Reports

Xenon Fluorosilicate and Related Compounds

Abstract. *The reaction product of Xe, F_2, and SiF_4 in a glow discharge has been shown to have a composition approximating Xe_2SiF_6. It and a similar hexafluorophosphate are unstable at room temperature. A stable hexafluoroantimonate is formed from Xe, F_2, and SbF_5 at 250°C.*

The initial announcement of the preparation of a salt of xenon(I), $XePtF_6$ (*1*), was followed by reports of the preparation of $XeRhF_6$ by Bartlett (*2*) and of the "adduct" Xe-RuF_6 by Chernick *et al.* (*3*). These were prepared by combination of the noble gas with the noble metal hexafluoride. On the basis of the magnetic susceptibility the first of these was characterized as $Xe^{I}Pt^{V}F_6$, although in the absence of electron-spin resonance data there appeared to be no good reason for preferring this formulation over $Xe^{II}Pt^{IV}F_6$. More recently Bartlett (*4*) has provided more evidence for the $Xe^{I}Pt^{V}F_6$ formulation by metathetical reactions in IF_5. Bartlett (*2*) has also reported the formation of brick red $Xe(PtF_6)_2$ by the action of Xe on excess solid PtF_6 or by pyrolysis of $XePtF_6$. More recently Peacock and co-workers (*5*) have reported the formation of yellow, diamagnetic $XeF_2 \cdot 2SbF_5$ by reaction of XeF_2 or XeF_4 with SbF_5 and of straw-colored $XeF_2 \cdot 2TaF_5$ from XeF_4 and TaF_5. These are suggested to be covalent compounds of xenon(II).

We have prepared a salt of xenon which appears with little doubt to be a compound of xenon(I). When a 2:1 mole ratio of xenon and fluorine at a total pressure of less than 10 mm was passed in glass apparatus at −78°C through a 6500- to 7000-volt glow discharge, a white crystalline solid was deposited on the walls of the vessel. This solid was stable at −78°C, but upon warming to room temperature slowly decomposed to gaseous products among which Xe and SiF_4 were found by mass spectral analysis. The gaseous decomposition products were hydrolyzed in 10-percent aqueous KOH, and the silicon and fluorine content of the solution was determined by standard analytical methods. These, combined with the volume of xenon liberated, in a typical case gave a composition for the solid of $Xe_{2.8}SiF_{5.8}$. A similar run carried out with a 2:1:1 mole ratio of xenon, fluorine and silicon tetrafluoride gave a product having a 2.2:1 atom ratio of xenon to silicon. In the case of the 2:2:1 ratio about 0.35 g of product was obtained. Although it is possible to obtain molecular addition compounds under conditions such as these—as has, indeed, been suggested for the Xe-RuF_6 "adduct"—it is a little more difficult to imagine a ternary Xe-F_2-SiF_4 adduct of proportions so fortuitously close to the composition Xe_2SiF_6 and the formulation $(Xe^+)_2SiF_6^{--}$ seems to be the most reasonable.

A similar reaction with xenon, phosphorus pentafluoride, and fluorine produced a white-to-yellow solid, unstable at room temperature and containing both Xe and PF_5 as judged by mass spectral and infrared analyses of the decomposition products. On the other hand, heating a mixture of the gases at 220°C for 10 hours in a nickel bomb and passing the gases into a trap at −78°C produced nothing containing xenon.

However, when 0.153 mole of SbF_5, 0.0435 mole of Xe, and 0.0410 mole of F_2 were heated in a nickel bomb at 250°C for 12 hours, a xenon-containing, pale yellow solid resulted which reacted vigorously with water with release of xenon. This did not sublime below 100°C, whereas the compound reported by Peacock (*5*) sublimed at 60°C in vacuum. Our compound is presumed to be $XeSbF_6$.

If the radius of the Xe^+ cation is similar to that for Na^+ (*6*) and the lattice energy for Xe_2SiF_6 is similar to that for Na_2SiF_6 (*7*), the molar enthalpy for the reaction

$$2\,Xe(g) + F_2(g) + SiF_4(g) \rightarrow Xe_2SiF_6(c)$$

is about −40 kcal. If it is assumed that the entropy of Xe_2SiF_6 is the same as that of Cs_2SiF_6, ΔS for for the reaction is about −134 entropy units and ΔF is about 0 at 298°K. Since the reverse of this reaction is the expected decomposition reaction, the calculations correspond to the qualitatively observed stability. Similar calculations indicate that $XeBF_4$ should be stable up to about 150°C, but that $KrBF_4$ should be unstable down to within a few degrees of absolute zero.

