Elemental Carbon as Interstellar Dust [and Discussion]

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Elemental carbon as interstellar dust

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C_{60} has not yet been detected in primitive meteorites, a finding that could demonstrate its existence in the early solar nebular or as a component of presolar dust. However, other allotropes of carbon, diamond and graphite, have been isolated from numerous chondritic samples. Studies of the isotopic composition and trace element content and these forms of carbon suggest that they condensed in circumstellar environments. Diamond may also have been produced in the early solar nebula and meteorite parent bodies by both low-temperature–low-pressure processes and shock events. Evidence for the occurrence of another carbon allotrope, with sp hybridized bonding, commonly known as carbyne, is presented.

1. Introduction

At the same time that buckminsterfullerene was being conceived as a molecule of possible astrophysical significance, a number of much older forms of carbon were about to enjoy a new lease of life because of their discovery as presolar grains in primitive meteorites. Ever since the 1960s, it has been recognized that carbonaceous chondrites were a host for noble gases of anomalous isotopic composition (Anders 1981). The carriers of a litany of components, enjoying names such as Xe(HL) (also called CCF-Xe), s-Xe, Ne-E(L), Ne-E(H), etc., were believed to be unidentified carbon species called C_δ, C_β, C_α and C_ϵ respectively, themselves exhibiting unusual or exotic isotopic compositions (Swart *et al.* 1983*a*; Carr *et al.* 1983). In 1987, C_δ was shown to be diamond (Lewis *et al.* 1987) the meteorite mineral which contained Xe(HL) and nitrogen whose isotopic composition was greatly enriched in the light isotope ^{14}N (Lewis *et al.* 1983). This was almost immediately followed by the recognition (Bernatowicz *et al.* 1987) of C_β and C_ϵ as SiC, with over a factor of two ^{13}C more than the average solar system concentration. A little later came the identification of graphite, also ^{13}C enriched, as the Ne-E(L) related phase C_α (Amari *et al.* 1990). Other minor carbon containing entities, with non-descriptive but operationally defined names, e.g. C_λ (Ash *et al.* 1988), $C_\aleph$, C_κ (Ash *et al.* 1990), C_θ (Tang *et al.* 1987), H-C_δ (Verchovsky *et al.* 1992) have been suggested as presolar from their isotopic compositions or their associations but as yet absolute identifications are lacking. As SiC is not a carbon allotrope, a discussion of its importance as a presolar grain is not relevant in the context of this meeting and is given elsewhere (Pillinger & Russell 1993). Herein, the elemental carbon components which have been encountered in primitive meteorites or which have a related provenance are considered.

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2. Separation and analysis of carbon components from meteorites

Elemental forms of carbon make up only a small part of the fabric of meteorites. They are hidden within a morass of organic matter, much of it indigenous, but some contamination added to the extraterrestrial samples accidentally during their sojourn on Earth. Fortunately the species of interest are robust and can withstand very harsh processing to isolate them from their immediate habitat. Thanks to the pioneering work of Tang *et al.* (1988), all the forms of carbon we are interested in can be extracted from meteorites with mineral acids such as HF/HCl and oxidizing conditions involving reagents like H_2O_2, NaOCl and $Cr_2O_7^{2-}$. To concentrate diamond $HClO_4$ is also used; only diamond is believed to be stable in $HClO_4$, but this is not an immutable fact. Much of the work discussed in this paper has used a technique known as stepped combustion (Swart *et al.* 1983*b*). Therein samples are heated through a series of temperatures, in the presence of oxygen, so that they are converted to carbon dioxide and released in order of increasing stability. Stepped combustion has been applied extensively to residues prepared up to and including $HClO_4$ stage of treatment. A derivative of stepped combustion, preparative precombustion, has been used with samples treated with HF/HCl (Ash *et al.* 1990). The carbon converted to CO_2 during any combustion reaction can be analysed for its isotopic composition using mass spectrometry. Specialized techniques have had to be developed to measure the smallest samples used (Carr *et al.* 1986; Prosser *et al.* 1990; Yates *et al.* 1992*a*, *b*). Carbon phases almost always co-exist with nitrogen which is released simultaneously during the combustion; because N exists in only trace abundance, static mass spectrometers (Wright *et al.* 1988) and appropriate handling techniques (Boyd *et al.* 1988) have had to be developed specifically for the investigations discussed here. Below, some isotopic data acquired by ion probe analysis are also included. However, this technique has a restricted application except in cases where individual grains can be located and mounted for study.

