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CARBON AND NITROGEN ISOTOPES IN TYPE II SUPERNOVA DIAMONDS

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ABSTRACT

We construct a model for the origin of the abundant nanometer diamonds found in meteorites. We interpret them as interstellar particles that were grown during the expansions of supernova interiors. The physical setting and the chemical-vapor-deposition process that we describe present clear reasons both for the small sizes (nm) of the diamonds and for their mean isotopic composition being not greatly different from solar. To delineate the isotopic requirements for collections of diamonds (which are too small for analysis individually) we present measurements of carbon and nitrogen isotopes obtained by stepped combustion of diamond collections. Our model for the growth of supernova diamonds is motivated by a series of postulates, unremarkable as single postulates, that together produce a successful calculation. The computed growth occurs in the continuously mixing envelopes of expanding Type II supernova remnants. It provides a good characterization of these facts: (1) the C isotopic composition is not far from solar; (2) both carbon and nitrogen become isotopically lighter as the diamonds are combusted; (3) the C/N ratio changes during combustion; (4) the diamonds are individually tiny; (5) collections of diamonds are carriers of Xe-HL. We show that the isotopic gradient during combustion may be interpreted in this model as either an isotopic gradient within each diamond or as a correlation between isotopic composition and size of individual diamonds contained in the bulk collections.

Subject headings: dust, extinction — meteors, meteorites — nuclear reactions nucleosynthesis, abundances — supernovae: general

1. INTRODUCTION

This paper presents a chemical-reaction model for the growth of the small diamonds that are found to be distributed abundantly throughout the primitive chondritic meteorites. The growth occurs by chemical vapor deposition (CVD) cycles, a nonequilibrium process. The growth site is argued to be within the interiors of expanding young supernova remnants, specifically at a mixing interface between the He-shell material and the hydrogen envelope. It is there, beginning ~ 1 yr after core collapse, that abundant carbon from the He shell mixes with abundant hydrogen from the envelope—precisely the needed chemical constituents for the nonequilibrium reactions with hydrocarbon molecules. It is the dynamics of that chemistry that selects diamond correlation for growth, rather than the graphitic ground state of solid carbon. The latter had been the prior expectation for carbon condensates based on ideas of thermodynamic equilibrium in a slowly cooling gas. The slowness of this CVD chemical process results in the small (nanometer) diamond sizes. The hydrogen stabilizes the tiny structures against graphitization. The diamonds survive the expansion and slowing of the supernova interior, their growth complete long before mixing with circumstellar matter occurs. Surprisingly to some, the calculated growth produces diamonds of nearly solar isotopic composition, because ^{13}C -rich carbon is associated with the hydrogen, which mixes with the ^{12}C -rich He shell.

The structure of this paper is as follows: an historical introduction in this § 1; isotopic data for C and N obtained by us (C. T. P. and S. S. R.) using stepped combustion of diamonds in § 2; the physical postulates motivating the supernova scenario

in § 3; supernova mixing prescription and calculations of diamond growth in § 4; and final discussion in § 5.

The discovery of abundant tiny (1–4 nm) diamonds in meteorites (Lewis et al. 1987) came as a great surprise, as did the demonstration that they collectively carry isotopically anomalous xenon, which had been known for a decade to reside in carbonaceous residue of acid dissolution of bulk meteorite samples (Lewis Srinivasan, & Anders 1975; Lewis, Gros, & Anders 1977). If these diamonds in meteorites are all presolar, being as much as 0.1% of meteoritic matter, or equivalently up to 3% of meteoritic carbon (Huss & Lewis 1994b), the interstellar medium contains an incredible 10^{16} diamonds per g if interstellar carbon is also 3% diamond by mass. They must have substantially survived the aggregation processes for the meteorite parent bodies in the solar accretion disk. Some infrared spectroscopic evidence of abundant interstellar diamonds is presented by Allamandola et al. (1993). The Xe-HL component within diamond collections, being fairly normal except for large enrichments of the two heaviest and the two lightest of xenon's nine stable isotopes, seems to have been implanted in the diamonds by nonthermal collisions between the diamonds and high-speed Xe gas. That this occurred within the expanding supernova interiors was developed in a parallel line of works (Clayton 1975a, 1976, 1981, 1989; Howard, Meyer, & Clayton 1992). What has been suggested in those papers is that the diamond growth and Xe implantation had to occur prior to mixing of the supernova ejecta with the interstellar medium (ISM) in order to have the chance to record such highly anomalous xenon, and that the hydrodynamic collisions between diamonds and Xe gas must have favored the appropriate

velocities for those parcels of gas containing xenon that had received a burst of neutron irradiation having fluence $\tau = 0.07$ mbarn⁻¹ in the explosion itself (to produce the two heaviest isotopes) and for other gas parcels that had been the source of the *p*-process nucleosynthesis (to produce the two lightest isotopes). The *r*-process production near the supernova core (Meyer et al. 1992) and *s*-process production in the He shell must have been excluded (or disfavored) by the lack of appropriate relative velocities between diamonds and these gas pockets. See Howard et al. (1992) for the discription of these arguments. Although these arguments are both interesting and useful, they derive from a rare-gas trace constituent within the diamonds.

The present work turns attention to the growth of the diamonds themselves. We interpret them as SUNOCONs, a useful acronym (Clayton 1978) distinguishing any SuperNOVA CONDensate from other types of interstellar dust (STARDUST, NEBCONs and PRESOLCONs; Clayton 1978); but unlike the thermal equilibrium condensate envisioned in most discussions of SUNOCONs, we regard the diamonds as being instead the result of specific sequences of nonequilibrium chemical reactions. Such chemical sequences in the gas phase have been studied experimentally (Angus & Haymann 1988) and are called CVD. The reactants are primarily molecules, mostly hydrocarbons. Equilibrium thermal condensation in hot gas motivated the first prediction of interstellar diamonds by Saslaw & Gaustad (1969), who suggested that diamonds might thermally condense (i.e., an equilibrium condensate) as a metastable form of solid carbon, considering that the energy difference between diamond and graphite is so small and the required rearrangement so great. Equilibrium also motivated the physical idea (Nuth 1987; Badziag et al. 1990) that surface energy would in fact make diamond the ground state for sufficiently small diamonds (less than 5 nm). As interesting as these ideas are, they both run afoul of the observation that, within supernovae, the large mass densities of carbon are of the ¹²C isotope, leading to the criticism that such thermal condensations of diamond should be overwhelmingly isotopically light. The CVD process that we will utilize circumvents that criticism. Collections of diamonds from meteorites are characterized by the isotopic abundance ratio ¹²C/¹³C = 93, as we show below, only slightly greater than the solar value 89. This near normalcy has raised scepticism over their being anything as exotic as SUNOCONs despite the anomalous Xe that at least a subset of them contains. However, near normalcy of carbon isotopically is one of the simple consequences of the supernova scenario for their CVD growth that we will describe.

A parallel line of research, the technique of stepped combustion (combustion of the diamond collection while incrementally increasing the temperature of the sample) combined with mass spectrometric analysis of the C and N isotopes released by the combustion of diamond isolated from primitive chondrites, showed that both the carbon and nitrogen are isotopically anomalous in bulk (carbon only slightly [Swart et al. 1983b] so but nitrogen very anomalous [Lewis et al. 1983]) and that their isotopic compositions even vary during combustion (Russell, Arden, & Pillinger 1991). These results are discussed in § 2 below, wherein we also present some new data. The nitrogen released during combustion is sufficient for every diamond to contain several atoms and is highly ¹⁴N-enriched, adding to the evidence that at least some component of these samples is presolar. We present some of those data in this

paper and attempt to fit them into a model of diamond growth within supernovae. What we describe in the present work is the way these observations suggest a new astronomical research program based on the vapor deposition growth of diamonds in supernova envelopes. Because of enormous complexities that will require decades of effort to resolve, our discussion features postulational and intuitive elements rather than only deductive elements. Our aim will be a clear physical description of the picture, whereas our few calculations will be of only a survey nature, designed more to lend credence to this new picture than to fix the answer. If we are correct a new astronomy of supernova remnants is possible. It is another variant of “cosmic chemical memory,” the generator of these new astronomies (Clayton 1982).

But first consider a major limitation of this study: viz., the data derive from collections of diamonds rather than from individual diamonds. Those problems are summarized next.

1.1. Collections of Diamonds: Xenon

All measurements, including those reported here, are made on large collections of interstellar diamonds rather than on single diamonds, which individually contain only a few thousand C atoms, and less than 20 N atoms. Only a very tiny fraction (one in 2×10^6) of diamonds contain even a single atom of Xe. At least 10^9 diamonds are required to even measure a Xe isotopic composition. It has not been possible to distinguish between individual diamonds. For this reason our scenario will attempt to achieve only the “mean diamond.” This objective may be inappropriate, however. Two especially important cases illustrate the potential pitfall. Because only one in a million diamonds has even a single Xe atom contained within it, we have no way to be sure that a given diamond had the opportunity to implant both Xe-H and Xe-L; to the contrary, some may encounter Xe-H-rich gas and others Xe-L-rich gas, with the final mix containing Xe-HL. We will take this to be the case because the efficiency for diamond encounters with Xe-L gas must be an order of magnitude lower than the efficiency for encounters with Xe-H gas, as we now show.

