# Condensation of Carbon in Radioactive Supernova Gas

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**Chemistry resulting in the formation of large carbon-bearing molecules and dust in the interior of an expanding supernova was explored, and the equations governing their abundances were solved numerically. Carbon dust condenses from initially gaseous carbon and oxygen atoms because energetic electrons produced by radioactivity in the supernova cause dissociation of the carbon monoxide molecules, which would otherwise form and limit the supply of carbon atoms. The resulting free carbon atoms enable carbon dust to grow faster by carbon association than the rate at which the dust can be destroyed by oxidation. The origin of presolar micrometer-sized carbon solids that are found in meteorites is thereby altered.**

Supernovae of type II are explosions of massive stars consisting of concentric shells of evolved nuclear compositions (*1*). High levels of $^{56}$Co radioactivity produced abundant amounts of energetic Compton electrons (*2*) and He$^{+}$ ions (*3*) within the expanding ejecta of type II supernova 1987A (SN 1987A) for several years. The chemically inert CO molecules that were formed by the radiative association of C atoms with O atoms can be destroyed through ionization and dissociation of the CO molecule by fast electrons and by charge-transfer collisions of He$^{+}$ ions with the CO molecules (*3*). Consequently, the total mass of CO molecules in SN 1987A was only $\sim 5 \times 10^{-3}$ times the mass of the sun at ~200 days after the explosion (Fig. 1) (*3*), whereas the total mass would have been two orders of magnitude greater in the absence of radioactivity. As a result, the C was made up of mostly free neutral atoms in the moderately ionized ejecta (*3*) of SN 1987A, which synthesized more of the O than the C (*1*). The atomic C vapor pressure was higher than expected under thermodynamic equilibrium at a temperature of ~1000 K (*3*). Such supersaturation occurred in other type II supernovae as well, enabling rapid condensation within them of C into solid dust, even in gases that have higher abundances of O than of C (*4*).

This possibility differs from conventional astronomical wisdom (embodied in the statistical equilibrium of slowly cooled gases containing C and O atoms), which states that the element of lesser abundance will be consumed in the tightly bound (11.09 eV) CO molecule, so that the chemistry of the remaining gas will be dominated by the more abundant element. This paradigm of equilibrium chemistry, which has worked well for envelopes of asymptotic giant branch stars (*5*), has been used (*6, 7*) to explain the origin of micrometer-sized graphite and SiC grains [found in meteorites (*8*)] that were formed in supernovae, as indicated by their distinct isotopic compositions (*7, 9–12*). However, with the CO trap deactivated, the compositions of dust formed in supernovae are dictated by kinetic chemistry rather than by equilibrium chemistry.

To investigate the growth of C dust in supernova ejecta, we explored the chemistry of large C clusters and integrated the coupled differential equations governing the molecular abundances to be expected in SN 1987A. We considered a gas containing equal numbers of C and O atoms, bathed in the expected fluxes of Compton electrons and x-rays, and expanding with time $t$ so that its density declines as $t^{-3}$. We included abundance equations for C clusters with up to $10^{12}$ C atoms to study the growth of micrometer-sized C grains. Molecules with 100 or less atoms were treated individually in the model, whereas clusters with $10^{m-1}$ – $10^{m}$ atoms ($3 \leq m \leq 12$) were grouped together and treated as a single species because it was not possible to include them individually in any numerical calculation.

Our chemical model contained many types of chemical reactions for large C molecules, some of which may play roles in interstellar chemistry (*13–16*). In the dense primarily neutral gas of the supernova ejecta, the C molecules grow successively by repeated radiative associations with C atoms

$$C + C_{n-1} \rightarrow C_n + h\nu \qquad (1)$$

where $n$ is an integer and $h\nu$ is the energy of the radiative quantum. Although reaction 1 is slow, with a typical value of the rate coefficient of $\sim 10^{-17}$ cm$^3$ s$^{-1}$ for small molecules such as $C_2$ (*17*) and $C_3$, its rate coefficient increases rapidly for larger molecules because their numerous vibrational modes absorb and distribute the collision energy so that it rarely accumulates in a dissociative channel (*18*). Reaction 1 may, however, be slowed (*19*) in the presence of competing exothermic reaction channels

$$C + C_{n-1} \rightarrow C_m + C_{n-m} \qquad (2)$$

unless energy barriers exist that are greater than the thermal energy of the molecules (*20*); $m$ is any integer less than $n$. For the linear C chains with their thermochemical properties and molecular states listed in (*14*), reaction 2 is exothermic for odd $n$ and may proceed rapidly. But for even $n$, reaction 2 is endothermic or involves a change in the total spin of the molecular system so that it may have a large energy barrier. Reaction 1 is slowed whenever reaction 2 is fast. Therefore, reaction 1 may proceed slowly for odd $n$ and rapidly for even $n$. We assumed rate coefficients of $10^{-13}$ cm$^3$ s$^{-1}$ for odd $n$ and $10^{-10}$ cm$^3$ s$^{-1}$ for even $n$ (Table 1).