3. The occurrence of diamond in meteorites

Diamonds were first recognized in extraterrestrial materials when, within the space of a year or two, separate researchers reported their presence in the Novo Urei ureilite (Ierofeieff & Latchinoff 1888) and two iron meteorites, Magura (Weinschilling 1889) and Canyon Diablo (Foote 1891). During the next hundred years other ureilites (Vdovykin 1970) and at least one more iron meteorite (Clarke *et al.* 1981) were found to contain diamond. It was generally considered that diamond (or maybe more correctly, lonsdaleite, the hexagonal crystalline form of mineral) was a transformation product of graphite induced by impacts on Earth or in space (Lipschutz 1964). The diamonds discussed below have all been found in unshocked primitive meteorites, where the possibility of high-temperature–high-pressure reactions are precluded.

(*a*) C_δ *nanometre-sized, interstellar diamonds*

The diamonds first recognized by Lewis *et al.* (1987) have now been traced to every class of chrondritic meteorite (Alexander *et al.* 1990; Huss 1990; Russell *et al.* 1991) and are known to occur as a component within the matrix. The amounts available for extraction reach a maximum of 900 ppm but decline to nothing in higher petrologic grades. The cut-off point in unequilibrated ordinary chondrites is about type 3.6 but for enstatite chondrites the type 4s still contain diamond. Progressive

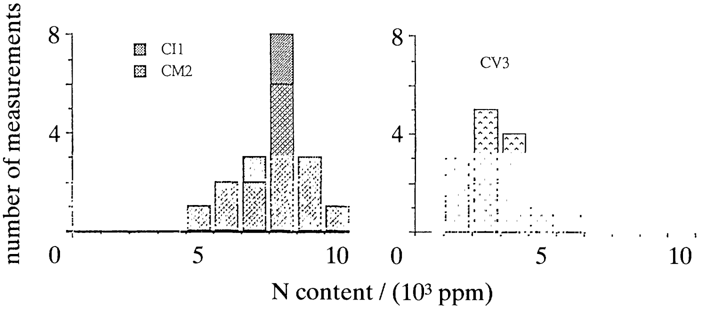

Figure 1. Nitrogen abundance in diamonds from various meteorite types.

metamorphism is believed to be the process responsible for destroying diamonds on the meteorite parent bodies; some possible metamorphic reactions have been proposed (Alexander *et al.* 1990).

A feature of the diamonds found in primitive meteorites, indeed the property which led to their isolation, is their very small particle size and ability to form a colloidal suspension in alkaline solutions. The particles precipitated from aqueous ammonia exhibit crystallites which have an average size of less than 3 nm (Lewis *et al.* 1989) equivalent to only *ca.* 2000 atoms of carbon. Electron diffraction patterns (Fraundorf *et al.* 1989; Gilkes *et al.* 1992) confirm the diamonds are cubic rather than hexagonal; the latter would be expected if shock was involved in their production. The particle size distribution is log-normal which suggests that either the grains have been size sorted or were in a state of growth rather than comminution (Lewis *et al.* 1989). It has been proposed that the apparent acidity of nanodiamonds is a property conveyed by carboxylic groups situated at corner sites on a cubic structure. Such a model is in surprisingly good agreement with data obtained by differential titration (Lewis *et al.* 1989). A question that has to be asked is, are the carboxyl groups original or a happenstance caused by harsh oxidative acid treatments used in isolation of the diamond? An attempt made to oxidize terrestrial microdiamonds to convert any peripheral dangling C atoms to carboxyl groups proved unsuccessful (Russell *et al.* 1992*a*). Of course, it is not possible to duplicate the conditions under which nanodiamond might occur, for example, as a continuous intergrowth with less robust forms of carbon which could be degraded to acid groups.