Bulk supernova ejecta must be more enriched in light Xe (Xe-L) isotopes than in heavy isotopes (Xe-H), considering that supernovae are the sites of origin of all ^{124,126}Xe (the light *p*-process isotopes) but that the neutron burst responsible for the Xe-H enrichment accounts for only a small fraction of bulk ^{134,136}Xe, the heavy Xe isotopes, which are primarily produced in the true *r*-process. So if Xe-L represents *p*-process production, the Xe-L component must be more overabundant than the Xe-H component in the combined yields of Type I and Type II supernovae. The equality of the observed overabundances must mean, on this picture, that the diamonds simply encountered Xe-H more often than Xe-L. This is an accident of history containing information about young supernova remnants. The true *r*-ejecta has hardly been encountered by the diamonds at all, for if it had been, the implanted Xe would have a large ¹³¹Xe excess. One can imagine exceptions to these conclusions, however. For example, it is conceivable that the *p*-process yield is also not encountered by the diamonds, and that Xe-L represents not true *p*-process but some minor light-isotope enrichment, in which case we could not conclude that the diamonds have sampled the Xe-L and the Xe-H with differing efficiencies. But because the process enriching ^{124,126}Xe in supernovae must be rather similar to the *p*-process, and because the *p*-process does happen in the supernova mantle by ordinary thermal processes, we hold it

likely that Xe-L is a significant component of true *p*-process material. Huss & Lewis (1994a, b) have reviewed the inability to separate Xe-H from Xe-L within differing diamond collections, and our interpretation is that the mixture of diamonds with differing histories has just not been separable—at least not yet. The general picture developed here affirms the likelihood that Xe-H and Xe-L are ultimately separable because, as presolar diamonds of probably differing histories and differing chemical memories, they may be separable by some other factor as well, as one of us predicted long ago (Clayton 1976).

1.2. Collections of Diamonds: Carbon

Another potential pitfall of seeking individual diamonds having the composition of mean diamonds is the isotopic composition of the carbon. Because the bulk carbon in diamonds has almost solar isotopic composition, one sometimes hears it said that these diamonds cannot be SUNOCONs. Our scenario based on vapor deposition will rationalize the almost normal isotopic composition of the mean diamonds (about 3%–4% enriched in ^{12}C compared to the usual terrestrial standard), as well as their mean isotopic change during combustion. Although this success addresses the objection that diamonds cannot be SUNOCONs, it is nonetheless irrelevant if the chondritic diamonds have some other major site of origin in addition to supernovae. It would then be inappropriate to expect the C composition of the Xe-HL bearing diamonds to equal that of mean interstellar diamonds. One runs such a risk in taking the carbon composition of the Xe-HL bearing component to be the same as the bulk mean. One might also be surprised if supernovae are the only sources of interstellar diamonds. Nonetheless, we feel that the exercise of regarding the mean diamond as a SUNOCON is instructive. It presents a target, and our results will evaluate that target and lay the foundations for a more comprehensive picture.

The carbon (and nitrogen) isotopic variations within the SUNOCON component would have to be much larger than in the bulk diamonds if the anomalous diamonds were but a small fraction of the total—for example, if the SUNOCON diamonds were mixed with much more numerous diamonds made in the solar system. This uncertainty is the main stumbling block to quantitative application of the model to be presented, emphasizing the need for a technique for separating diamonds into different families. We also warn that the individual diamonds must of necessity have widely varying C-isotope ratios. The typical diamond (by number) has 1000 C atoms and therefore only ~ 11 ^{13}C atoms, so that even the smallest fluctuation (one atom) is a large 10% variation in isotopic ratio. Bearing in mind the much smaller number of N atoms per crystal, this argument demonstrates that the N isotopic composition will vary even more remarkably between individual diamonds, with most containing pure ^{14}N ! We therefore can assert that the lack of evidence of carbon variability is a result of the huge number of diamonds in a measured sample rather than any suspected homogeneity within diamonds. They cannot be homogeneous.

2. STEPPED COMBUSTION OF DIAMONDS: CARBON AND NITROGEN ISOTOPES

Only diamonds isolated from the CM2 meteorite class by a procedure described by Russell et al. (1991) are considered here. This is because diamonds are very abundant in this meteorite type and have apparently been less (although not the least [Newton et al. 1994]) affected by parent body processes than

those isolated from other groups (Alexander et al. 1990; Huss 1990). Huss & Lewis (1994b) discussed their abundance in other meteorite classes.

The diamonds are combusted in a controlled oxygen environment to release CO_2 and N_2 . The combustion is performed in increments of increasing temperature (Russell et al. 1991; Swart et al. 1983a), and the gas released from each temperature step of the combustion sequence is individually analyzed by mass spectrometry of the CO_2 and N_2 molecules. The carbon isotope data were acquired using a VG SIRA 24 mass spectrometer, which measures microgram amounts of CO_2 to a high precision (± 0.05 parts per thousand). Nitrogen isotopes were measured to $\pm 0.5\%$ – 1% precision on a static vacuum mass spectrometer. Carbon yields during stepped combustion were determined with a capacitance manometer in a calibrated volume (accuracy $\pm 1\%$), while nitrogen abundance is from the calibrated mass spectrometer response.

2.1. Carbon Isotopes: Experimental Results

Although there is evidence that diamond acid residues can be separated (Verchovsky et al. 1994), the chemical resistance of our samples operationally defines them as a single phase, i.e., diamond. The diamond typically combusts between 400 and 550 C. Stepped combustion acts on materials in such a way that the finest grains or the surfaces of larger diamond particles should burn first (Wright & Pillinger 1988) and so are measured in the first combustion steps. Thus the material combusting at the lowest temperature was arguably the last condensed. Figure 1 shows very clearly that as diamond samples burn the isotopic composition progresses from heavier ($^{12}\text{C}/^{13}\text{C} = 91.3$) to lighter ($^{12}\text{C}/^{13}\text{C} = 92.5$) values. This 3.8%

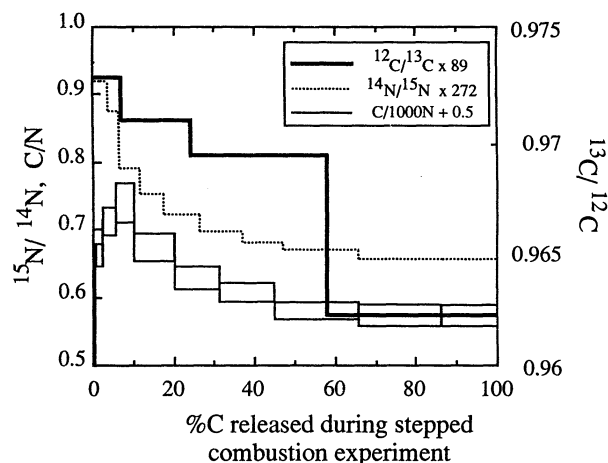


FIG. 1.—The isotopic composition of carbon (heavy line, right-hand ordinate) and of nitrogen (dashed line, left ordinate) released by diamond combustion as a function of the fraction of the carbon that has been combusted. The errors experimentally on these isotope ratios are smaller than the widths of the lines used to plot them; i.e. they are very accurate. Also shown are upper and lower limits to the C/N mass ratio (solid-line boxes). Each quantity has for convenience been plotted in normalizations shown in the box: $^{13}\text{C}/^{12}\text{C}$ multiplied by 89 so that the terrestrial ratio would plot as unity; $^{15}\text{N}/^{14}\text{N}$ so the terrestrial ratio (1/272) would also plot as unity; and a C/N ratio offset from zero so that 100 would plot as 0.6. These data are from a sample of the class CM2 chondritic meteorite Cold Bokkeveld. Typical sample size was 100 micrograms, about 10^{16} individual diamond grains. Both nitrogen and carbon releases become isotopically lighter as the combustion proceeds to completion (100% released). The last released are either the centers of the diamonds or the largest diamonds, depending on the interpretation, and are respectively about 3.8% and 35% lighter than terrestrial for carbon and nitrogen.

deficiency in ^{13}C relative to the international standard in the final release is in itself not sufficiently anomalous to identify the diamonds as presolar, even though it is accurately measured and is reproducible. Materials even more rich in ^{12}C are frequently encountered among terrestrial samples (particularly biological ones) but not usually in meteorites; nevertheless it cannot be regarded as demonstrably anomalous. More eye-catching is the greater than 1% decline in ^{13}C seen during the stepped combustion. Such a trend is in the opposite sense to a kinetic isotope effect, which dictates that light isotopes react faster and thus preferentially $^{12}\text{CO}_2$ first; so this trend must be an inherent feature of the samples. These carbon data have been presented previously by Russell et al. (1991).