Once synthesized, a linear C chain is removed by atomic C to form a larger molecule by reaction 1 or to produce smaller molecules by reaction 2 and by a reaction with atomic O

$$O + C_n \rightarrow CO + C_{n-1} \qquad (3)$$

Reaction 3 is slow for $n = 3$ because of, in part, the existence of an energy barrier of ~0.1 eV (*21*). It may be slow for other odd $n$ (*21*), with a typical rate coefficient of $10^{-13}$ cm$^3$ s$^{-1}$, but for even $n$, reaction 3 is probably rapid with a typical rate coefficient of $10^{-10}$ cm$^3$ s$^{-1}$ (*16*), approaching its collisional limit. The destruction of the CO molecule is dominated by energetic electrons (*3*) because the CO molecule is chemically inert. In contrast, molecules that are not chemically inert can be destroyed predominantly by chemical reactions rather than by energetic electrons.

The fractional abundances relative to that of atomic C of the linear C chains as a function of size $n$ (Fig. 2) were obtained by numerically integrating the chemical rate equations from 100 to 500 days after the

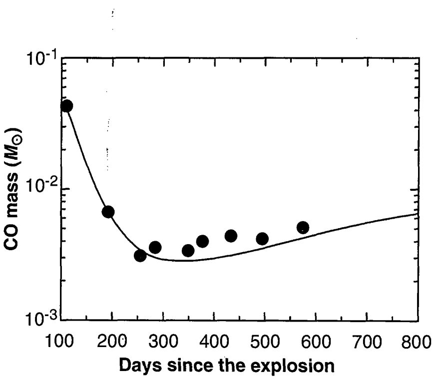

**Fig. 1.** Comparison of the masses of CO in SN 1987A, which were derived from spectral observations (circles) and predicted by chemistry (curve) from (*3*). $M_{\odot}$, mass of the sun.

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explosion of SN 1987A, just before the observations of dust formation at ~530 days (*22*). The fractional abundances did not change greatly with time because they became locked in to their steady-state values at 50 to 100 days and later were frozen out because of the slowing of the reactions as the gas became more diffuse but still dense enough to prevent photodissociation of the molecules. The fractional abundances decrease steeply from unity for C to $\sim 10^{-12}$ for $C_3$ because, for these small molecules, the radiative association time scales are very long (several months per molecule) in comparison with the oxidation time scales (1 s to 1 hour). The fractional abundances of the C molecules are lower than that of CO, which is $\sim 10^{-2}$ per C atom, because the destruction of small C molecules by atomic O is much faster (one per second to a few per hour) than the destruction of CO by energetic electron impact (one per day). As $n$ increases from 3 to 24, the abundances of the C molecules decline more slowly from $10^{-12}$ to $10^{-18}$ because the radiative associations are more effective for the larger molecules.

As the linear C chains become larger, they are isomerized to the more stable ringed molecules, which grow more rapidly than the linear molecules. The conversion to cyclic structures may occur at the stable monocyclic $C_{24}$ molecule (*15*). It may also occur at smaller molecules (*23*), allowing even more C dust grains to condense in supernovae than the number of grains predicted here. We assumed that the neutral reactions involving these ringed molecules were mostly associative and that, therefore, oxidation does not occur at a rate that is sufficient to provide a competitive destruction mechanism (*14*). If oxidation were more rapid than C association, the growth of large C clusters would be hindered and C would not condense in supernovae.

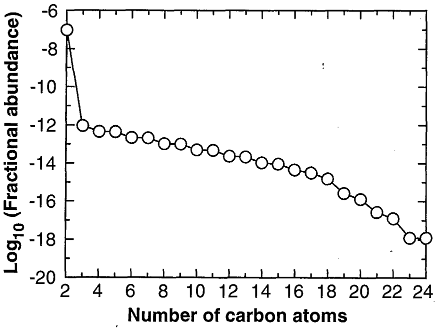

**Fig. 2.** The calculated fractional abundances of the linear C chains in relation to that of atomic C before the onset of dust condensation in SN 1987A.