Among the most novel properties of C_δ is its ability to incorporate nitrogen. Terrestrial diamonds mined from kimberlite/lamproite source rocks, or found as placers, on occasion have nitrogen contents as high as 3000 ppm (Boyd *et al.* 1987) but the majority of samples contain 1000 ppm or much less (Deines *et al.* 1987). The diamonds from primitive chondrites have N abundances which extend from 2000–10000 ppm (figure 1) (Russell *et al.* 1991). Although there is a meteorite type dependent pattern in the data, models that attempt to explain that the results on the basis of gas loss, during simple metamorphic processing, do not work (Russell *et al.* 1992*b*). The major problem, and a quite remarkable feature of the N concentrations within the diamond, is the uniformity of N isotopic composition, the average of 22 determinations being -343 ± 16 ‰ (Russell *et al.* 1991). (Herein isotopic compositions are discussed using the δ convention as enrichments or depletions relative to a standard, where for example $\delta^{13}\mathrm{C}(‰) = 1000\,[(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sample}} - (^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{std}}]/(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{std}}$.) If metamorphism is the cause of diminishing N content, it must be that high N diamonds are preferentially destroyed (Fisenko *et al.* 1992) without major isotopic fractionation. Whenever diamond-rich fractions are step-combusted the earliest temperature fractions have higher C/N ratios suggesting that either the finest grains or the surfaces of larger particles are nitrogen depleted (Russell *et al.* 1991) or perhaps have another carbon containing component present. At the same time the carbon isotopic compositions tend towards values enriched in the ^{12}C and nitrogen toward values enriched in ^{14}N. The shift in carbon isotopic composition is no more than 5‰ whereas δ^{15}N changes by more than 300‰. Such observations are indicative that a 'pure' phase is not being sampled thus C_δ may be only a hiding place for other minor but more interesting components. It is, however, difficult to envisage what the co-existing material is unless it is another form of elemental carbon resistant to the reagents used. It is claimed that diamond-like carbon is observed in the electron micrographs (Fraundorf *et al.* 1989; Blake *et al.* 1988) but a test carried out on a-C synthesized by a chemical vapour deposition (CVD) process revealed that such material is easily destroyed by $HClO_4$ (Pillinger *et al.* 1989); the apparently amorphous material seen may be fine-grained crystalline diamond incorrectly oriented for lattice imaging (Gilkes *et al.* 1992). As several investigators have suggested that presolar diamond might form around stars by a process akin to CVD (Lewis *et al.* 1987; Pillinger *et al.* 1989) an investigation of various samples made by this method has been performed. Fine-grained, micrometre-sized, CVD diamonds produced in a methane/hydrogen plasma burn sharply at relatively low temperatures. A sample made by sputtering a graphite target with argon gave residue, after treating with $Cr_2O_7^{2-}$ and $HClO_4$ to remove diamond-like material, which was enriched in ^{13}C by the order of 160‰ (Gilkes *et al.* 1992). An alternative suggestion (Blake *et al.* 1988) for the diamond formation mechanism is grain–grain collisions in the interstellar medium which transform amorphous carbon and graphite to the sp^3 hybrid allotrope. It may be relevant that diamonds have also been found in detonation soot (Blake *et al.* 1988; Greiner *et al.* 1988).