2.2. Nitrogen Content and Isotopic Composition: Experimental Results

Nitrogen abundance and isotopic composition can be monitored simultaneously with carbon release as a function of stepped combustion temperature to give the C/N ratio to a precision $\pm 20\%$ and $^{14}\text{N}/^{15}\text{N}$ to a far greater precision (± 0.5 parts per thousand) than the effects recorded here. Figure 1 also contains new nitrogen data from a somewhat more pure diamond residue (called CBJA) than was available to Russell et al. (1991). The C/N ratio of the diamond also varies as the experiment progresses. The early steps of the combustion yield very low C/N values, with the nitrogen released being similar in isotopic composition to terrestrial values and presumably reflecting a small input from atmospheric nitrogen that has become absorbed on to the diamond surface. After that initial combustion, the C/N ratio rises quickly to a peak value of around 250 before declining to a "plateau" composition during the bulk of the combustion at around 100; i.e., the diamond contains about 1% nitrogen. The isotopic composition of the nitrogen changes as the C/N evolves in that the nitrogen in the first temperature steps is enriched in ^{15}N relative to that which burns last. Not only is the decline in ^{15}N content during combustion significant, but the absolute 35% deficiency in bulk ^{15}N is in this case so large as to indicate a presolar origin for the N-bearing portion. And because the average diamond contains many (about 20) N atoms, this is strong circumstantial evidence for a presolar origin of a large fraction of the diamonds. The composition of small grains or surface diamond is difficult to define because of the possibility of air contamination ($^{14}\text{N}/^{15}\text{N} = 272$), but the first crystallized diamond is well constrained at $^{14}\text{N}/^{15}\text{N} = 419 \pm 5$. The data we show in Figure 1 are consistent with earlier measurements obtained from less pure diamond samples.

In the model presented below, we interpret the changing isotopic composition during combustion to two separate physical possibilities: (1) as a radial gradient in the isotopic structure of the mean diamond, with the centers being isotopically lighter in both C and N isotopes and richer in N overall; (2) as a particle size spectrum, with the smaller particles being isotopically heavier than the larger ones. Possibly, the smaller diamonds have mixed somewhat with solar composition. These two possibilities are indistinguishable by the stepped combustion data we have at present, but the model will be shown to predict both effects.

3. THE TYPE II SUPERNOVA MODEL

We accept the arguments (Clayton 1989; Howard et al. 1992) that supernovae of Type II are the sites for producing

both Xe-H and Xe-L. Type II supernovae share with Type I the bulk p -process nucleosynthesis, probably roughly equally. Woosley et al. (1990) confirmed the availability of the required neutron burst in Type IIs called for by calculations of Xe-H production. Type II origin is also indicated by the Kr isotopic anomalies coupled with the p -process theory of light-isotope nucleosynthesis. Degassing of diamond collections reveals a deficiency of ^{78}Kr in the Kr-L component with respect to solar abundances and an excess of $^{124,126}\text{Xe}$ in the associated Xe-L component. Type I supernovae may more easily produce an excess at ^{78}Kr with respect to the general level of p -nucleosynthesis (Howard, Meyer, & Woosley 1991), so Type II better fits a ^{78}Kr deficit. Nonetheless, this reasoning is not very secure, and the circumstantial Kr and Xe isotopic data could mislead. What must be addressed is this: how do Type II supernovae grow diamonds and what is their isotopic composition?

For clarity we choose to begin by listing assumptions and arguments that will be used to interpret C and N data from stepped combustion of diamond collections. Because these assumptions will lead to a successful calculation, but one that follows from a very complicated model, it is our hope that emphasizing the assumptions will make that calculation seem more understandable. Each assumption is by itself moderate, though open to questions of its own, but the careful reader will discern how they conspire to lead us to that final complicated model, which, if simply stated from the outset, might seem hopelessly detailed for scientific plausibility. In the next sections we will defend these assumptions only slightly, recognizing that although they must be oversimplifications they are nonetheless needed to proceed quantitatively. In our final discussion we consider the effects of these assumptions being false.

1. Diamonds grow by CVD on a seed condensate nucleus. This deposition is not an equilibrium process (thermal condensation). It is kinetic and has been extensively studied in the laboratory (e.g., Angus & Hayman 1988).

2. Seed nucleation is a thermal condensation of minimal "molecule scale" carbon clusters. The seed nucleus abundance locally depends, according to classical nucleation theory, on a high power of the density of C atoms (e.g., $n = 10$ for 10-C atom adamantane, or $n = 4$ for clusters of 4 SiC particles; etc.). We assume that no nitrogen condenses thermally in these seed nuclei, although that can occur, considering that some refractory nitrides do exist.

3. Carbon solids cannot nucleate if bathed in much more abundant oxygen. Even if CO molecules cannot lock up C atoms in those environments, the hot O would combust any particles that attempt growth. In the subsequent low-temperature phase of deposition growth, on the other hand, ambient oxygen is not destructive, and even helps! Howard et al. (1990) showed that C/O ratios between 0.83 and 1.0 were very efficient in growing crystalline diamond, whereas other ratios produce instead graphite, soot, and amorphous carbon. The model we present will naturally occur in ambient ratios near C/O = 1.

4. Subsequent growth of diamond by CVD requires the presence of hydrogen to form diamond. H bonds to dangling C bonds on the surfaces of nanometer diamonds stabilize their structures and prevent graphitization (Frenklach 1989). Graphite growth, on the other hand, is chemically etched away by the H bath. Therefore, diamond growth requires mixing with the H-rich Type II supernova envelope. This is another

reason to select Type II; viz., Type I, totally lacking hydrogen, cannot grow diamonds by this process. In the growth equation to be presented later, equation (2), the exponent s on the H density expresses the requirement for hydrogen.

5. Assumptions 2 and 3 require the carbon to nucleate in the He-burning shell material where the greatest C concentration exists (after expansion and cooling, of course, which will require about a year) and to grow diamonds by admixing with H-rich material above the He zone. The He-burning convective shell had previously been singled out by Clayton (1981) as the birthplace of Xe-HL carbonaceous carriers by virtue of it being the only C-rich zone (i.e., $C/O > 1$) of the Type II supernova. The carbon interior to the He shell will, on the other hand, never contribute to the vapor growth, as it has no hydrogen within it and has far more O than C.

6. Diamonds grow by vapor deposition at a rate about 0.1% of the kinetic rate of collision with carbon atoms (if C were atomic at the same carbon density), judging from the laboratory experiments (e.g., Angus & Hayman 1988). We modeled those experiments to determine that 0.1% efficiency with respect to atomic collision rates constitutes a good rule. This assumption has the merits of simplicity and plausibility, but by suppressing the true chemical network of reactions it also suppresses any information that they would give in a more complete chemical calculation. We show below that the supernova gives diamonds of the observed size with this assumption. Thermal equilibrium condensates (e.g., graphite) might be expected to grow to sizes 100 times larger.

7. Type II supernovae are mixed by instabilities at the time of explosion. These cause interpenetration of matter with both overlying and underlying strata of the initial supernova. Observations of SN 1987A and explosive hydrodynamics (Fryxell, Mueller, & Arnett 1991) indicate that such mixing occurred (e.g., McCray 1993, and references therein).

8. Reverse shocks and asymmetries maintain turbulence, which slowly decays as the remnant expands. The turbulence causes continuing collisions between fluid elements during the subsequent expansion. That expansion assumes approximately a Hubble-like homology relationship for velocity versus radial position, but the decaying turbulence continues to collide fluid elements with decreasing violence (i.e., with relative velocity much less than flow velocity). By the time that solid particle growth commences (~ 1 yr) a significant spectrum of compositional mixings may exist.

9. Xenon is implanted when diamonds collide with Xe bearing gas at speeds of order $1 \text{ eV nucleon}^{-1}$. Lower speeds cannot implant Xe. At higher speeds the Xe projectile would penetrate and disrupt the tiny diamond. Turbulent mixing provides the required relative velocities near 10 km s^{-1} between diamonds and Xe. Such kinetic energy is much smaller than solar wind implantation in lunar soil, for example, but an order of magnitude greater than thermal energies in the supernova after 1 yr of expansion. This assumption is not central to the issue of diamond growth but is germane to the overall picture of them as SUNOCONS.

10. Gas composition mixes much more slowly (at the molecular level) by chemical diffusion. The supernova mixing can be thought of as stirring a drop of ink into water, which first winds up as inhomogeneous ribbons of ink and on much longer timescales diffuses the ink into the surrounding water. The diamonds nucleate in the C-rich matter (ink) but grow as H envelope (water) dilutes it.

11. Carbon seed nuclei condense after ~ 1 yr, when the tem-

perature of the He-burning shell has fallen below 1500 K. Dust condensation is accompanied by a rapid transition to an infrared object, and cooling becomes so efficient that the kinetic temperature falls to a value closer to 500 K. Vapor growth of diamond continues thereafter, until truncated by the rapidly falling density (as t^{-3}). Although the initiating nucleation was very nonlinear, the subsequent CVD growth is either linear in density, or varying with a low power of the density (depending on the identity of the molecular species that affects the H replacement by C on the diamond surfaces). In the reference calculations that we will present, we will take the growth rate to be linear in the density, although the general growth eq. [2] below) should in some reaction networks allow for a higher power of dependence upon density.

