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17. In the model the parent material for C atoms is CH_4 . The recent detection of CO ice in infrared spectra of Triton's surface (18) suggests that photolysis of CO could be an additional source of C atoms.
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25. Early measurements of three-body reactions of C atoms with N_2 to produce CNN and with H_2 to produce CH_2 have been made (26) at 300 K. We are not aware of data regarding the electronic structure of CNN, so we assumed that C simply attaches to N_2 without disturbing the N_2 triple bond. In trial model runs we then assumed that loss of CNN occurs by photolysis (rate $\sim 5 \times 10^{-4} s^{-1}$) to yield C and N_2 , and by reaction with N and H atoms (rates $\sim 1 \times 10^{-10} cm^3 s^{-1}$) to yield CN, CH, and N_2 . The resulting column abundance of C atoms in the model was reduced by an order of magnitude, and the peak C^+ density decreased to about $7 \times 10^3 cm^{-3}$. However, it must be emphasized that the lack of laboratory data on gas-phase CNN makes this result highly uncertain; most likely, CNN does not form at Triton's low temperatures. The recombination reaction of C atoms with H_2 is thought to have a large activation energy (27) and is assumed to be negligible in Triton's atmosphere.
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A New Type of Meteoritic Diamond in the Enstatite Chondrite Abee

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Diamonds with $\delta^{13}C$ values of -2 per mil and less than 50 parts per million (by mass) nitrogen have been isolated from the Abee enstatite chondrite by the same procedure used for concentrating C δ , the putative interstellar diamond found ubiquitously in primitive meteorites and characterized by $\delta^{13}C$ values of -32 to -38 per mil, nitrogen concentrations of 2,000 to 12,500 parts per million, and $\delta^{15}N$ values of -340 per mil. Because the Abee diamonds have typical solar system isotopic compositions for carbon, nitrogen, and xenon, they are presumably nebular in origin rather than presolar. Their discovery in an unshocked meteorite eliminates the possibility of origins normally invoked to account for diamonds in ureilites and iron meteorites and suggests a low-pressure synthesis. The diamond crystals are ~ 100 nanometers in size, are of an unusual lath shape, and represent ~ 100 parts per million of Abee by mass.

The presence of diamond in extraterrestrial samples [ureilites (1) and an iron meteorite (2)] was first reported over a century ago. It now seems that a number of processes must have been involved in the formation of such meteoritic diamonds. A mechanism similar to that for the formation of diamonds on Earth at high pressures is unlikely in meteorites because their parent bodies are believed to be no more than a few hundred kilometers in diameter and so would not reach the required high pressures. In Canyon Diablo, the iron meteorite from Meteor Crater, Arizona, cubic diamond is intergrown with hexagonal lonsdaleite, which is usually associated with shock processing. The diamonds were thus believed to be produced in the terrestrial impact event (3). Recognition of the diamond polymorphs in an Antarctic iron meteorite that showed no evidence of terrestrial shock, however, implied that at

least some diamonds were formed before the iron meteorite reached Earth (4). Most, but not all, ureilites [for example, ALHA 78019 (5) is an exception] contain diamond in amounts up to 1% by weight (1) in matrix veins intergrown with graphite and lonsdaleite (6). The favored explanation for the origin of these diamonds is formation by shock during collisions in space (6, 7). An alternative mechanism to shock, akin to chemical vapor deposition (CVD), has also been suggested (8).

Whatever the exact mechanism of formation of the ureilite and iron meteorite diamonds, their existence can almost certainly be explained by processes acting in the solar system at some time. The situation is clearly different for the carrier of isotopically anomalous N (9) and Xe [Xe (HL) (10)], sobriquet C δ , which was identified as diamond with a particle size of typically 3 nm (11). C δ diamond is present in virtually all types of primitive carbonaceous and ordinary chondrites (12, 13) and the enstatite chondrites Indarch (13, 14) and Qingzhen (13); C δ diamonds from different meteorite classes show a variation of a factor of 6 in N content and a 5 per mil range in C isotopic composition (15). The N and Xe isotopic compositions suggest that C δ diamonds were produced as circumstellar

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grains (9) and not as a result of shock after the meteorites or their parent bodies consolidated. In ordinary chondrites the abundance of C δ falls as a function of petrologic grade, suggesting that the diamonds are destroyed by oxidative metamorphic events (12, 13). To explore this process for a class of meteorites formed in a reducing environment, we examined the enstatite (EH4) breccia Abee. We were anticipating minimal amounts of C δ . In fact, C δ was not detectable; surprisingly, however, another variety of diamond was discovered.