As already mentioned, C_δ is contaminated by Xe(HL) but the amounts of xenon are so small that only about one diamond crystal in 2×10^6 actually contains a xenon atom. The predominance of heavy and light xenon isotopes (hence the name Xe(HL)) requires an origin involving nucleosynthesis in a supernova (Clayton 1976); however, for diamonds to condense at all it is necessary to invoke their formation in a carbon star likely to be a red giant (Lewis *et al.* 1987). To accommodate these apparently incompatible conditions has required rather specific formation models to be invoked. One ingenious way to circumvent the problems has been to suggest origin in a binary star (Jorgensen 1988) another involves condensing diamonds in the He shell of a type II supernova, the only place in a massive star which is C-rich enough (Clayton 1989). Both the above proposals require that the xenon is incorporated into the diamond by a trapping mechanism probably ion implantation (Clayton 1981) after the crystal solidified and its trace content of nitrogen was fixed (Russell *et al.* 1991). No astrophysical means has yet been found to establish the diamond carbon isotopic composition at the observed $^{12}C/^{13}C = 93 \pm 0.5$ very close to the overall Solar System (probably 89); a carbon star origin would intuitively be ^{13}C enriched, the supernova hypothesis leads to ^{13}C content relative to ^{12}C of 10^{-4} (Clayton 1989). In some ways it would be much more satisfactory if C_δ could be further fractionated to separate Xe(H) and Xe(L), two components of different C isotope abundance and a specific nitrogen carrier; many have tried but so far to no avail (Schelhaas *et al.* 1990; Nichols *et al.* 1991; Lewis & Anders 1989; Russell *et al.* 1990).

Lewis *et al.* (1989) have discussed the possibility of detecting diamond in interstellar space. They argue this might only be achieved if C_δ like particles make up 10% of the total carbon budget. Allamandola *et al.* (1993) have observed a few percent of tertiary sp^3 carbon atoms in several protostars, possibly thereby confirming the predictions of Saslaw & Gaustad (1969) who were the first to suggest that diamond could be an interstellar grain.

(*b*) C_δ *in other places*

The fact that C_δ is such a resilient phase has encouraged the search to be carried to a variety of environments. For example, it has been known since the very earliest trace element analyses of the lunar regolith that a 1–2% (by mass) equivalent of carbonaceous chondrite debris survives from the great welter of impacts occurring over the last 3–4.5 billion years (Wasson & Baedecker 1970). To investigate whether any vestige of C_δ is included amongst this detritus, an HF–HCl residue of lunar soil was step combusted monitoring nitrogen isotopes as a fingerprint (Brilliant *et al.* 1992). Isotopically light nitrogen (-74‰) was observed over the correct temperature range to be indicative of about 2 ppm of relict interstellar grain material surviving. Unfortunately the normal method of concentrating diamond is inappropriate for experiments involving lunar samples because crystals 3 nm in size would be completely amorphized by continuous bombardment with the solar wind flux. Therefore, not surprisingly a sample of the HF/HCl residue processed with oxidizing acids afforded no evidence of residual diamond by TEM or isotopic fingerprinting. Experiments to prove the existence of interstellar diamond on the lunar surface will have to be more subtle.

Cosmic dust (micrometeorites less than 1 mm in size) are thought to be a likely source of primitive chondritic material. Such grains could be both asteroidal or cometary in origin. If the latter is true, then they might have brought to Earth copious quantities of presolar grains. Studying individual cosmic dust grains as though they were the equivalent of hand specimen conventional meteorites is a very exacting task but not without its rewards. In one instance a cosmic dust grain collected as part of the NASA high altitude programme was found to have lonsdaleite fragments (Rietmeijer & MacKinnon 1987). A much broader brush experiment has been attempted using samples of cryoconite (a sediment found in seasonal melt water pools on Greenland (Maurette *et al.* 1987)). After treatment of a specimen with HF/HCl, $Cr_2O_7^{2-}$ and $HClO_4$ according to the normal procedures for isolating diamond, the residue was step combusted using a special low blank procedure (Yates *et al.* 1992*a*, *b*). Although only 100 °C steps could be utilized, carbon dioxide liberated over the temperature régime 400–500° had an unusually low $\delta^{13}C$ of -34.4 ± 0.4‰, in keeping with the presence of C_δ. Transmission electron microscopy reveals the presence of a very fine grained diamond reminiscent of C_δ. Detailed isotope measurements are needed to resolve whether this has any relation to the material found in carbonaceous chondrites. In trying to estimate what the abundance of the diamond might be in cryoconite cosmic dust a number of assumptions have to be made. However, a concentration in excess of the maximum observed by Huss (1990) for CI matrix is arrived at suggesting unmelted micrometeorites might be very primitive.