12. Nitrogen substitutes for C in the diamond structure at about the 1% level (e.g., Russell et al. 1991). It does not need to await later high-velocity implantation, as noble gases do. We take N to be deposited chemically along with C in the CVD process. Nitrogen is virtually absent in the He-burning convective shell, so that it cannot thermally condense within the nucleations that are begun in that material. The nitrogen is attached as a part of the CVD process of vapor growth of the diamonds. As we will see below (Fig. 3), the nitrogen exists in presupernovae of Type II as a ^{14}N -rich pocket in the upper He zone and H-burning shell and a less ^{14}N -rich surface zone of about 15 solar masses of H envelope.

13. The diamonds, even though tiny, are not permanently confined to the matter in which they first nucleated. Turbulent convective transport gradually moves the seeds into other nearby mass elements, with which they mix. Alternatively, we can imagine nearby gases slowly diffusing into a mass element containing a nucleation cluster. We are not able to describe the physical mixing in a quantitative way at the present time. We postulate without computation that this transport is a natural consequence of the turbulent mixing toward ever finer mass scales and of the t^{-3} reduction in the mass density (which has fallen to near $10^{-15} \text{ g cm}^{-3}$ at $t = 1000$ days). The migration occurs when low-mass, thin-fluid elements collide. This is essential in allowing the carbon nuclei to encounter not only H but also Xe-HL.

4. DISCUSSION OF MODEL AND CONSEQUENCES

4.1. Diamond Size

Diamond growth by CVD in supernovae can be expected to produce particles of the correct size. To establish this we compare the measured rates of CVD deposition in the laboratory with the C-atom flux in a medium having the same C density of atomic carbon. If C atoms having density n_C stick to a surface with probability α when they hit it, the kinetic growth rate would be (Wickramasinghe 1967, pp. 57–58)

$$dr/dt = \alpha n_C v_T M_C / \rho_d, \quad (1)$$

where $v_T = (kT/2\pi M_C)^{1/2}$ is the normal component of the thermal speed of C atom of mass M_C and ρ_d is the density of diamond. The carbon density n_C is determined by the ambient density and the carbon mass fraction within it. For laboratory conditions studied by Angus & Hayman (1988) at $P = 6000 \text{ Pa}$ and $T = 1000\text{--}2000 \text{ K}$ in a gas that is 1% carbon, this would give a kinetic limit ($\alpha = 1$) to diamond growth equal to 3 cm hr^{-1} . On the other hand, the experiment actually recorded growth at 0.003 cm hr^{-1} , which is a factor 1000 smaller than the kinetic limit. We therefore scale that result to the super-

nova environment in a simple way by taking the CVD growth rate to be 0.1% of the corresponding kinetic limit for C atoms having the same number density.

Notice that we are not saying that the deposition actually is of gaseous C atoms. It is actually some hydrocarbon such as acetylene C_2H_2 (Frenklach 1989; Howard et al. 1990) that is the major active molecule in the addition process. In the actual process, an H atom bonded to the surface vertex of the small diamond (thereby stabilizing it) is abstracted away by the arrival of the hydrocarbon molecule, which leaves behind a C atom in its place. Instead of equation (1) the true equation is

$$dr/dt = k_1(n_C)^r(n_H)^s = k_2\rho^{(r+s)}(X_C)^r(X_H)^s, \quad (2)$$

where r and s are the power-law dependences on n_C and n_H , respectively, of the densities of the true molecular reactants that moderate the diamond growth. For example, if acetylene is indeed the key gaseous reactant, its abundance in the gas will depend upon both n_C and n_H in ways that can be determined only by integration of a chemical reaction network responsible for the manufacture of the acetylene (Frenklach 1989). During acetylene growth the reaction network will be expected to have $r = 2$ and $s = 2$; however, after a year of supernova expansion we hold it more likely that the acetylene-forming reactions have become very slow and their number density therefore decreases owing to expansion only. But those chemical questions require further study. In the second form of equation (2), ρ is the bulk density of the gas and X is the mass fractions for C and H. Rate coefficients k_1 and k_2 are those appropriate for this equation. We do not model that atomic level chemistry. We simply assume that it happens, whatever the actual chemical path, at a rate that is 0.1% of the kinetic limit of C atoms if they were monatomic. This way of scaling experiment to supernova seems adequate for the exploratory paper, because it matches experiment. In the long run the actual chemical paths must be understood and modeled. We write equation (2) at this point to contrast the true situation to the idealized equation (1) which we use only to set the scale of particle growth, and also to support later discussion when CVD growth occurs in a gas whose composition is changing owing to mixing.

Returning to the supernova comparison, then, we take the density to be $1 \times 10^{-15} \text{ g cm}^{-3}$ at $t = 1000$ days after the explosion; we take the carbon to be 1% of the matter as appropriate to the mixing zones of the supernova to be described below; and we take the density to subsequently decline in proportion to $(1000 \text{ days } t^{-1})^3$. This gives a kinetic limit to the initial growth rate at $t = 400$ days when dust growth may commence equal to 470 nm yr^{-1} . The corresponding temporal integration with falling density then gives the kinetic limit to the entire growth of roughly 520 nm radius. Taking 0.1% of that value as the true CVD growth rate gives final particle radius $5.2 \text{ \AA} = 0.52 \text{ nm}$. Roughly then, diameters of 1 nm are expected. With the compositional model for the growth zone that we define in the next section the final diamond sizes will be comparable to this simple estimate. This is indeed a typical size for observed diamonds, which are found to be distributed in a lognormal distribution of sizes with median diameter of 2.6 nm (Lewis, Anders, & Draine 1989). The lognormal distribution is typical of growth processes rather than fragmentation processes. We cannot suppose that high accuracy can be associated with such a simple argument; only that it is a plausible estimate and it gives the correct order of magnitude for the observed diamonds. This establishes supernova interiors as a candidate venue for the observed diamonds.

4.2. Mixing Model for CVD Growth

Figure 2 shows the radial composition of a portion of a $25 M_\odot$ star (Weaver & Woosley 1993 model S25S7A). It is a fair representative of the class of massive core-collapse Type II supernovae. As a class these models have implications for the ISM diamonds. We infer the general behavior of this class of supernova models with the aid of this particular $25 M_\odot$ model and the 13 postulates of the previous section. For brevity in subsequent discussion we will refer to postulate number j by the reference (no. j). What Figure 2 shows is the spherically symmetric unmixed onion-like structure immediately after shock wave passage. It does not display the oxygen-dominated matter, which we take to be irrelevant to both thermal nucleation and to CVD growth of diamonds. It also does not show the constant composition all the way to the surface (at $m = 25 M_\odot$). Nor does it show the nature of the partially mixed object a year later when diamond growth begins.

The outgoing shock wave plus its attendant heating and overpressure amplifies certain instabilities to smooth radial expansion of the gas ball, which after shock passage contains a severe overpressure throughout. These turbulent interpenetrations remain part of the later structure but decay during its subsequent expansion (nos. 8, 9). At later times each gram of material contains a linear admixture of various fluid layers shown here. The reader must visualize the Figure 2 structure after $\sim 1 \text{ yr}$, already mixed into ribbonlike structures by turbulence (no. 10), but now also mixing at the molecular level as the dust begins to grow. A reliable description of the compositional structure at that time can only be guessed at because it must contain a complex spectrum of mixings.

The carbon interior to $m(r) = 6.7 M_\odot$ radial mass coordinate is bathed by 20 fold more abundant oxygen and so can neither nucleate carbon nor grow diamonds (no. 3), and we tentatively assume that inability to remain even later after any mixing

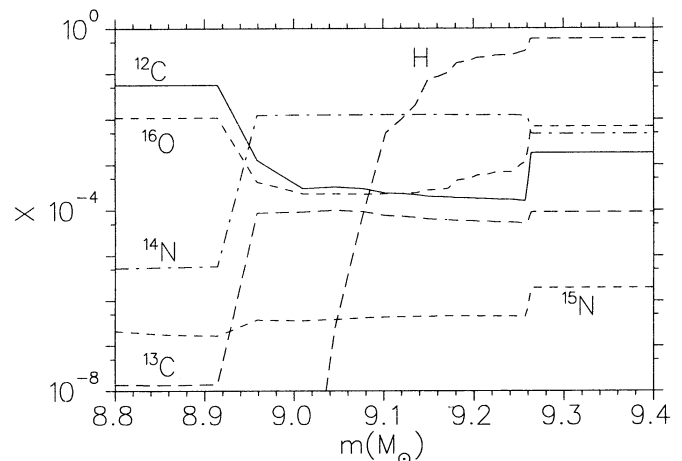


FIG. 2.—The composition profile of a $25 M_\odot$ presupernova star, displayed as mass fractions vs. the radial enclosed mass coordinate from model S25S7A of Weaver & Woosley (1993). The ^{12}C -rich He burning shell exists between $6.7 < m < 9.0 M_\odot$, with a He cap of $0.3 M_\odot$ that is ^{14}N -rich. The hydrogen-rich envelope extends from $9.3 M_\odot$ to the surface at $25 M_\odot$. For our mixing routine zone 1 is the ^{12}C -rich top $0.07 M_\odot$ of the He-burning shell (just inside $m = 9.0$), zone 2 is its He cap of $0.305 M_\odot$ of H-free matter, and zone 3 is the bottom $0.38 M_\odot$ of the H envelope. Their compositions in bulk are in Table 1. The “growth zone” for the diamonds in our reference calculation is a uniform mix of zones 1 + 2 diluted gradually by zone 3, which introduces H and ^{13}C . That H envelope (zone 3) has $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{N}/^{13}\text{N}$ ratios that are about 4.1 and 9.7 times greater than terrestrial ratios respectively owing to their earlier containment with the initial hydrogen-burning core.

with the H-bearing envelope. Therefore, we neglect all carbon interior to the He-burning shell at $m(r) = 6.7 M_{\odot}$. Diamonds nucleate and grow from the C initially located above $m(r) = 6.7 M_{\odot}$. We now drop the reminder that m is a radial coordinate and its units are M_{\odot} .