The sample of Abee had been sawn as a slab from the interior of a larger fragment some time before 1960. Because the sample had been cut, a special effort was made to ensure that it was not contaminated by diamonds from the sawing operation. The surfaces of the Abee slab were etched in acid (9 M HF–1 M HCl) for 5 min so that an initial mass of ~86.8 g was reduced by 1.4 g. We calculate that this operation removed a layer, on average 70 μ m thick, from the exposed surface of the sample. The residual block of meteorite was cleaned by ultrasonication in water, washed in acetone, dried, broken into chips, and processed according to our standard procedure for isolating C δ diamonds (15, 16), which was modified from the method reported by Lewis *et al.* (11). After treatment with HF–HCl, CS₂,

Cr₂O₇²⁻, and HClO₄, we obtained a yield of 134.5 ppm of insoluble residue. Four analyses showed that carbonaceous material made up an average of 77.5% by weight of this residue; the remainder was mainly oxide minerals. Powder x-ray diffraction gave a pattern consistent with the idea that the C was well-crystallized cubic diamond. A scanning electron microscope investigation revealed that the diamonds were unlike C δ isolated from other primitive chondrites. The Abee diamonds were typically between 100 nm and 1 μ m in size, rather than of nanometer dimensions of C δ diamond (17). Most crystals were clumped into rounded aggregates 20 μ m in diameter (Fig. 1A). Transmission electron microscopy showed that the diamonds have a face-centered-cubic structure; both platy and lath-shaped crystals were evident (Fig. 1, B and C). Electron diffraction data (17) confirmed the diamond identification. In addition, a few SiC crystals are evident (Fig. 1D); these contain many stacking faults, and electron diffraction suggests that they are a hexagonal polytype. In contrast, most SiC grains identified in primitive chondrites have a cubic structure (18).

We made stable isotopic measurements (19) of C and N (20) of the Abee diamond, using stepped combustion techniques (21). Little C was combusted at

temperatures below 400°C (Fig. 2A): the peak yield of CO₂ occurred in the 550° to 575°C steps [compared to 490° to 500°C for C δ (15)]; some C was still being burned at temperatures as high as 800°C. The C isotopic composition ($\delta^{13}\text{C}$) rose from a value below –20 per mil that is probably indicative of terrestrial contamination [known to be between –20 and –30 per mil (21)] to a plateau of -1.86 ± 0.24 per mil. The overall bulk $\delta^{13}\text{C}$ measurement from repeat analyses was -2.2 to -2.5 per mil. A $\delta^{13}\text{C}$ value of -1.86 per mil is distinct from that of most terrestrial diamond samples, which have a mean $\delta^{13}\text{C}$ value of -5.5 per mil (22); only a few (~1%) diamonds, from specific locations (for example, New South Wales), have $\delta^{13}\text{C}$ values higher than -2 per mil. When the stepped combustion was continued up to 1250°C, small amounts of C burned, but no high $\delta^{13}\text{C}$ values, such as are seen in carbonaceous chondrites (23) and attributed to SiC (24), were observed.