Another environment that has been successfully searched for nanodiamonds is the Cretaceous–Tertiary boundary layer. Carlisle & Braman (1991) carried out the now time honoured acid dissolution procedure on samples from Knudsen's Farm, Alberta, Canada. They found 45 ppb of a white fraction 97% carbon almost entirely 3–5 nm diamonds. Without any corroborating evidence the authors jumped to the conclusion that the diamonds must have derived from a primitive meteorite in their estimation a C2 chondrite, thus claiming the first tangible evidence for a giant impact at the end of the Cretaceous. The presence of nanodiamonds has now been independently confirmed (Gilmour *et al.* 1991, 1992). However neither carbon isotopic composition or nitrogen abundance and δ^{15}N values are similar to values encountered for C_δ form of diamond in primitive meteorites. Thus Gilmour *et al.* (1992) favour an origin for the diamonds in the impact event or the associated fireball plasma. Despite these findings, Carlisle (1992) still adheres to an interpretation involving a direct meteorite input basing his arguments on an isotopic analysis for which no experimental details are available (Wright 1992).

(*c*) *Non-*C_δ *diamond*

Prospecting for nanodiamonds in meteorites has led to the discovery of two, maybe three other types of meteorite diamond. During an effort to explore the metamorphic stability of C_δ under reducing conditions the enstatite (EH4) chondrite Abee was studied (Russell *et al.* 1992*a*). It was anticipated that the relatively high grade meteorite would be virtually devoid of nanodiamonds; indeed it was, but amongst the oxidized acid residues, was found 100 ppm of diamond having a needle or lath-like morphology. The crystals that are 100 nm to 1 μm in length (i) burn at temperatures higher than C_δ (ii) can be extracted into alkaline solution, (iii) have δ^{13}C of -1.8 ± 0.24‰ and (iv) contain only 50 ppm N of δ^{15}N 0 to -20‰. The isotopic characteristics of Abee diamond are on the borderline of terrestrial kimberlite/lamproite stones (Galimov 1991; Boyd *et al.* 1987). Since the meteorite sample studied had surfaces which had been cut in undocumented circumstances, there was some concern about contamination by fragments from the saw blade, although every effort to exclude such a possibility was made. The evidence, however, that totally eliminates a terrestrial origin comes from noble gas measurements. Abee diamonds contain abundant cosmogenic neon which not only suggests they are indigenous to the meteorite but argues that the crystals were well distributed during cosmic irradiation. None of the information available for the new diamonds indicates a presolar origin, and since Abee is also unshocked it may transpire that low temperature low-pressure synthetic processes were active in the early solar nebula. Interestingly the morphology of Abee diamond resembles needle like crystals made by CVD (Seitz 1992). Abee diamonds could just be related to those which have been known about in ureilites for almost 100 years (Russell *et al.* 1992*a*).

Another meteorite which has been shown to be a new source of diamond is the very unusual chondrite Acfer 182 found in the Sahara. This meteorite is a reasonably large sample of class of meteorite first encountered as an 11 g pebble on Antarctica; it is distinguished by abundant small chondrules, calcium aluminium rich inclusions, 15% (by vol.) metal and the highest δ^{15}N values encountered for a bulk meteorite (Grady & Pillinger 1990, 1992, 1993). As Acfer 182 is a primitive chondrite it was surveyed for the presence of C_δ which is indeed present (Grady & Pillinger 1993). However, in the residue from the usual acid treatments, larger diamonds have also been found including a crystal almost 10 μm across with distinctive radial growth features suggesting a shock transformation. Further separations will be needed in order to obtain isotopic data for this new group of diamonds.