In the He-burning convective shell $6.7 < m < 9.0$ carbon is very abundant, being about $X_C = 7\%$ of total mass. Thermal nucleation of the first stable carbon clusters occurs within those portions of the partially mixed matter that are still dominated by this He-shell component at a postshock time of ~ 1 yr, because the abundance of C_n clusters is, according to nucleation theory, proportional to X_C to the n power (nos. 2, 5). Early nucleations that remain in matter from this zone will grow large graphite particles, probably 100–1000 times larger than the diamonds considering that graphite could grow at the kinetic limit. This could grow micron-size graphite SUNOCONS, which allows not only isotopic measurements of carbon within individual particles, but of trace elements as well. Such graphite particles will be ^{12}C -rich and ^{18}O -rich in their trapped oxygen and may be represented by one such well-known particle (Hoppe et al. 1992). However, the surest way to identify a SUNOCON will be large excess of ^{44}Ca owing to their condensation before (< 100 yr) the abundant radioactive ^{44}Ti has decayed, as predicted 20 yr ago (Clayton 1975b).

Table 1 shows how we simplify the supernova structure (Fig. 2) to a subsequent mixing of three zones. Zone 1 is the top layer ($0.07 M_{\odot}$) of the C-rich He-convective-burning shell, which in total stretches between $6.7 < m < 8.9$. For numerical survey we arbitrarily take that top layer to be $0.07 M_{\odot}$ and imagine that it is instantaneously mixed at shock passage into zone 2. Mechanically we regard the shock to impulsively inject that $0.07 M_{\odot}$ through the dropping density at the interface into the lower density zone-2 material. "Instantaneous mixing" means, for this application, not physically instantaneous but rather that the two zones are mixed much earlier than $t = 1$ yr, when the nucleation commences. Zone 2 is N-rich matter between $8.9 < m < 9.3$. It has consumed hydrogen and is therefore a part of the He shell, but is outside the convective shell where He has been fused into carbon. For our simplest calculation we take zones 1 and 2 to have mixed before the subsequent mixing with zone 3 and associated diamond growth occurs. Zone 3 is the bottom $0.38 M_{\odot}$ of the convective H envelope, which extends in its totality between $9.3 < m < 25$. We take the zone 3 mass to equal that of the mixed zones 1 + 2 on the grounds that its mass capable of being mixed should be comparable to the mass injected into it by the shock, which at their interface moves through the density gradient. This is not a physical requirement of mixing theory or of the basic model we are presenting. Rather it should be viewed as a plausibility allowing the calculation to proceed. Table 1 lists the total masses of key nuclear species for these three total zones. We then choose a simple numerical algorithm for the subsequent mixing of

zone 1 + 2 with zone 3. That mixing is envisioned as occurring more slowly than the turbulent instabilities that initiated it. That slower diffusive mixing produces a changing chemical composition for CVD growth of the diamonds, which require (no. 4) the hydrogen of zone 3 in contact with the nucleations of zone 1 (in this case the combined zone 1 + 2).

A key consequence of this description insofar as application to the observed meteoritic diamonds is concerned is the ^{13}C -richness and the ^{14}N -richness of the hydrogen envelope. The former explains why the diamonds are not, if they are indeed SUNOCONS, ^{12}C -rich, essentially eliminating that often heard objection to the idea. The second requires that SUNOCON diamonds be ^{14}N -rich, as they are found to be (Fig. 1), even if the N deposited by CVD were totally from the H envelope. Some mistakenly regard the H envelope as consisting of the initial material from which the massive star formed. But that is not the case. The initial hydrogen-burning core was much larger than it is finally at H exhaustion; therefore the He core has outside of it matter that has been made ^{14}N -rich isotopically as well as C-poor and N-rich. These features are central to the thesis of the paper.

To the above we must specify a model for the microscopic mixing of zone 3 into the zone 1 + 2 bearing the carbon-cluster nucleations. For this survey we treat this in a very simple way. At regular time intervals Δt a small mass Δm of zone 3 is switched with an equal mass of zone 1 + 2. Then the new composition of zone 1 + 2 is computed. The size of the time step is initially unspecified, but we later choose it to be 13.3 days in our reference calculation. The mass exchanged at each time step is also arbitrary, but we choose it to be $0.01 M_{\odot}$ in that reference calculation. Each composition asymptotically approaches the bulk composition of the summed zones. What this produces is a zone 1 + 2 composition that is increasingly enriched in hydrogen and ^{13}C , both of which are overwhelmingly in zone 3 initially. The H is required for CVD growth by postulate (no. 4). The particle becomes more ^{13}C -rich as it grows. This can result in diamonds that have a gradient in their isotopic composition, as was found in the data (Fig. 1). Figure 3 shows the relevant abundance ratios in the growth zone (1 + 2) as the mixing steps proceed. Once the time step Δt of the mixing is chosen, the time-step abscissa of Figure 3 can be expressed in supernova time since explosion, and the onset of nucleation (which we take as $t = 400$ days) identified. It is these trends of composition versus time that determine the gradient of isotopic composition within layered deposition as well as the variations of particle size with starting time for their growth. The last, variations in the starting time for the growth, will be shown to also produce correlations between particle size and mean isotopic composition. We prefer to show $^{13}\text{C}/^{12}\text{C}$ ratios in the figures although we use the inverse, $^{12}\text{C}/^{13}\text{C}$, in discussion because its solar value (89) is better known and is invariably used in discussion.

For our numerical computation of diamond size and com-

TABLE 1
MASSES AND BULK COMPOSITIONS OF THE MIXING ZONES

| Zone | Mass-range | Mass (M_{\odot}) | X_{H} | X_{C} | X_{N} | $^{12}\text{C}/^{13}\text{C}$ | $^{14}\text{N}/^{15}\text{N}$ |
|-------|-------------|----------------------|----------------|----------------------|--------------------|-------------------------------|-------------------------------|
| 1 | 8.885–8.955 | 0.070 | 0 | 0.057 | 5×10^{-6} | 1.5×10^6 | 1.78 |
| 2 | 8.955–9.26 | 0.305 | 0.088 | 5.3×10^{-4} | 0.014 | 5.44 | 3.02×10^4 |
| 1 + 2 | 8.885–9.26 | 0.375 | 0.071 | 0.011 | 0.011 | 167 | 1.44×10^4 |
| 3 | 9.26–9.64 | 0.38 | 0.587 | 0.0019 | 0.0048 | 21.5 | 2630 |

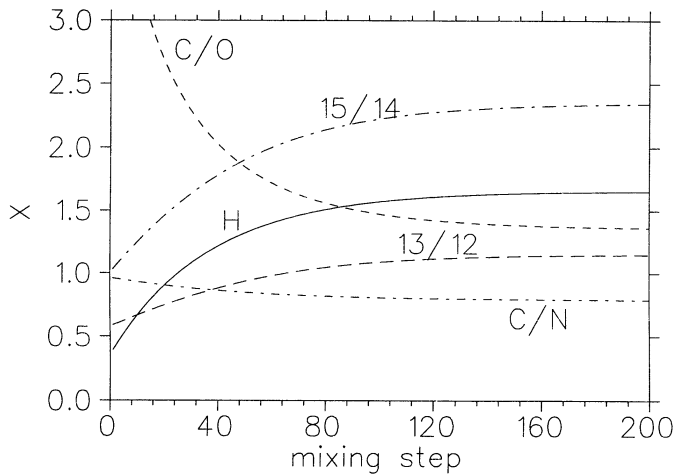


FIG. 3.—The composition of the continuously mixing “growth zone” where the diamonds are proposed to grow by CVD. During each mixing time step a mass $0.01 M_{\odot}$ from zone 3 is exchanged with an equal mass from the fully mixed zones 1 + 2. This causes H and ^{13}C to grow in the “diluted” zone 1 + 2, which is where the diamond seeds nucleate. The C/O abundance ratio declines only slightly during this mixing. The total masses and bulk compositions of these zones are in Table 1. For improved visual resolution these differing ordinate scales are used: C/O = atomic abundance ratio; $H = 5X_H$, the hydrogen mass fraction; $^{13}\text{C}/^{12}\text{C} = 89$ ($^{13}\text{C}/^{12}\text{C}$) so that the terrestrial ratio ($^{13}\text{C}/^{12}\text{C} = 1/89$) would plot at unity; $^{15}\text{N}/^{14}\text{N} = 50(^{15}\text{N}/^{14}\text{N})/(^{15}\text{N}/^{14}\text{N})_{\odot} = 50 \times 273(^{15}\text{N}/^{14}\text{N})$, so that the ordinate value 2 represents a $^{15}\text{N}/^{14}\text{N}$ ratio that is 1/25th of the terrestrial ratio (1/273). The C/N ratio is smaller than the solar ratio (3.23), and this N richness may contribute to the N richness of the diamonds, but their relative efficiencies for incorporation by CVD are not known. Our standard reference calculation for CVD growth starts that growth at mixing time step 30, which is also assumed to be at $t = 400$ days.