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24 December 1963

Origin of Diamonds in the Ureilites

Abstract. *Diamonds in two of the three diamantiferous stony meteorites (ureilites) show a pronounced crystallographic orientation. This suggests that the diamonds were produced by shock during breakup of the meteorite's parent body rather than by high gravitational pressure.*

In previous papers (*1, 2*) on the origin of meteoritic diamonds (Table 1) I concluded that the diamonds in the Canyon Diablo iron were formed by conversion of graphite as a result of the shock of impact of the meteoroid with the earth. The subsequent finding of coesite and stishovite (*3*) in the sandstone around the Canyon Diablo crater indicates shock pressures of at least 100 kbar. The successful shock-induced conversion of graphite to diamond in the laboratory (*4*) also lends strong support to the shock origin of Canyon Diablo diamonds.

Diamonds also occur in a rare type

Table 1. Identification of diamonds in ureilites and the phases identified in individual diamonds.

Meteorite	Recovered mass (kg)	Phases identified
Dyalpur (*21*)	0.26	Diamond, graphite, α-iron
Goalpara (*10*)	2.7	Diamond, graphite, α-iron, troilite, chromite
Novo Urei (*22*)	1.9	Diamond, graphite, α-iron, clinopyroxene

of stony meteorite, the ureilites (*5*). These meteorites, however, are too small (Table 1) to have hit the earth at speeds much greater than terminal velocity, and this implies that the diamonds could not have been formed during the impact of the ureilites with the earth. I therefore suggested (*1*) that the diamonds in these meteorites were formed by some preterrestrial shock—probably the one occurring during catastrophic breakup of the ureilites' parent body. In this paper I report on an x-ray study of meteoritic and synthetic diamonds which was 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 0.12 Å (Fig. 1) and to decrease the interplanar spacing (*c*-axis) by about 1.86 Å. If a randomly oriented infinite distribution of graphite crystallites is assumed, 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 (*6*). The resulting diamonds should exhibit a preferred crystallographic orientation. Diamonds formed by hydrostatic (gravitational) compression, on the other hand, will show no such structure since hydrostatic pressure acts isotropically in a medium. In fact, the situation may not be quite so simple because of complicating effects due to secondary and rarefaction (reflection) waves. Therefore, a preferred orientation should be apparent in at least some instances of diamonds formed by shock. The absence of such an orientation, however, cannot rule out the formation of diamonds by shock.

Specimens from all three ureilites 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 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 (*7*). In this experimental arrangement, a polycrystalline aggregate would be indicated by uniform ellipses centered on the x-ray outlet port, while preferred orientation would be evidenced by enhancement of segments of these ellipses. Large single crystals would be indicated by single spots, while deformed single crystals would be evidenced by asterism of these spots in directions approximately perpendicular to the ellipses.

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 Φ, corresponding to the ends of the preferred orientation zones in each set of normals to the reflecting planes, were measured (*8*) and then plotted on a polar stereographic net graduated in 2° increments (*9*).

The composition and sizes of the diamonds in the ureilites vary. All of the discrete diamond grains that I have analyzed are polycrystalline ag-

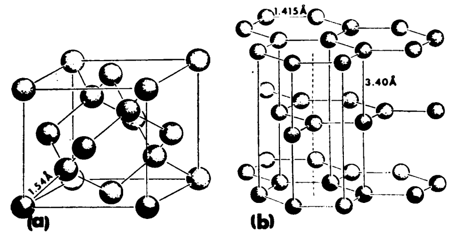

Fig. 1. Crystal structures of diamond (*a*) and graphite (*b*) [after Taylor (*9*)].

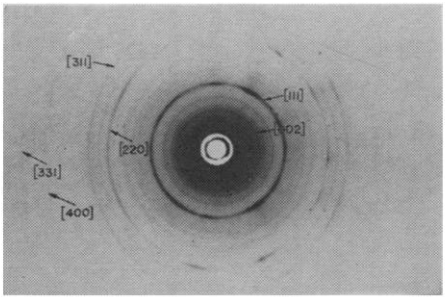

Fig. 2. Zirconium-filtered MoKα x-ray pattern of nonrotated diamond grain from Goalpara (× 2). The graphite [002] plane shows that the graphite is polycrystalline and randomly oriented. The diamond [111], [220], [311], [400], and [331], on the other hand, shows preferred orientation.