Stepped combustion analysis of 'pure' C_δ diamond fractions separated as colloids in ammonia are always accompanied by a small amount of carbon characterized by a slightly elevated δ^{13}C. This additional material burns at temperatures higher than the main portion of the sample (Ash *et al.* 1987). Recently, it was found that diamond-rich residues particularly for the meteorites, Efremovka, Allende, Inman and Krymka contain a xenon component which is released by combustion at the same temperature as this carbon (Verchovsky *et al.* 1991, 1992). The isotopic composition of the new xenon, which has been named H-C_δXe (H denoting high temperature), is quite distinct from all other forms of the noble gas seen earlier (Verchovsky 1992). Gas of this isotopic composition had however been spotted (Lewis & Anders 1989) during one of the numerous attempts to separate Xe(H) and Xe(L) but at that time the possibility of another carbon component of higher stability than C_δ but associated with it was not considered. It is now very clear that the more stable carbon is 1000 ppm of the C_δ residue and its Xe (and other gases) content is much higher than the nanodiamonds (Verchovsky *et al.* 1992). The great stability of H-C_δ, i.e. resistance to the most oxidising acids suggests that it may be some other form of diamond. An interesting observation in this respect is that larger diamond crystallites have occasionally been seen by TEM within C_δ or similar residues (Fraundorf *et al.* 1989; Gilkes *et al.* 1992*a*). Such an observation is consistent with C_δ affording diamond X-ray diffraction data (H. J. Milledge, personal communication).

3. Other elemental forms of carbon in primitive meteorites

One of the enormous benefits of seeking diamond, or for that matter SiC, as presolar grain material is the incomparable resistance of the mineral to chemical attack. Other species are far more difficult but not impossible to isolate.

(*a*) *Graphite*

From the very earliest stepped combustion experiments performed on meteorite acid residues, it was known (Carr *et al.* 1983) that the carrier of Ne-E(L) burnt at a temperature somewhere between that of Xe(HL) and s-Xe/Ne-E(H). A sample enriched in Ne-E(L) liberated a small amount of carbon with $\delta^{13}C = +340‰$ which burned at around 650 °C. Very similar δ^{13}C values were encountered at about this temperature during stepped combustions of a variety of samples, processed in different ways, surprisingly including some treated with $HClO_4$. The evidence seemed to point strongly to the conclusion that C_α, the Ne-E(L) carrier was only slightly enriched in ^{13}C. The same carbon isotopic composition was also observed at approximately 650 °C in an HF/HCl residue of the Allende meteorite which had been extensively precombusted to remove low stability amorphous carbon (Ash *et al.* 1990). A problem with equating this result with the presence of C_α is that Allende is a meteorite which contains little if any Ne-E(L) (Frick & Pepin 1981). To reconcile the data Ash *et al.* (1990) suggested that C_α might be degassed in Allende; a new name $C_\aleph$ was introduced to distinguish the gas-poor from the gas-rich component. Interestingly, when carried to extreme the precombustion experiment revealed for the first time the existence of carbon enriched in ^{12}C (Ash *et al.* 1988). A minute component (only 0.1 ppm) burning at about the correct temperature for graphite combustion became apparent after many hours of precombustion.

In an effort to track the carrier of Ne-E(L) further, Amari *et al.* (1990) dispensed with the use of the most powerful oxidants (i.e. $HClO_4$) substituting NaOCl and alkaline H_2O_2 to remove stubborn organic phases. After treatment a residue from the Murchison meteorite was separated according to density. Ne-E(L) was found specifically in a sub-class of dense, rounded graphite grains 1.5–6 μm in size, the most convincing experiments being carried out using a focused laser to degas individual grains for mass spectrometric studies (Nichols *et al.* 1992). In addition to the dust grains, the residues contained other forms of graphite including aggregates of 0.1 μm spherules and even euhedral graphite crystals. Isotopic composition of various of these components have been measured by ion microprobe. Aggregates give normal solar system values for carbon but have abundant nitrogen up to 300‰ enriched in ^{15}N (Amari *et al.* 1990). The dense spheres are among the most exotic particles yet studied. Many have ^{12}C/^{13}C ratios which range from 0.09 to 16 times the solar system value of 89. The most ^{12}C enriched grains have a ^{12}C/^{13}C ratio of 1440, far in excess of values observed for carbon stars, which do not go beyond 97 (Lambert *et al.* 1986) although in principle these could be higher. It seems to be clear that the ubiquitous δ^{13}C of +340‰, measured for stepped combustion, is due to the averaging of all these various components. However, the mix seems to be amazingly consistent and it is difficult to understand why stepped combustion is not able to resolve at least partially the dense graphite spheres from the sub-micrometre sized aggregates.