position we employ a standard reference choice of parameters. These correspond to setting time step 30 equal to 400 days after the explosion, when the ambient isotopic composition was $^{12}\text{C}/^{13}\text{C} = 108.7$. Integration of the growth equation gives a particle at 800 days of radius 1.25 nm having bulk composition $^{12}\text{C}/^{13}\text{C} = 92.68$. Further growth adds decreasing amounts of matter annually, with an asymptotic mass only 33% greater than at 800 days. By day 1600 $^{12}\text{C}/^{13}\text{C} = 91.7$ and the radius is 1.58 nm, which corresponds to a diameter only slightly greater than the observed median diameter 2.6 nm (Lewis et al. 1989). Figure 4 shows how three composition features of the diamonds so grown depend upon the choice of initial mixing time step; (bottom) the initial $^{13}\text{C}/^{12}\text{C}$ ratio at the time step, which is also equated to 400 days; (middle) the bulk isotopic ratio after the diamond has grown to 1600 days; (top) the surface isotopic ratio for the last matter deposited (at day 1600). This figure, along with the reasonable size of the resulting diamonds, constitutes our basic computational result.

4.3. Isotopic Gradient in Particle Structure

For simplicity we have taken the thermal nucleation of carbon clusters to occur at day 400, at which time we begin the CVD growth onto that nucleus. In that case the nuclei have the mean isotopic composition of the growth medium at day 400, which is also the composition of the first CVD carbon added. It is possible of course that the nucleations happen considerably earlier, when the growth zone was even more ^{12}C -rich, and somehow survive unchanged until CVD growth takes off as H is admixed. But that seems needlessly hypothetical for an initial survey, so we take the nucleations to have the same C

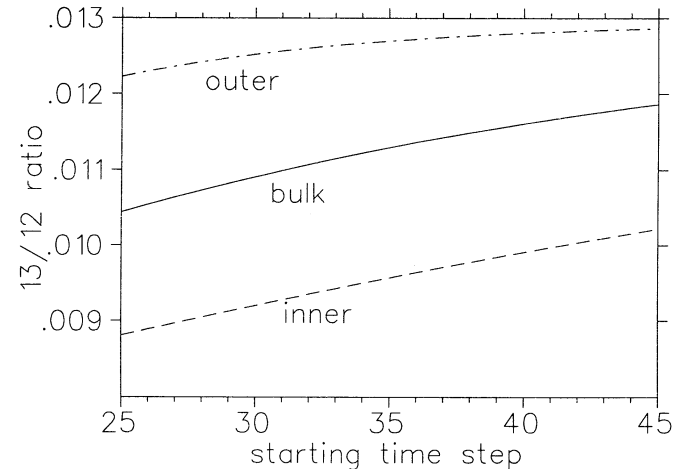


FIG. 4.—Diamond sections (vertical) as a function of the initial mixing step at day 400. CVD growth has occurred between day 400 and day 1600. The three curves (bottom, middle, top) show respectively the $^{13}\text{C}/^{12}\text{C}$ isotopic ratio for the first material added (near day 400) by CVD, the bulk of the entire diamond after growth continues until day 1600, and the last material added (near $t = 1600$ days). These are displayed as a function of the initial time step within our mixing algorithm (Fig. 3) when growth first begins; i.e., the initial time step equated to $t = 400$ days. The earlier in the mixing that 400 days falls, the more ^{12}C -rich are the diamonds (for all three measures displayed), because the ^{12}C richness of the growth zone is declining with time (Fig. 3). These diamonds all grow to the same final radius (1.58 nm) because they all have been taken to grow during the same density decline occurring between day 400 and day 1600. They are identical diamonds, but their composition depends on how advanced the mixing is when CVD begins, i.e., on the initial mixing time step as shown here.

isotopic composition as the first C deposited by CVD. Nor do we know the sizes of the thermal nuclei, although we tentatively suggested 10-C-atom adamantane above. Although the question of the nucleus is interesting, we will hereafter not include them, owing to their unknown numbers of C atoms, in our results to be displayed.

The CVD growth requires hydrogen (no. 4) and therefore also ^{13}C , which is enriched in the H-bearing matter overlying the He zone. Quantitatively the mixing relation is almost linear and would have the form

$$^{13}\text{C}/^{12}\text{C} = 1.2 \times 10^{-5} (H/^{12}\text{C}) \quad (3)$$

for the simplest binary mix, namely between zone 1 nucleations, where $H/C = 0$ and $^{13}\text{C}/^{12}\text{C} = 0$, and zone 3 where the hydrogen and the ^{13}C reside with the bulk ratio $H/C = 3700$ and $^{13}\text{C}/^{12}\text{C} = 1/21.5$ (see Table 1). Figure 3 displayed the relation in the growth zone more completely. The CVD adds a mix of ^{13}C and ^{12}C containing of order 1000 ^{12}C atoms total. The successive layers of CVD deposits are increasingly more ^{13}C -rich according to Figure 3 and to equation (2) above. This expectation assumes that carbon self-diffusion at particle temperatures of several hundred kelvins is too small to homogenize the particles. This makes the diamonds isotopically heavier on their outsides.

Chemical questions make it difficult to be as specific about nitrogen content. Because N is a trace element rather than the basic diamond constituent, its concentration in the diamonds depends upon how well it competes with carbon in the chemical cycles of deposition. We lack controlled experiments to guide the N deposition rate. Figure 3 and Table 1 show that the C/N element ratio in the mixing zone [(1 + 2) diluted by 3] is near unity and declines only slowly, i.e., there are no great

variations in the bulk chemistry of the medium. These ratios in the range $0.8 < C/N < 1$ are however several times smaller than solar, a fact that may help explain the high nitrogen content (about 1%) of the diamonds. But the actual ratio deposited must be determined by theoretical and experimental studies that are lacking to date. We therefore can only observe that if N is about 1% as efficient as C in getting deposited into the growing diamonds, the SUNOCON diamonds modeled here will have about the observed C/N ratio.

Another problem for the N content is that the $^{14}\text{N}/^{15}\text{N}$ ratio is everywhere larger than terrestrial by substantial factors. The ratio 1.44×10^4 in initially mixed zone (1 + 2) is 53 times greater than terrestrial; and the envelope zone 3 that dilutes it carries the ratio 2630, which is 9.7 times the terrestrial value (see Fig. 3). Therefore the diamond growth must of necessity inherit $^{14}\text{N}/^{15}\text{N}$ ratios much greater than terrestrial. The chondritic diamonds, on the other hand, are only some 50% greater than terrestrial. What this suggests is that the N content of the diamonds is not entirely from their SUNOCON component, or that chemical interactions subsequent to the ejection of the SUNOCONS are able to add isotopically more normal nitrogen. Evidence for the addition of some normal material is provided by noble gas data. There are at least three components of xenon in diamonds; exotic Xe-HL and two planetary components, P3 and P6, of roughly "normal" (i.e., solar system-like) isotopic composition (Huss & Lewis 1994a). P3 may be carried in separate diamond crystals, and P3 is thought to reside on the crystal surfaces. Similarly, the nitrogen may be interpreted as a mixture of exotic and normal material, with normal nitrogen located in separate diamonds from a different source and/or on the grain surfaces, added after the crystal formation. The first opportunity for surface addition must occur as the SUNOCONS, moving at about 1000 km s^{-1} , collide during their first Myr with many times their own mass in the process of slowing to random interstellar speeds. Some N may have been implanted then. It remains to be shown that the diamonds can survive this phase. Subsequent opportunities occur during the roughly 10^9 yr of mean interstellar lifetime for refractory dust, and finally in the warmer denser thermal environment of the solar accretion disk. Such considerations lie outside the scope of this paper, but they illustrate that the cosmic memory of SUNOCON diamonds will be very complex. Although the nitrogen contributions in diamonds are not fully understood at this time, what can be noted as very suggestive are two results of our simple modeling: (1) Because the $^{14}\text{N}/^{15}\text{N}$ ratio in the model is at least 10-fold terrestrial, the ^{14}N -richness of the chondritic diamonds does seem to point to a SUNOCON component within them; (2) The last N added to the SUNOCON is isotopically heavier than the first N deposited, which emulates the gradient seen in the stepped combustion (Fig. 1). The second point is no better than mildly suggestive, however, once we view the N content as a mixture of some kind between supernova N and normal N, for in that perspective the changing isotopic ratio measured during combustion can simply be attributed to a changing ratio in the mix of the two N components. Our purpose, however, is to describe the SUNOCON model clearly so that such subsequent considerations may be more accurately attempted.

