous papers (1,3) on the subject of the origin of meteoritic diamonds (Table 1) I concluded that the diamonds in Canyon Diablo formed by the shock conversion of graphite during impact of the meteoroid with the Earth. The subsequent finding of coesite (3) and stishovite (4) in the sandstone around the Canyon Diablo crater indicate shock pressures of at least 100 kb. The shock-induced conversion of graphite to diamond (5) also lends strong support to the shock origin of Canyon Diablo diamonds.

The ureilites (6) however are too small (Table 1) to have hit the Earth at speeds much greater than terminal velocity implying that the diamonds could not have formed during the ureilites' impact with the Earth. I therefore suggested (1) that the diamonds in these meteorites were formed by some pre-terrestrial shock - probably the one occurring during catastrophic breakup of the ureilites' parent body. It is the purpose of this paper to report on an x-ray study of meteoritic and synthetic diamonds undertaken to examine this suggestion.

The direct conversion of graphite to diamond is not a complex one. It is necessary only to increase the interatomic distance within individual carbon planes by 0.13 Å (Figure 1) and decrease the interplanar spacing (c-axis) by about 1.85 Å. Assuming a randomly oriented infinite distribution of graphite crystallites, it should be possible to determine whether a given diamond aggregate was produced by shock, inasmuch as only those graphite crystallites with c-axes parallel to the direction of motion of the shock will be converted to diamond. The resulting diamonds should exhibit a preferred crystallographic orientation ("fiber"). Diamonds formed by hydrostatic (gravitational) compression, on the other hand, will show no such structure since hydrostatic pressure acts isotropically in a medium. In the actual case the situation may not be quite so simple because of complicating effects due to secondary and rarefaction (reflection) waves. However, a preferred orientation should be apparent in at least some diamonds formed by shock.

Experimental

Specimens from all three ureilites were used in this study. I should like at this point to very gratefully acknowledge the loan of the Dyalpur meteorite (Dr. E. Olson, Chicago Natural History Museum), and Goalpara and Novo Urei meteorites and thin sections (Dr. E. P. Henderson, U. S. National Museum). I should also like to thank P. S. DeCarli (Stanford Research Institute), Dr. R. H. Wentorf Jr. (General Electric Research Laboratory) and M. Waxman (National Bureau of Standards) for their gifts of synthetic diamonds produced by various techniques.

Specimens were prepared for x-ray analysis by carefully carving or chipping them out so as not to affect the possible orientation of the crystallites within each fragment. The specimens, each of which weighed less than about 0.1 mg, were then examined by previously described diffraction techniques and equipment (2) to determine their composition. Fortunately the other phases present in the specimens did not possess diffraction lines which would interfere with those of diamond.

After verification of the presence of diamond in the fragment, the specimen was studied with a Unicam Model S.25 Single Crystal Goniometer (Unicam Instruments Ltd., Cambridge, England).

Stationary x-ray photographs were taken every 10° with iron-filtered CoKα (for the (111) diamond planes) and zirconium - filtered MoKα (for the (220) and (311) planes of Goalpara diamond). The angles ρ and ψ corresponding to the ends of the preferred orientation zones in each set of normals to the reflecting planes were measured (7) and then plotted on a polar stereographic net graduated in 2° increments (8) using both clockwise and counter-clockwise rotation. The most significant information was obtained from the stereographic projections plotted in clockwise rotation and these were used in the discussion which follows.

Ureilitic Diamond Composition and Size Distribution

All of the discrete diamond grains which I have analyzed are polycrystalline aggregates consisting of diamond, randomly oriented polycrystalline graphite, and other phases (Table 2).

The $\alpha_1 - \alpha_2$ doublet of the diamond (331) plane provides a useful measure of the average crystallite size. From its lack of resolution in Goalpara, Zachariasen (9) has estimated the diamonds to be ~100 Å. The diamonds from Dyalpur and Novo Urei on the other hand are relatively quite large, with those from Dyalpur being considerably larger than 300 Å.

Orientation

Figure 2 is a magnification (2x) of the diffraction pattern of a Goalpara diamond. It should be noted that the diamond reflections indicate pronounced preferred orientation while the graphite is randomly oriented. Stereographic projections of the diamond [111], [220], and [311] directions (Figures 3 a,b,c,) reveal very striking patterns. The angles indicated on each projection are those which that simple cubic plane makes with its (311) plane (10). As may be seen, agreement is quite good indicating that the oriented planes in the diamond are probably those parallel to (311).

It is well to pause at this point and note that the preferred orientation of diamond indicative of formation by an anisotropic process is present in Goalpara and (as will be seen) in Novo Urei also. Natural terrestrial diamonds have never been reported to contain preferred orientation nor does an extensive monograph (11) on these structures in terrestrial rocks and minerals make mention of this "fabric" in diamond.

Previous x-ray studies of hydrostatically-produced synthetic diamond (12, 13, 14) do not indicate preferred orientation. The two samples which I studied do not show such orientation.