For an associative rate coefficient $k_n(\mathrm{C}) = 10^{-10}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ for $n > 24$ and a C number density $\rho_t(\mathrm{C}) = 10^{10}(t/t_0)^{-3}\ \mathrm{cm}^{-3}$, where the starting time $t_0 = 2 \times 10^7$ s,

$$\frac{dn}{dt} = k_n(\mathrm{C})\rho_t(\mathrm{C}) = (1\ \mathrm{s}^{-1})(t/t_0)^{-3} \qquad (4)$$

Integrating Eq. 4 to infinity yields the limiting size for the maximum number of C atoms in a grain as

$$n(\max) = t_0(\mathrm{seconds})/2 = 10^7 \qquad (5)$$

For this model, the fractional abundance is constant to $n = 10^7$, beyond which it declines because of the limit on the C fluence. However, the calculated mass fraction summed over all the C clusters with $10^{m-1}$ to $10^m$ atoms increases as $n$ increases to $n = 10^8$ before declining (Fig. 3) because of the increasing molecular mass and the increasing number of C clusters that was included in the grouped clusters. This binned mass fraction can be converted to binned and unbinned number fractions by dividing by $n$ and $n^2$, respectively. A cluster with $n = 10^7$ has a diameter of 0.06 μm, which is ~2% of the size of the large supernova graphite particles, which contain at least $10^{12}$ atoms (*7*).

To achieve a cluster size in excess of 0.1 μm within the expansion time, $k_n(\mathrm{C})$ must grow with $n$, which may occur because of the larger surface area of the macroparticles (*24*). A growth model that assumes $k_n(\mathrm{C}) \propto n^{2/3}$ for $n > 24$ produced a larger population of the micrometer-sized dust particles (Fig. 3). It predicted that the greatest mass fraction resides in the largest graphite particles. This may account for the meteoritic observations that most of the supernova graphite particles seem to be large (0.8 to 20 μm), with mass fractions of the order of $10^{-5}$ (*7*, *9*). Even if all radiative associations (reaction 1) are 10 times slower than the assumed rate or if the C/O abundance ratio is reduced from unity to one-half, the largest C particles would only have been four orders of magnitude less abundant than those shown in Fig. 3. In the case of reduced radiative association rates, the ionic radiative associations may play a more important role in enhancing the growth of large C clusters.

**Table 1.** Rate coefficients of reactions of linear C chains $C_n$ ($n < 24$).

| Reaction | Reactants | Products | $k$ ($\mathrm{cm}^3\ \mathrm{s}^{-1}$) | $n$ | References |
|---|---|---|---|---|---|
| 1 | $C + C_{2n-1}$ | $C_{2n} + h\nu$ | $10^{-17}$ | 1 | *17* |
| | | | $10^{-10}$ | >1 | *13* |
| 1 | $C + C_{2n}$ | $C_{2n+1} + h\nu$ | $10^{-17}$ | 1 | Estimated |
| | | | $10^{-13}$ | >1 | Estimated |
| 2 | $C + C_{2n}$ | $C_m + C_{2n-m+1}$ | $10^{-10}$ | >1 | *13* |
| 3 | $O + C_{2n+1}$ | $CO + C_{2n}$ | $10^{-12}$ | 1 | *21* |
| | | | $10^{-13}$ | >1 | *21* |
| 3 | $O + C_{2n}$ | $CO + C_{2n-1}$ | $10^{-10}$ | | *16* |

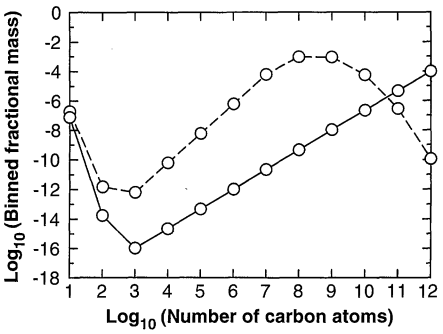

**Fig. 3.** The calculated fractional masses of the C clusters in relation to that of atomic C summed over those containing $n = 10^{m-1}$ to $n = 10^m$ C atoms for both the flat model (dashed line) and the growth model (solid line). The flat model assumes that the rate coefficient $k_n(\mathrm{C})$ is independent of $n$ for $n > 24$; the growth model assumes that it is proportional to $n^{2/3}$ for $n > 24$. The latter assumption reduces the abundance of $C_n$ for intermediate values of $n$ but increases it for the very large particles.

These models show that C dust can grow to sizes as large as a few micrometers within the expanding supernova interior, even if O is more abundant than C. With the CO trap deactivated by radioactivity in a supernova, the conventional distinctions between C/O > 1 and C/O < 1, which normally determine whether C or oxide grains condense, are no longer valid. Instead, the compositions of dust grains in supernovae are dictated by kinetic chemistry. The growth of C dust in supernovae is maintained by the association of dust with abundant free C atoms and is only moderated by oxidation. Carbon particles within O-rich gas may substantially alter the spectral evolution of supernovae and contribute to infrared emission and to cooling.