The abundance of N released simultaneously as the diamond was combusted was low (Fig. 2B), amounting to less than 50 ppm of the mineral. The C/N ratio was 2.0×10^4 , much greater than the equivalent value of 80 to 270 measured for C δ (15). Three times as much nitrogen ($\delta^{15}\text{N} = 22.7 \pm 1.0$ per mil) was liberated between 700° and 900°C as in the low-temperature steps. These data indicate that a second indigenous N component of unknown affinity is present in this residue. The net C/N

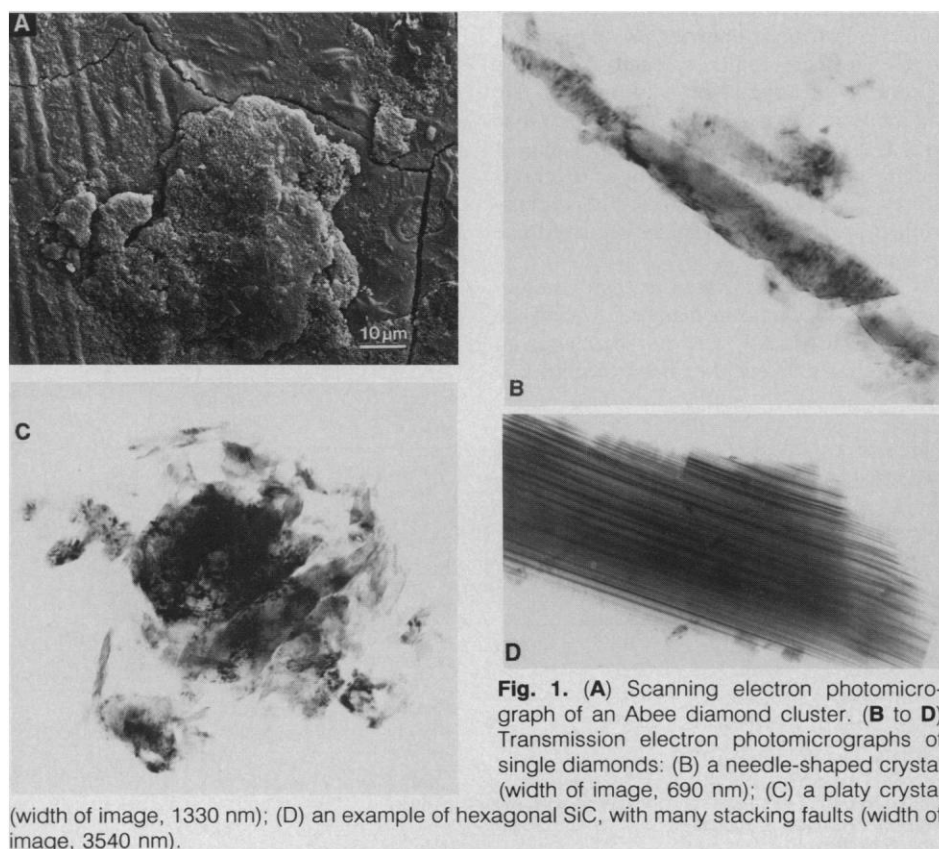


Fig. 1. (A) Scanning electron photomicrograph of an Abee diamond cluster. (B to D) Transmission electron photomicrographs of single diamonds: (B) a needle-shaped crystal (width of image, 690 nm); (C) a platy crystal (width of image, 1330 nm); (D) an example of hexagonal SiC, with many stacking faults (width of image, 3540 nm).

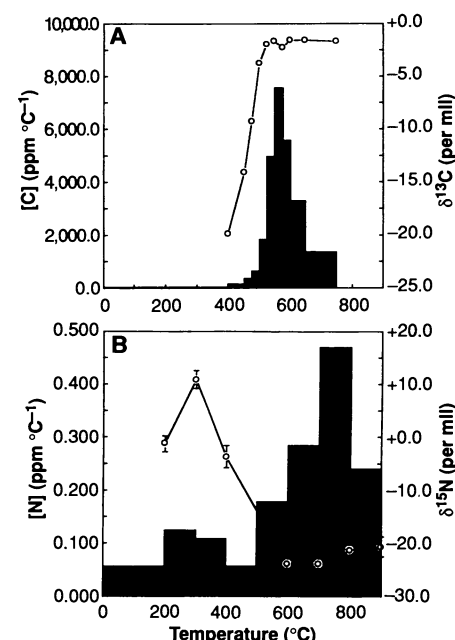


Fig. 2. (A) Stepped combustion profile of C from the Abee diamond; the histogram gives yield information and the line graph corresponds to the isotopic composition. (B) Stepped release profile for N.

ratio of this component was ~50, allowing for the tailing of the C peak.