(*b*) *Carbynes*

Like many other subjects the quest for the identification of presolar grains was not without its false starts. Material with polyyne or cummulene structures was first claimed to have been made in the 1960s, but in 1968, El Goresy and Donnay found ‘white carbon’ with a distinctive X-ray diffraction pattern within a graphite-rich gneiss from the Ries Meteorite crater in Bavaria. This new allotrope of carbon was given the mineral name chaoite. Shortly after it was identified in a meteorite, the Havero ureilite (Vdovykin 1972). During the late 1970s the number of possible carbynes grew as species of different chain lengths were proposed (Whittaker & Wolten 1972). About this time also cyano polyacetylenes of increasing chain length were being identified as interstellar molecules (Morris *et al.* 1976). With various pieces of circumstantial evidence accumulating (Whittaker *et al.* 1981) proposed carbynes as anomalous noble gas host phases; Webster (1981) suggested they might contribute to interstellar dust. The idea that the C_δ, C_β, etc., might be almost entirely carbynes was very soon refuted by detailed TEM studies (Smith & Buseck 1981*a*); indeed the notion that carbynes were the third crystalline allotrope of carbon was questioned (Smith & Buseck 1982).

Although the possibility of carbynes in primitive meteorites fell into disrepute for ten years, a considerable literature on the existence of an allotrope involving sp hybridized carbon, mostly Russian, but also Western (Heimann *et al.* 1983, 1984) has built up in the subject. Kudryavtsev *et al.* (1992) give single crystal X-ray data. While attempting to study C_δ with high resolution TEM (Gilkes *et al.* 1992) found crystalline regions with interplanar spacings higher than diamond, silicon carbide and graphite. Selected area electron diffraction studies and lattice images from several of these particles match figures obtained for chaoite. EDX spectra confirm that silicon is absent so that the grains are not the contaminants suspected in earlier studies (Smith & Buseck 1981*a*, *b*, *c*, 1982). Repeated attempts have been made to obtain electron energy loss spectra (EELS) for specific particles fully identify some kind of carbyne. These experiments have been frustrated because of the instability of the tiny grains in the electron beam. This, however, might itself be indicative that the particles are the sp allotrope by analogy to the work of Kudryavtsev (1992). EELS data with a characteristic K edge distinct from amorphous carbon, graphite and diamond have been obtained from unspecified areas; the absence of Si edges again rules out the possibility of contamination by silicates. Similar results TEM and EELS data have been obtained from putative carbyne material deposited in the laboratory during a plasma are experiments (Gilkes & Pillinger, unpublished results).

(*c*) C_{60} *in Meteorites*

Almost as soon as buckminsterfullerene was proposed as a form of carbon, the idea of searching for the C_{60} structure as an interstellar grain in meteorites was suggested (Heymann 1986). Indeed C_δ nanometre-sized diamonds were found as a result of an erroneous 'hunch' that C_{60} might be the carrier of Xe(HL) (Lewis *et al.* 1987). The isolation of buckminsterfullerene in quantity has allowed its properties to be evaluated (Gilmour *et al.* 1991; Heymann 1991) so that a more directed search may be conducted to investigate its role as a presolar grain constituent of primitive meteorites. Tests performed with authentic C_{60} samples show that like diamond and SiC, buckminsterfullerene is stable in all the reagents used to isolate interstellar grains from meteorites including oxidising acids, even $HClO_4$. With respect to combustion properties C_{60} burns at variable temperatures but this is probably a feature of the crystal size rather than molecular dimensions. It seems likely that C_{60} would burn at or around the same temperature as nanometre sized diamonds; the lowest combustion temperatures observed with authentic samples being *ca.* 400 °C. Interestingly, isotopic compositions measured during stepped combustions indicate that the $\delta^{13}C$ for C_{60} is about 12‰ heavier than the likely isotopic composition of the graphite rods from which it was made. This may reflect an isotopic fractionation during the synthesis or could be due to the purification during HPLC extraction.