It has long been thought (*25*) that supernova C grains condense only within the C-rich gas expanded from the previous He-burning shell of supernovae. However, the C in that shell is almost isotopically pure $^{12}$C, whereas the supernova graphite particles contain substantial amounts of $^{13}$C (*9*). Striving to avoid O under the presumed requirement of thermochemical equilibrium, previous studies (*7*, *9*) interpreting the isotopic ratios measured in the supernova C particles have labored to mix external matter into this $^{12}$C-rich shell without increasing the O abundance to a value greater than that of C. The problem faced by this restriction is the set of isotopic ratios measured in these particles (*10*): The $^{28}$Si-rich Si and the radioactive $^{44}$Ti (*9*, *11*) are separated by a huge mass of O from the

$^{12}$C-rich shell, and the $^{13}$C that would ameliorate the $^{12}$C purity and the $^{15}$N excess that is common in supernova particles (*7*, *9*) both lie in O-rich gas. The large overabundance of daughter element $^{44}$Ca of 60-year radioactive $^{44}$Ti in some of these supernova particles (*9*, *10*) unequivocally demonstrates their supernova origin (*11*). Our results liberate the analysis from the problems caused by trying to avoid O-rich gas.

These same principles also enable oxides to grow within supernova gas having $C > O$. Possible evidence of such an oxide grain has been reported (*26*) in a corundum ($Al_2O_3$) grain from the Semarkona meteorite with a large excess of $^{18}$O. This large $^{18}$O excess exists in the He-burning shell of the supernova, which is also the only supernova shell that has $C > O$ (*1*, *25*), a composition that would otherwise be expected under thermochemical equilibrium to prevent condensation of an aluminum oxide solid by locking up the O in CO molecules. The radioactivity in supernovae maintains free $^{18}$O atoms in the C-rich shell. However, because the $^{18}$O excess in this grain is only of a factor of 3.2 (*26*) (so that its condensation requires admixture of a large amount of $^{16}$O), it cannot be concluded that condensation began in the He-burning shell—only that it utilized gas from that shell. Maintenance of free C and O atoms by radioactivity may enable C grains and oxide grains to condense from the same gas.

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# A Semiconductor-Based Photonic Memory Cell

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**Photonic signals were efficiently stored in a semiconductor-based memory cell. The incident photons were converted to electron-hole pairs that were locally stored in a quantum well that was laterally modulated by a field-effect tunable electrostatic superlattice. At large superlattice potential amplitudes, these pairs were stored for a time that was at least five orders of magnitude longer than their natural lifetime. At an arbitrarily chosen time, they were released in a short and intense flash of incoherent light, which was triggered by flattening the superlattice amplitude.**

Storing light for appreciable amounts of time is not an easy task because light is always propagating. In principle, light can only be stored directly by guiding its path in a loop back to the origin [for example, in a cavity in which a light beam is folded back and forth between two mirrors or a whispering gallery–type resonator (*1*)] or by guiding the light along a coil of optical fiber (*2*). However, to reach delay times of the order of $1\ \mu s$, one must use mirrors that lose very little light to obtain the necessary 300 reflections in a 1-m-long cavity, or equivalently, one must use 300 m of fiber to form the loop. Another recently realized approach to light storage uses Anderson localization (*3*); for this method, the light path is prolonged by passing it through a nonabsorbing but highly scattering medium. In addition to being bulky, these techniques in general do not allow for easily variable delay times.

For optical signal processing (*2*) and pattern recognition, however, one would like to store the photonic signals in an array of pixels that can be implemented on a chip. Analogous to an electronic memory where electrons are stored in a capacitor, each pixel could act as an optical memory for intermediate storage or delay of selected optical bits. Such memory cells are the most important part that is still missing from an optical network unit (*2*). Ideally, such a device would be a small container in which an incoming optical signal could be stored for an arbitrarily chosen time and then be released again as light. The switching speed should be of the order of 1 gigabit/s for local area network applications. Attempts to develop this device rely on a hybrid solution, in which a "smart pixel" (*4*) registers the light with a conventional detector, converting it to an electrical signal that is then stored in an electronic memory cell. At a given time, the signal can be reconverted to light by using, for example, a laser diode as an emitter. This approach, however, is a complex solution requiring many different techniques and components for a single pixel.

Here, we report the realization of a conceptually different, yet simple and potentially very efficient, storage cell for optical energy, which is based on a field-effect tunable lateral potential modulation in the plane of a semiconductor quantum well (QW). In such a cell, light energy can be locally accumulated and stored for many microseconds by convert-

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