We analyzed the noble gas contents and isotopic composition in a 0.4-mg split of the Abee diamond residue by a combination of pyrolysis and combustion steps (Table 1). The C abundance inferred from combustion up to 600°C (~64%) was in reasonable agreement with the C analysis. Major release of noble gases occurred during combustion at 500° and 600°C, whereas the preceding pyrolysis steps, although performed at higher temperatures, liberated only minor amounts. The gases released included large amounts of cosmogenic ^3He and ^{21}Ne (25), in abundances similar to the concentrations measured for bulk Abee (26). These high abundances coupled with the release pattern, which closely follows that of C combustion (Table 1), demonstrate that these cosmogenic gases are contained in the C phase and consequently that the diamonds are indigenous. The presence of large amounts of cosmogenic Ne in diamond is somewhat surprising, because Ne cannot be produced from C. The most likely explanation is that the Abee diamond is widely dispersed throughout the meteorite so that it acquired significant amounts of spallation Ne by recoil from the surrounding silicates. Trapped Xe and other gases were also released in the combustion steps but $^{136}\text{Xe}/^{132}\text{Xe}$ is much lower than for Xe (HL). An upper limit for the abundance of Xe (HL) in the Abee diamonds is $<1 \times 10^{-9} \text{ cm}^3 \text{ STP}$ (standard temperature and pressure)/g, less than 1/300 of the concentration thought to be typical (13) of C δ diamonds. It is conceivable that the Abee diamonds do not contain any Xe (HL). The low abundance of ^{20}Ne ($<6 \times 10^{-8} \text{ cm}^3 \text{ STP/g}$) is 1/1000 of the typical value for C δ (27), showing that C δ cannot be more than 0.1% of the residue. Unlike the cosmogenic gases, trapped noble gases do not appear to be uniformly distributed in the carbonaceous material because in the 500°C combustion step the ratio of

trapped gas to C is significantly higher than in the 600°C step. Hence, we cannot rule out the possibility that some or all of the trapped gases could be carried by a subfraction of the diamonds or by an unidentified carbonaceous phase.

An unusual feature of chondritic (C δ) diamonds is their ability to form a colloidal suspension in alkali. This property, thought to be due to carboxylic acid groups on the tiny diamond crystals (28), was accidentally brought to light for C δ and became instrumental in identifying the N and noble gas carrier (11) as diamond. Abee diamonds treated with NH_3 (pH = 8) produced a milky suspension, only a fraction (mostly larger diamond grains, with some oxide minerals) of which could be concentrated in a centrifuge. On acidification, the Abee diamonds reprecipitated and settled out as a gray deposit. We investigated the possibility that the acid moieties on diamonds were created by the harsh oxidizing treatments used in the isolation procedures by treating a terrestrial diamond grinding powder (0.25 to 1 μm) with $\text{Cr}_2\text{O}_7^{2-}$ and HClO_4 . We could not reproduce the properties of the Abee or C δ samples. The indigenous nature of Abee diamond is therefore indicated by (i) the C isotopic composition, which is unusual for terrestrial diamond, (ii) the presence of cosmogenic noble gases, (iii) the texture of the diamond crystals, and (iv) their ability to form a colloidal suspension in NH_3 . Furthermore, the combustion properties, N abundance, noble gas measurements, microscopy, and C and N isotope data confirm that the diamond in the residue isolated from Abee is not a variety of C δ diamond (Table 2) but is a type of diamond new to chondrites. The higher temperature of combustion is in agreement with its observed size range.