Consider first the set of identical mean diamonds that emerges from our reference calculation (nominally 1.58 nm in radius for initial time step = 30) which is displayed in Figure 4. Their carbon isotopes vary from $^{13}\text{C}/^{12}\text{C} = 0.00920$ in the first layers deposited on the nucleus to 0.0125 for the last layer

deposited at $t = 1600$ days. The relation is almost linear and can be expressed as the gradients

$$d(^{13}\text{C}/^{12}\text{C})/dr = 0.0022 \text{ nm}^{-1}, \quad d(^{12}\text{C}/^{13}\text{C})/dr = -19 \text{ nm}^{-1}, \quad (4)$$

where r is the radial position within the diamond. The bulk composition of these identical diamonds is $^{13}\text{C}/^{12}\text{C} = 0.0109$ in the CVD layers (about 99% of the entire particle) and could be slightly smaller if a more ^{12}C -rich nucleus were included. The bulk ratios are satisfyingly close to the measured bulk composition ($^{12}\text{C}/^{13}\text{C} = 92.5$) to allow one to regard the entire collection of diamonds as being SUNOCONS as far as carbon isotopes are concerned. Furthermore, the gradient in equation (3) above is reasonably close to the gradient of the composition with stepped combustion (Fig. 1) to allow the possibility that the radial structure of the diamonds has recorded that gradient. This interpretation becomes more complicated and more interesting if the diamonds have a size spectrum, as observed by Lewis, Anders, & Draine (1989).

4.4. Growth Time Variations; Isotopic Composition versus Size

We cannot expect that all diamonds had equal time available for growth, because their nuclei will have formed at differing times. Nucleation is an equilibrium process between formation and disruption. A cluster may move up and down in size many times before it grows to the stable size for accommodating further growth. If nucleation and growth is taken to begin at 400 days, say, as we have done in our nominal calculation, we must admit the possibility of some beginning at 360 days, say, and some at 440 days. Because of the t^{-3} dependence of the density upon time, these starting time variations map into particle size variations. Because the carbon isotopic composition is changing with time, furthermore, the late nucleating particles will not only be smaller but also more ^{13}C -rich. Our nominal calculation gives these dependences between starting time, final size, the bulk isotopic composition:

$$\begin{aligned} t_i = 360 \text{ days}; \quad r_f = 2.02 \text{ nm}; \quad ^{12}\text{C}/^{13}\text{C} = 95.0, \\ t_i = 400 \text{ days}; \quad r_f = 1.58 \text{ nm}; \quad ^{12}\text{C}/^{13}\text{C} = 91.7, \\ t_i = 480 \text{ days}; \quad r_f = 1.02 \text{ nm}; \quad ^{12}\text{C}/^{13}\text{C} = 88.8. \end{aligned} \quad (5)$$

These sample results are in particle size entirely consistent with the analytic integral of ρ over time, because we model the CVD as linear in the ambient density, and the C and H mass fractions are only slowly changing after the early mixing epoch. Since $\rho \propto t^{-3}$, that integral scales the particle size in proportion to t_i^{-2} . The bulk isotopic composition depends, of course, on the model for mixing. What we have used is a mean composition, evolving with time as the zones mix more completely. Figure 5 displays both the bulk composition and the diamond size (*right-hand ordinate*) for different start times for growth within the standard nominal calculation (400 days = time step 30).

It will be evident from Figure 5 that the gradient during combustion (Fig. 1) may equally well derive from the spectrum of particle sizes. That physical idea gives a correlation of the observed direction and magnitude (eq. [5]). This does not imply that it is the correct idea, but it does save the SUNOCON picture embarrassment on that point.

Variations in local composition at each time may be more important than variations of starting time for the determination of particle size. We have not modeled such variations in

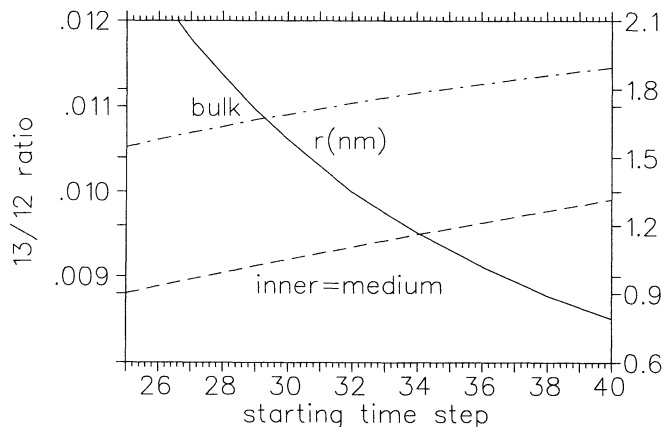


FIG. 5.—Differing starting times for CVD growth in the reference calculation. The bulk carbon isotope ratio (*upper curve*) and that within the first carbon deposited (*lower curve*) of diamonds that begin growth at differing times in the reference calculation (wherein step 30 = 400 days). Also shown as right-hand ordinate is the final particle size. Particles beginning their growth before day 400 grow to larger final size and are more ^{12}C -rich than those that begin growth at later times. This effect introduces a correlation between final diamond size and their isotopic composition. The smaller diamonds are more ^{13}C -rich. Because they should combust first, this sense is the correct one for the observed correlation (Fig. 1). However, the relative numbers of the diamonds of differing size are not obtainable from this calculation.

the degree of mixing. Our nominal model takes the CVD medium to have everywhere that mean composition shown as a function of time in Figure 3. The actual mixing, however, will have a complicated spectrum at each time. We therefore do not claim to have isolated the most important physical aspect of this process; to the contrary, we believe that a more realistic description of the mixing spectrum is the next improvement needed for this class of models.

A reason to suspect mixing fluctuations is the observed spectrum of particle sizes (Lewis et al. 1989). This lognormal distribution $dN/d\ln a$ has the largest number of small particles and decreases with particle radius as $\exp[-(\ln a/a_0)^2/2\sigma^2]$, with mean radius $a_0 = 1.3$ nm and $\sigma = 0.47$. This means that the number $dN/d\ln a$ falls by one power of e for each doubling of particle size, with observed radii ranging from 0.4 nm to 3.3 nm. A simple spread in starting times as described above does not seem promising, because to grow small particles would require more particles nucleating and beginning their growth late rather than early. That may or may not be expected physically. Two ideas may be very relevant to the problem of the size spectrum: (1) a spectrum of compositions at each time during the mixing may produce a spectrum of sizes; (2) the local depletion of free carbon by a large number density of nucleations will produce a large number of small particles. With respect to point (1), we remind the reader that our calculation has been simplified to that of a single time-dependent composition. The hierarchy of turbulent mixings followed by diffusion will naturally produce a rich spectrum of local compositions. Since both carbon mass fraction X_C and hydrogen mass fraction X_H enter into the growth rate (at fixed mass density), the actual kinetics may easily produce rather differently sized particles in the available time. The dependences on mass fractions are not likely to be linear in equation (2). With respect to point (2), we remind the reader that we have calculated the growth without carbon depletion, which is correct if only a small fraction of the C deposits in the diamonds (or other C-bearing solids). What we have calculated is the growth of a mean test particle. But if

there exist key zones for diamond growth that deplete all of the local carbon, a sudden burst of abundant nucleation must of necessity result in many small diamonds. This issue is entwined with the bulk supernova yield of diamonds, a point we return to at the end. We recommend future studies from both points of view.

5. CONCLUSIONS AND DISCUSSION

We have shown that scaling of the CVD process for kinetic growth of diamonds from the laboratory results to the supernova environment produces diamonds of nanometer size, comparable to the meteoritic diamonds. This allows, but does not require, those diamonds to be SUNOCONS.

We have shown that modeling of the process produces diamonds of almost solar carbon isotopic composition. This counters the allegation that the diamonds could not be SUNOCONS because SUNOCONS should be very abnormal isotopically (usually stated as being almost pure ^{12}C in conversation). Our results allow the SUNOCON interpretation.

We have shown that the isotopic ratio $^{13}\text{C}/^{12}\text{C}$ increases gradually from the centers of the diamonds to their surfaces if those diamonds are able to remember (without interior equilibration) the deposition sequence. We presented experimental data from stepped combustion that show such an isotopic gradient. The very smallness of the gradient, being only about 1%–2% is consistent with the small changes that our simple mixing model produced. However, such a small gradient could be some different physical effect.

We have shown that the $^{15}\text{N}/^{14}\text{N}$ also increases from particle center to surface in the deposition sequence. This also agrees with the sense shown in the particle data we have presented. However, the actual diamonds are only ^{14}N -rich by 50%, whereas the depositions from the model are very much richer in ^{14}N . So although the direction of ^{14}N richness is suggestive of some correctness to this picture, the absolute value is quite off. One way to save this picture then is to have the N-bearing SUNOCONS carry only a modest fraction (say 10%) of the total N in the diamond collections, with the other N being near solar isotopic composition. Extending the work begun by Verchovsky et al. (1994) may help resolve this problem.