Although C_{60} itself has not yet been discovered, graphite particles similar to those reported by Ugarte (1992) have been found in HF/HCl by insoluble residues of meteorites such as Allende (Smith & Buseck 1981*b*) and Adrar 003 (Gilkes & Pillinger, unpublished results); whether these are seeded by C_{60} is an open question.

Although it is necessary to continue to look for C_{60} in primitive meteorites as an interstellar grain, it might be more appropriate to seek its hydrogenated counterparts since it is difficult to find astrophysical environments which are hydrogen free. Nothing is yet known about the properties of species of the form $C_{60}H_n$ under the conditions prevailing during extraction of primitive meteorites. The solubility of C_{60} in organic solvents means that in the past it might have been removed from acid residues during the work up treatment, particularly in samples extracted with CS_2 to remove sulphur. Acid residues of various meteorite have been extracted with dichloromethane and extracts analysed by HPLC. None of these samples showed any evidence of C_{60}. Nevertheless infrared adsorption bands attributable to C_{60} have been observed in the interstellar spectrum (see other contributions in this volume) so the search will continue. Interestingly C_{60} has been identified in a terrestrial Precambrian coal from the Karelia region of Russia. Such a material will represent a good model for meteorite studies.

4. Conclusion

The first steps in any new discipline are always slow and tentative but once they have been made, growth of the subject is almost always exponential. Such has been the case for C_{60} and the discovery of interstellar grains in meteorites. Both these subjects are new areas of science involving carbon, demonstrating the spectacular scope in the chemistry of this unique element.

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Discussion

H. W. Kroto (*University of Sussex, U.K.*). A current controversy suggests that carbynes were due to the presence of an artefact. Furthermore, all the materials you have shown are essentially supposed to be condensed polyynes. I have yet to see any evidence to support the claim that they contain significant numbers of triple bonds.

C. T. Pillinger. We have endeavoured to prove that this might be carbyne by recording the electron energy loss spectrum. Unfortunately the material is very unstable in the electron beam required, so we have been unable to obtain any spectra from the regions where we believe such grains are. They may well differ from graphite, amorphous carbon and from other forms of carbon that we know about, including C_{60}; furthermore, they don't have silicon edges. So this is a carbonaceous phase, that has an electron diffraction pattern, which seems to match a material called chaoite, the 'white carbon' found in the Ries crater. I know you are worried about the stability of these samples. It is known that carbynes can be stabilized by attaching metals to the ends of the chains and one reason why I might now be able to have carbynes to hand is that extra atoms may be attached to the chains. This would possibly provide a link to the long chain triply-bonded carbon species containing nitrogen atoms. More information will be available if we obtain an EEL spectrum, which would tell us whether the material contained nitrogen or not. We are working on the problem, and I like to believe that about 20 years ago another allotrope of carbon was discovered.

R. C. Haddon (*AT & T Bell Laboratories, U.S.A.*). How much of this material do you actually possess? What about the surface of the diamond grains, presumably they have to be terminated with something?

C. T. Pillinger. We have enough material to see, about 30 grains. With a 200 atom grain, you must terminate the bonds on the surface. Now we know that hydrogen can terminate the bonds. I think there is an absorption at *ca.* 3 μm; the grains may therefore contain some hydrogen. The mean size for these diamond particles is 2000 atoms, although there are certainly diamonds which are smaller. Another point about the diamond grains is that they appear to have carboxyl groups attached, and this enables us to extract them from the meteorite. But whether the carboxyl groups are introduced as a result of our treatment, or whether they are there originally, is not clear. Characterizing nanocrystals is not very easy.

S. Iijima (*NEC Corporation, Japan*). Could you comment on other work in which C_{60} has been found in Nature?

C. T. Pillinger. It has been found in shungite; a Precambrian coal from Karelia. I have a sample of shungite which we have tried to extract with toluene to see whether we could obtain a spectrum with peaks corresponding to C_{60}. This is very recent data and our initial results are not promising.

S. Leach (*Observatoire de Paris-Meudon, France*). Do any of the diamonds contain colour centres due to metallic impurities?

C. T. Pillinger. There are no metal impurities in these diamonds high enough to give that kind of response.