The lack of associated isotopic anomalies in C, N, or Xe in diamond from Abee argues against, but does not preclude, an interstellar source. Abee does contain free

graphite (29), and therefore the possibility that the diamond formed in the asteroid belt or on impact with Earth must be considered. Minster *et al.* (30) have suggested that Abee was situated close to the surface of its parent body and so was shocked by surface impacts during the early stages of solar system history. However, Abee does not have a shocked petrologic texture (for example, it is free of shocked veins), and so it seems unlikely that this process would have been extreme enough to have initiated the formation of diamond from graphite.

Interstellar diamonds are believed to form in circumstellar environments by CVD (11), and it has been suggested that this process could also occur in the early solar system (31). Abee diamonds could also have been produced by this mechanism, in which case their coarse grain size compared to C δ could be a result of a difference in the formation environment (for example, Abee diamond could also have been formed in a dust-poor region where opportunities for nucleation were limited). A third possibility is that diamond formed as a result of substantial radiation by high-energy particles, which are believed to produce carbonado diamond (32), from organic matter and coal.

Although it is generally supposed that the diamonds in ureilites and iron meteorites are shock-produced in some parent body-related process, this is far from definite. They could be primordial and connected in some way to the new diamond type now found in a chondrite of the enstatite class. There is evidence for genetic links between the three meteorite groups: (i) Ramdohr (33) recognized obscure minerals (niningerite and oldhamite) common in enstatite meteorites in the opaque part of the ureilite matrix; (ii) on the basis of trace element studies, Wasson

Table 1. Noble gases in the Abee diamond residue (in units of $10^{-8} \text{ cm}^3 \text{ STP/g}$). Subscript t and c refer to the trapped and cosmogenic components, respectively, of He and Ne. P, pyrolysis step; C, combustion step.

Temperature (°C)	Combusted C (μg)	$^{20}\text{Ne}_t$	^{36}Ar	^{84}Kr	^{132}Xe	$^{136}\text{Xe}/^{132}\text{Xe}$	$^3\text{He}_c$	$^{21}\text{Ne}_c$
510 P		<0.3	13	<0.06	<0.07			<0.03
400 C	<9	<0.6	2	<0.04	<0.02		<0.5	<0.02
600 P		<0.3	5	<0.04	<0.03		<0.05	<0.02
500 C	130	3.3	267	1.46	1.08	0.325	7.3	0.75
700 P		<0.2	7	<0.04	<0.02		<0.5	<0.03
600 C	123	1.6	79	0.41	0.68*	0.329*	5.9	0.74

*The original fraction for Xe analysis was lost as a result of a breakdown of the mass spectrometer. A split was stored in the extraction line and analyzed 10 days later. Isotopic systematics suggest that some air Xe had accumulated during that time, but less than 50% of the analyzed fraction.

Table 2. A comparison of Abee diamonds and C δ .

Characteristic	Abee diamond	C δ
Combustion temperature (°C)	550 to 575	500
$\delta^{13}\text{C}$ (per mil)	-1.8	-32 to -38
Xe-HL content ($\text{cm}^3 \text{ STP/g}$)	$<10^{-9}$	$2 \text{ to } 3 \times 10^{-7}$
^{20}Ne content ($\text{cm}^3 \text{ STP/g}$)	$<10^{-7}$	1×10^{-4}
N content (ppm)	<50	2,000 to 10,000
Color	Gray	Brown
Reaction in NH_3	Milky solution	Brown solution
Grain size	<1 μm	~2 nm
Shape	Lath-shaped	Spheroidal

et al. (34) suggested that the graphite in enstatite chondrites may have come from the same source as the graphite in ureilite veins; (iii) O systematics imply that the enstatite chondrites and IAB irons lie on a mixing line (35); and (iv) O data for howardites, eucrites, IAB irons, and group I ureilites (36) can be attributed to the fractionation of a single homogeneous reservoir.