One speculative possibility is that the actual diamond mix contains a ^{15}N -rich diamond. It could be from some other source (nova, say) or even from supernovae themselves! There does exist a very ^{15}N -rich region in the O-Ne shell, which is the source of origin of the Xe-L that must be implanted in the diamonds (Howard et al. 1992). That ^{15}N is created by neutrino interactions with oxygen during the core bounce neutrino transfer (Woosley et al. 1990). It may conceivably appear, by implantation or by CVD, along with the Xe-L in those diamonds that were exposed to the Xe-L. We do not expect all SUNOCON diamonds to have had identical histories, as outlined in the Introduction. For the present paper these issues appear undecidable without further experimental evidence. Suffice it to admit a problem with the nitrogen isotopic composition.

5.1. Negating the Postulates

Our calculation has sufficient success to establish the possibility of a SUNOCON paradigm for the interstellar diamonds. However, our calculation could not proceed without a large number of postulates (§ 3). It is therefore advisable to question

the consequences of these postulates being false. We do this for convenience by the same postulate numbers:

Postulate 1: If the diamonds are not grown by CVD, it becomes a problem in fundamental chemistry to create them at all. Why diamonds? Nuth (1987) has advanced arguments that diamond could be the ground state for sufficiently small particles, so that they could then be equilibrium condensates. But in that case one would indeed expect SUNOCONS to be very ^{12}C -rich because the He shell is the only C-rich zone within supernovae (Clayton 1981) and its C is pure ^{12}C .

Postulates 2, 3, 5: The nucleation seeds of CVD growth need not themselves be carbon, so that it may be too restrictive to take the nuclei to be carbon clusters. If the seeds are nucleated in the envelope where H exists, however, one faces two problems: (a) those clusters would be in an O-rich bath, which Howard et al. (1990) showed to make mainly hydrocarbons rather than diamonds and (b) the CVD growth of the diamonds would produce ^{13}C -rich diamonds rather than (slightly) ^{12}C -rich diamonds. The meteoritic evidence is that carbon-rich dust is very common, so it makes sense to suspect the very C-rich He shell for the nucleations. SUNOCON seeds may also nucleate within matter interior to the He shell, and in principle diamonds could grow on them. They have the added problems of being farther from the hydrogen than the matter atop the He-burning shell, however, and of being carbon deficient with respect to oxygen.

Postulates 4, 5: If the CVD growth of diamond does not require H for stabilization, the diamonds would certainly employ the more abundant interior carbon, which is ^{12}C . But experiments do not work without H, and theory (Frenklach 1989) accommodates that fact. The consequence is that the H is associated with ^{13}C -rich carbon, so that mixing with the ^{12}C -rich carbon produces normal isotopic composition in a very natural way.

Postulate 6: The CVD growth rate need not be linear in the mass density, so that the observation that the laboratory growth rate is 0.1% of the kinetic collision rate for carbon need not apply to the much smaller density in supernovae. This would even be expected to be the case if the molecular composition must be continuously regenerated while the CVD growth occurs, because the active hydrocarbon molecule for CVD growth (e.g., C_2H_2) could have a very nonlinear concentration dependence (see eq. [2]). On the other hand, it does not seem unreasonable during the second year of the expansion, when the CVD growth is occurring, to regard the molecular composition as already fixed. In that case a 0.1% efficiency with respect to the kinetic limit for the supernova interior seems a sensible assumption. Nevertheless, when the kinetic paths for CVD growth are established, the molecular kinetics feeding it will merit detailed modeling. Frenklach's (1989) discussion of this seems quite relevant to such a calculation.

Postulates 7, 8, 10: Observations show that supernovae do mix, and two-dimensional hydrodynamic calculations confirm that they should (Fryxell et al. 1991). Instabilities seem routine when a strong shock wave moves outward into a region of suddenly lower density. "Mushroom-cloud" contours of published studies confirm that (Fryxell et al. 1991). We suppose that similar interpenetrations afflict the interface of the C-rich portion with the overlying portion of the He shell, and also the interface between the He zone and the hydrogen envelope. These instabilities are the first steps of a mixing hierarchy that will eventually allow carbon clusters to come into molecular

contact with the H-envelope matter. A turbulent cascade begins, mixing fluid ribbons, but ends as molecular diffusion. Such hydrodynamics needs no defense by us; rather, it is our own mixing scheme, which is very simplified and which reduces the entire spectrum of mixing histories to one typical history that needs clarification. If carbon clusters cannot find themselves increasingly in molecular contact with the H envelope, our picture and calculation become irrelevant. Such contact is not a foregone conclusion, because the carbon clusters are so small as to be merely molecules themselves, and will not easily decouple from their fluid environment. So molecular diffusion is necessary, and the question is how finely the turbulence can intertwine the fluids before diffusion must take over. Diffusion through large masses is also not possible within a year. So we regard a treatment of the mixing as a future target of any improved understanding. If interdiffusion is not facilitated in a manner resembling that which we invoke, the CVD growth needing hydrogen will simply have to occur in the envelope matter alone. But there the ^{13}C is 4 times too abundant, and the Xe is roughly solar.

Postulates 9, 10: If the mixing does not occur, it is hard to imagine how Xe-L and Xe-H, which originate within the original He core, is to be implanted into the diamonds. Speeds comparable to ejecta speeds will cause disruptive sputtering to the diamonds, not implantation, which requires the modest speed of several km s^{-1} . The diamonds cannot grow within the Xe-L bearing gas, because thermal relative speeds are not high enough for implantation. So velocity mixing by initial turbulence seems required to produce the right relative velocities.

Postulate 11: Carbon clusters may transiently form much earlier than 1 yr, but we are assuming that growth of diamond upon them by CVD takes off after ~ 1 yr of expansion and cooling. Slightly different starting times simply grow particles of slightly different size, as we demonstrated in § 3.4. Because the absolute size could not be computed very accurately in the first place, our model is clearly not very sensitive to the exact start time for the CVD.

It seems unlikely that the simplicity of our approach could stand the test of time. Nonetheless, our assumptions and description of growth may serve as a useful paradigm for the chondritic diamonds—at least for their SUNOCON component. That so many calculated properties fall close to the properties of observed diamond collections suggests that the chondritic diamonds do have in bulk a SUNOCON component, and that that component may grow very much in the manner we have assumed.

One might consider the growth of diamonds in stellar winds by the same CVD process. Asymptotic giant branch (AGB) star winds might be appealing except for the big *s*-process enrichment of Xe isotopes in AGB stars, which rules out that source for the diamonds carrying the Xe-HL. Wolf-Rayet star winds, on the other hand, do not have sufficient time and density to grow diamonds at the rates used in this work. This may be seen as follows. A W-R star losing $10^{-5} M_{\odot} \text{ yr}^{-1}$ at 2000 km s^{-1} has a wind density after 1 day as small as the supernova interior density after 1 yr. Both are of order $10^{-14} \text{ g cm}^{-3}$; therefore the integral of carbon number density over subsequent expansion time is much smaller for the W-R star than for the supernova. Such considerations lead up to the conclusion the supernova interiors are the best places to grow diamonds at the relatively slow rate of the CVD process. It is therefore conceivable that all diamonds may be SUNOCONS.

Finally, we consider whether this model can account for the apparently high number density of diamonds required in the ISM. The reader will note that we regard the diamonds in the solar system as a systematic ingredient of the ISM, resulting from countless past supernovae, and not from a single supernova that occurred near the forming solar system. If we assume for simplicity that the roughly 1% ratio of diamond mass to C mass in meteorites also applies to the entire ISM, it will be necessary for the SUNOCON growth of diamonds to consume 3% of the supernova yield of carbon. This efficiency is demanded roughly by the equality of supernovae and AGB stars yields of "new carbon" and the return of a comparable mass of old carbon by the AGB stars. A 3% efficiency for diamond production in supernovae appears to be reasonable (once one has accepted the existence of diamonds as reasonable). The mixing zones selected in Table 1 contained roughly $0.004 M_{\odot}$ of carbon, which is about 1% of the total carbon mass to be ejected from a Type II supernova of $25 M_{\odot}$. If we have correctly identified the only portions of the much larger zones (He shell plus H envelope) that actually do mix, the equality of these numbers would seem to require the entire carbon mass of those portions to be deposited on diamonds.

That seems rather extreme, but we ameliorate it with three comments. As we mentioned earlier, the preponderance of small diamonds in the lognormal distribution could be reflecting the exhaustion of carbon in those mixing zones where CVD growth is occurring. If so, it suggests that C nucleation may lead to virtually all of it condensing in the diamond-growing zones. Second, there is a much larger mass of He shell and envelope available for mixing, so we see no reason to suggest that it be limited to the portions of those zones that were selected for Table 1 and the associated mixing calculation. Third, the meteoritic concentration of diamonds may be enhanced in comparison with the average ISM, as would occur if most of the gaseous forms of C, but not the diamonds, were lost in the aggregation of the meteorites. This expectation is suggested by the meteorites themselves, which have 10 times less C than Si, rather than the other way around.

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