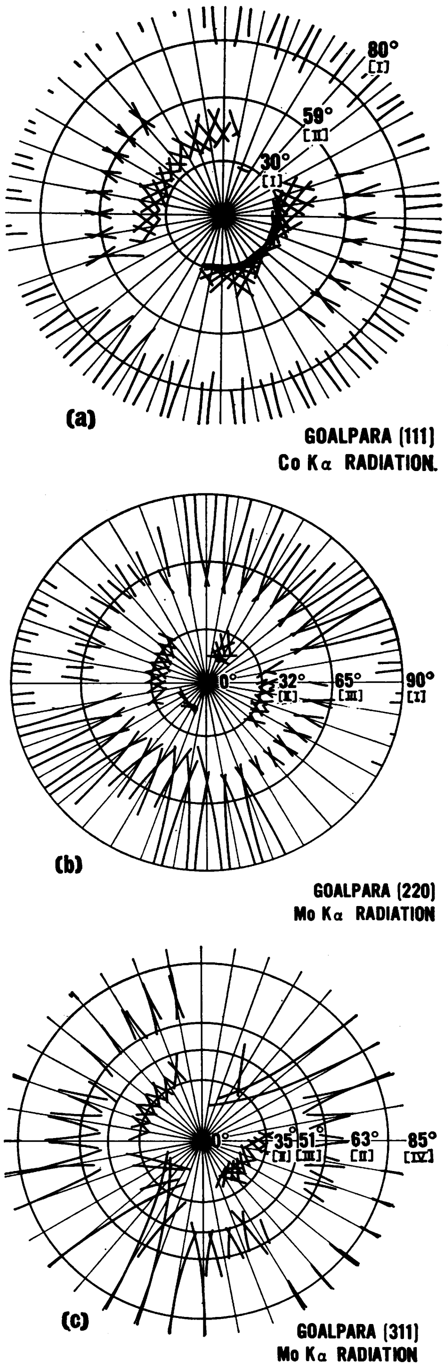

Fig. 3. Stereographic projections of Goalpara diamond (*a*) [111], (*b*) [220], and (*c*) [311]. The theoretical angles shown between each direction and the [311] are in agreement with the observed groupings.

gregates consisting of diamond, randomly oriented polycrystalline graphite, and other phases (Table 1).

The α_1-α_2 doublet of the diamond (331) plane provides a useful measure of the average crystallite size. From the lack of resolution of this doublet in Goalpara, Zachariasen (*10*) has estimated that the diamonds are about 100 Å. The diamonds from Dyalpur and Novo Urei on the other hand are relatively large; those from Dyalpur are very much larger than 300 Å.

The diffraction pattern of a Goalpara diamond is shown in Fig. 2. The diamond reflections indicate pronounced preferred orientation whereas the graphite is randomly oriented. Stereographic projections of the diamond [111], [220], and [311] directions (Fig. 3 *a, b,* and *c*) reveal very striking patterns. The angles listed on each projection are those which that simple cubic plane makes with its (311) plane while the roman numerals indicate the multiplicity of these angles (*11*). Agreement is quite good and indicates that the oriented planes in the diamond are probably those parallel to (311).

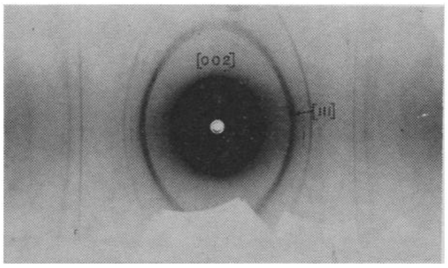

Fig. 4. Iron-filtered CoKα x-ray pattern of graphite partly converted to diamond by a 300-kbar shock. While the graphite is polycrystalline and randomly oriented, the diamond shows preferred orientation.