Synthetic diamonds produced by the anisotropic application of temperature and/or pressure, i.e. by flash-heating (15) or by 300 kb shock (Figure 4), possess oriented structures. The stereographic projections of these data show a grouping at about $\rho = 70^{\circ}$ for the former and a single "node" (compare with Figure 6) at about 40° for the latter. Diamonds produced by shock at pressures significantly lower than 300 kb are very polycrystalline and do not have detectable orientation. Thus, in accord with theory the only diamonds which exhibit preferred orientation were produced by some anisotropic process.

The x-ray pattern of a diamond from Novo Urei (Figure 5) is similar to that of 300 kb shock-produced diamond (Figure 4). The stereographic projection of the Novo Urei data (Figure 6) is different in character from that of Goalpara (Figure 3 a) - probably arising from differences in their pressure history.

Fortunately other phases present in these two meteorites can yield information on the ureilites' pressure-temperature history. Olivine from Novo Urei (Figure 7 a) is still reasonably single crystal, although it is fractured to some extent. Goalpara olivine on the other hand is heavily fractured (Figure 7 b) and in some regions shows signs of recrystallization along grain boundaries, indicating excursion into temperatures well above its melting point. Inasmuch as the only known natural process which can develop significant anisotropic pressure is shock, it appears reasonable that the diamonds in at least these two ureilites formed in this manner. It does not seem too extreme to suppose that the diamond formation and recrystallization of the olivine in Goalpara were cotemporaneous. Hughes and McQueen's data (16) on shocked olivine (dunite) indicate that even at the maximum pressure studied (700 kb), the temperature reached only 720°. At pressures of 400 kb, well into the diamond-forming region, the temperature rises to less than 200°. Thus, Goalpara which was shocked more severely than Novo Urei, was probably exposed to pressures considerably in excess of 700 kb.

Diamond from Dyalpur on the other hand shows no preferred orientation. It is possible that the diamonds in this meteorite were formed by gravitational pressure rather than by shock as in Goalpara and Novo Urei. Dyalpur's textural similarity to the other two ureilites would argue against different modes of diamond formation (Occam's Principle). We do know that diamond produced by shock at pressures well below 300 kb does not show preferred orientation and it may be that Dyalpur diamonds formed at these relatively low pressures. A more likely possibility is that the temperature of the Dyalpur graphite was high enough to allow the formation of well-crystallized diamond from shock-melted graphite. A similar interpretation has been advanced by Bundy (17) in order to explain the formation of very well-crystallized graphite by the flash-heating of fine-grained polycrystalline graphite. A detailed study of the mineralogy of the ureilites is presently being made (18) and should help in deciding between the two alternatives.

Mechanism of Shock Formation of Diamond

Figures 3a, 3b and 3c show certain features which may have bearing on the details of shock formation of diamond in Goalpara. First, there seems some degree of assymetry evident in the distribution of "groupings" in each set of normals. Second, there are two anomalous "nodes" present in the [220] which occur at about 30°. The former effect may be explained by lattice distortion of the diamond crystallites while the latter may be due to the presence of some diamonds formed by rarefaction waves or by secondary shocks. Another feature which may be of significance is that there appear to be only a few groupings at about 51°. This effect may only be an apparent one inasmuch as the zones in the Goalpara [311] are quite extended and markedly overlap the 51° line. The only other reasonable match for the groupings would be by planes parallel to the (210). Were these the oriented planes however, we would not expect the group at about 30° in the [220] or at about 60° in the [111]. It is possible that the observed distribution of axes is due to some combination of oriented (110) and (311) planes, although the available evidence favors the interpretation of the oriented planes being parallel to (311) only.

From meteoritic and artificially shock-produced diamonds some suggestions concerning the mechanism of shock conversion of graphite to diamond can be made. At pressures well below 300 kb polycrystalline fine-grained diamond apparently forms from polycrystalline graphite, possibly by compression of rhombohedral graphite only (6). From pressures of about 300 kb to well above 700 kb the solid-state reaction involves conversion of the basal (001) plane of graphite to diamond (311), or possibly some combination of (311) and (110). At very high pressures the conversion may involve the hypothetical "metallic carbon" postulated by Libby (18) or the formation of diamond from shock-melted graphite.

CONCLUSIONS

The simultaneous presence of graphite, diamond and kamacite in all of the ureilitic "diamonds" which I have investigated shows that these grains are not equilibrium assemblages. Studies at 60 (20) and 100 kb (21) show that graphite formed from diamond shows preferred orientation. In at least two meteorites, however, it is the diamonds which are oriented and in all diamondiferous meteorites the graphite is polycrystalline and randomly oriented. Thus, the graphite cannot have formed from diamond. On the other hand, theory predicts that shock-formed diamond would show preferential orientation. It thus appears that all meteoritic diamonds formed by shock rather than by gravitational compression of graphite (24).

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