A link between the diamonds is less easy to establish. Only a few isotopic data have been collected for diamonds from iron and ureilite meteorites, so their relation to Abee diamonds is uncertain. Vdovykin (6) reported a $\delta^{13}\text{C}$ value of -5.8 per mil for a diamond from Canyon Diablo and a similar value (-5.7 per mil) for diamonds from the ureilite Novo Urei. A more recent study has shown that at least nine ureilites (37) have bulk C $\delta^{13}\text{C}$ with a value of -2.2 ± 0.8 per mil, which may reflect the diamond composition because there is little evidence of fractionation between diamond and graphite (6). The $\delta^{13}\text{C}$ value in silicate inclusions from type IAB iron meteorites, -3 to -4 per mil, is systematically 1 to 2 per mil heavier than that of graphite nodules in the same samples (38). There are no N abundance or isotope measurements from diamonds in ureilite or iron meteorites; for the ureilites, however, where diamonds are abundant, bulk N concentrations are 25 to 35 ppm and most $\delta^{15}\text{N}$ values are close to 0 per mil (37). Trapped noble gases in ureilite diamonds are usually of higher abundance and have a lower $^{136}\text{Xe}/^{132}\text{Xe}$ ratio (39) than those of Abee-type diamond. However, the elemental ratios, particularly the high Ar abundance, are similar (40). As Abee is a breccia, we cannot exclude the possibility that it contains ureilite-like clasts, and so a search for Abee-type diamonds in carbonaceous residues of other enstatite chondrites is needed. C δ diamonds have been detected in residues of Indarch (EH4) processed according to the same protocol as Abee, but a minor amount of C appeared to burn at temperatures higher than that typical of C δ . Unfortunately, isotopic data from this fraction are affected by the presence of ^{13}C from SiC. Most of the C from relatively unprocessed carbonaceous residues of Qingzhen (EH3) and St. Saver (EH5) (41) burned from 500° to 700°C (slightly lower in the former), and $\delta^{13}\text{C}$ values were between -4 and -6 per mil; Daniel's Kuil, an EL6, liberated C with a $\delta^{13}\text{C}$ of $+5$ to $+7$ per mil at much higher temperatures (650° to 1000°C).

The presence of some diamonds with a $\delta^{13}\text{C}$ value of approximately -2 per mil and little or no N in chondrites, along with C δ diamond, could qualitatively explain the vari-

ability in $\delta^{13}\text{C}$ and N abundance of diamonds isolated from these meteorites. Russell *et al.* (15) demonstrated that residues having the lowest N contents are also those with the highest $\delta^{13}\text{C}$ values. These data could result from a mixture of C δ with a $\delta^{13}\text{C}$ of -38 per mil with [N] at $>10,000$ ppm and an N-free diamond with $\delta^{13}\text{C}$ near 0 per mil. Material balance calculations, however, do not satisfy the data uniquely. Indeed, C δ could be made up of diamonds from many sources, as is the case for SiC (42). The discrepancy between the combustion temperatures of C δ and Abee-type diamond would also need to be rationalized, although exothermic reactions that would promote combustion of the more stable Abee-type diamond could solve this problem (43).

There is a considerable need to subject diamonds from Abee (and, for that matter, diamonds from ureilites and iron meteorites) to the kind of scrutiny being given to the nanometer-sized component C δ . It may be that low temperature-low pressure (that is, nonshock) formation of diamond was an important process in the early inner solar system.

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17. Electron diffraction gives the following ring spacing (in angstroms) with values for authentic cubic diamond in parentheses: 2.06 (2.06), 1.25 (1.26), 1.07 (1.08), 1.03, 0.88 (0.89), 0.81 (0.80), 0.72 (0.73), and 0.68 (0.69). A grain size distribution was also acquired by electron microscopy, with the area of the lath-shaped grains used as an indicator of size. The results indicate that the diamonds do not conform to the log normal distribution observed for C δ diamond.
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$$\delta^{13}\text{C} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{std}}}{(^{13}\text{C}/^{12}\text{C})_{\text{std}}} \times 1000$$
 Standards for C and N are the belemnite from the Cretaceous Pee Dee Formation of South Carolina and air, respectively. The precision of measurements is ± 0.05 per mil for C and ± 2.0 per mil for N.
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