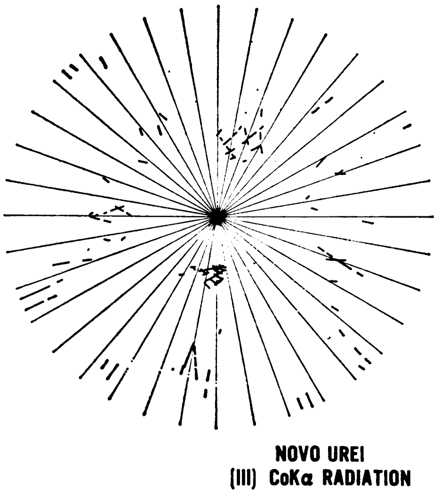

Fig. 5. Stereographic projection of Novo Urei diamond [111] directions. Although a pattern is evident, it is somewhat different in nature from that in Fig. 3*a*.

It is important to note that the preferred orientation of diamond, which is indicative of formation by an anisotropic process, is present in Goalpara and (as will be demonstrated) also in Novo Urei. Natural terrestrial diamonds have never been reported to contain preferred orientation and in an extensive monograph (*12*) on these structures in terrestrial rocks and minerals there is no mention of this "fabric" in diamond.

Previous x-ray studies of hydrostatically produced synthetic diamond (*13*) 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 or pressure or both, that is by flash-heating (*14*) or by a 300-kbar shock (Fig. 4), have oriented structures. The stereographic projections of these data show a grouping at about $\rho = 70°$ for the former and a single "node" (compare with Fig. 5) at about 40° for the latter. Diamonds produced by shock at pressures significantly lower than 300 kbar are very polycrystalline and thus do not have detectable orientation. Thus, in accord with theory, the only diamonds that exhibit preferred orientation were produced by some anisotropic process.

The x-ray pattern of a diamond from Novo Urei (Fig. 6) is similar to that of a diamond produced by a 300-kbar shock (Fig. 4). The stereographic projection of the Novo Urei data (Fig. 5) is different in character from that of Goalpara (Fig. 3*a*), possibly arising from a different alignment of the Novo Urei diamond relative to the x-ray beam or from actual differences in their pressure history.

Other phases in these two meteorites can yield information on the ureilites' pressure-temperature history. Olivine grains from Novo Urei (Fig. 7*a*) still appear to be reasonably good single crystals, although fractured to some extent. Goalpara olivine, on the other hand, is heavily fractured (Fig. 7*b*) and in some regions shows signs of recrystallization along grain boundaries, indicating excursion into temperatures well above its melting point. Since the only known natural process that can give rise to significant short-term anisotropic pressure is shock, it appears reasonable that the diamonds in at least these two ureilites were formed in this manner. It does not seem too extreme to suppose that the diamond formation and recrystallization of the olivine in Goalpara were contemporaneous. The data of Hughes and McQueen (*15*) on shocked olivine (dunite) indicate that even at the maximum pressure studied (700 kbar), the temperature reached only 720°. At pressures of 400 kbar, which is well in the diamond-forming region, the temperature rises to less than 200°. Thus, Goalpara, which was shocked more severely than Novo Urei, was

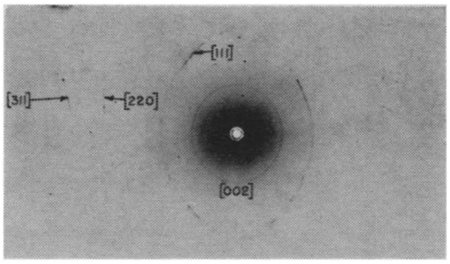

Fig. 6. X-ray pattern (iron-filtered CoKα) of Novo Urei diamond. The diamond crystallite orientation is similar to that shown in Fig. 4.

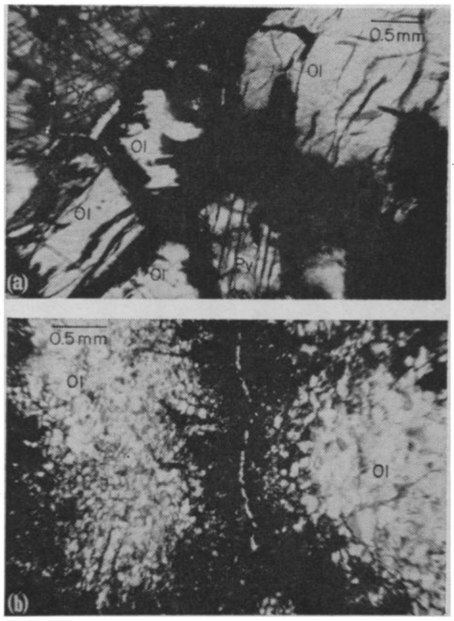

Fig. 7. Thin section of (*a*) Novo Urei ureilite and (*b*) Goalpara ureilite (both × 50). In (*a*), olivine (*Ol*) apparently still exists as single crystals although somewhat fractured. The clinopyroxene (*Py*) grains show cleavages. The opaque material is a graphite-diamond-kamacite mixture. In (*b*), the clinopyroxene grains are still apparently single crystals although some show an undulatory character under polarized light. Olivine grains (*Ol*) are badly shattered and in some locations are apparently recrystallized.

probably exposed to pressures considerably in excess of 700 kbar.

Diamond from Dyalpur shows no preferred orientation. One could suggest that the diamonds in this meteorite were formed by gravitational pressure rather than by shock as in Goalpara and Novo Urei. However, Dyalpur's textural similarity to the other two ureilites (particularly to Novo Urei (*16*) would argue against different modes of diamond formation by Occam's principle (see *17*).

Figure 3 (*a, b,* and *c*) shows certain features which may have bearing on the details of shock formation of diamond in Goalpara. First, some degree of asymmetry seems evident in the distribution of groupings in each set of normals. Second, there are two "nodes" in the [220] that occur at about 20°. 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°. These angles occur three times within the crystal (multiplicity III) and should be more prominent than the 63° angle which occurs twice (multiplicity II). 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 (220). 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 an examination of meteoritic and artificially shock-produced diamonds some suggestions can be made concerning the mechanism of conversion of graphite to diamond by shock. At pressures well below 300 kbar, polycrystalline fine-grained diamond is apparently formed from polycrystalline graphite, possibly by the compression of rhombohedral graphite only (*4*). From pressures of about 300 kbar to well above 700 kbar the solid-state reaction involves conversion of the basal (001) plane of graphite to diamond (311), or possibly some combination of (311) and (110). Only at very high pressures may the conversion involve the hypothetical "metallic carbon" postulated by Libby (*18*) or possibly formation from shock-melted graphite.

The simultaneous presence of graphite, diamond, and kamacite in all of the ureilitic "diamonds" that I have investigated shows that these grains are not equilibrium assemblages. This raises the question of whether they represented an arrested stage in the conversion of graphite to diamond, or vice versa. Studies at 0 kbar (*19*) and 100 kbar (*20*) 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 diamantiferous meteorites the graphite is polycrystalline and randomly oriented. Thus, the graphite cannot have been formed from diamond. On the other hand, the theory predicts that, under favorable circumstances, shock-formed diamond would show preferential orientation. It thus appears that all meteoritic diamonds were formed by shock rather than by gravitational compression of graphite.

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23. I am very grateful to Edward Anders for his many suggestions and comments during the course of this investigation. I also thank John Jamieson and Paul S. DeCarli, for many stimulating discussions, and E. C. T. Chao for his comments on the thin sections of the meteorites. I gratefully acknowledge the loan of the Dyalpur meteorite (E. Olsen, Chicago Natural History Museum) and the Goalpara and Novo Urei meteorites and thin sections (E. P. Henderson, U.S. National Museum). Gifts of synthetic diamonds produced by various techniques were received from R. H. Wentorf, Jr. (General Electric Research Laboratory), M. Waxman (National Bureau of Standards), and P. S. DeCarli (Stanford Research Institute). Miss Vida Milanovic and Miss Donna Reichel provided valuable assistance. The Materials Research and Development Section, NASA, lent equipment during the course of this research, which was supported in part by National Science Foundation grant G 14298.

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28 January 1964

Mossbauer Effect for Surface Atoms: Iron-57 at the Surface of η Al_2O_3

Abstract. *The Mössbauer effect has been observed for Fe^{57} atoms at the surface of η Al_2O_3. The Fe^{57} is trivalent, and the quadrupole splitting found is consistent with a surface location. Anisotropy of thermal vibration relative to the surface is observed.*

The Mössbauer effect offers a promising means of investigating both the electronic structure and the lattice dynamics of atoms at surfaces. The availability of materials with very large ratios of surface to volume makes it possible to prepare specimens whose surfaces contain large numbers of atoms showing this effect. Relatively conventional techniques of physical chemistry show that the atoms of interest are actually on the surface. For example, studies of the catalysis of *ortho*-to-*para* conversion in hydrogen have shown that