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12. J. M. Wood *et al.* [*J. Am. Chem. Soc.* **113**, 5907 (1991)] have shown by mass spectrometry that species containing $C_{61}O$ to $C_{66}O$ occur in the crude extracts of fullerene preparation. These were not isolated nor characterized further.
13. Properties of the diphenyl fulleroids Ph_2C_{61} to $Ph_{12}C_{66}$. C_{60}: MW (molecular weight) 720; UV-vis [λ_{max} (absorption maximum), cyclohexane] 212, 257, 328, 404, 542, 598, and 620 nm. Ph_2C_{61}: MW 886.882; ^{1}H NMR (CS_2, $CDCl_3$) δ 8.02 (dd, J = 7.5, 1.2 Hz, 4H), 7.42 (t, J = 7.5 Hz, 4H), and 7.32 (t, J = 7.5 Hz, 2H); fast-atom-bombardment (FAB) MS weak 887, stronger 720 (C_{60}); infrared (IR) (KBr) 3020 (w), 1600 (w), 1510 (m), 1495 (m), 1450 (m), 1430 (m), 1385 (w), 1185 (m), 1160 (w), 1080 (w), 1030 (w), 1000 (w), 755 (sh), 740 (m), 700 (s), 575 (w), 550 (w), and 530 (s) cm^{-1}; and UV-vis (λ_{max}, cyclohexane) 212, 258, 326, 429, 495, and 695 nm. Analysis (Anal) for $C_{73}H_{10}$: calculated (calcd) C, 98.86, and H, 1.14; found C, 96.81, H, 1.27, and N, 0.00. Ph_4C_{62}: MW 1053.104; ^{1}H NMR (CD_2Cl_2) δ 8.4 to 6.8 (m, br, 20H); FAB MS 1055 to 1052 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1585 (sh), 1495 (m), 1450 (m), 1380 (w), 1185 (w), 1160 (w), 1080 (w), 1030 (w), 1005 (sh), 840 (w), 800 (w), 740 (m), 700 (s), and 520 (br) cm^{-1}; and UV-vis (λ_{max}, cyclohexane) 214, 263, 327, and 510 nm; Anal for $C_{86}H_{20}$: calcd, C, 98.09 and H, 1.91; found C, 95.38, H, 2.48, N, 0.00, and 1.4% of residue. Ph_6C_{63}: MW 1219.326; ^{1}H NMR (CD_2Cl_2) δ 8.4 to 6.8 (m, br, 30H); FAB MS 1220 to 1218 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1585 (sh), 1495 (m), 1450 (m), 1380 (w), 1330 (w), 1180 (w), 1155 (w), 1080 (w), 1030 (w), 1000 (w), 835 (w), 740 (m), 700 (s), and 530 (br) cm^{-1}; and UV-vis (λ_{max}, cyclohexane) 260 (sh) and 492 nm. Anal for $C_{99}H_{30}$: calcd C, 97.52 and H, 2.48; found C, 94.29, H, 2.59, N, 0.00, and 2.4% of residue. Ph_8C_{64}: MW 1385.548; ^{1}H NMR (CD_2Cl_2) δ; 8.4 to 6.8 (m, br, 40H); FAB MS 1386 to 1384 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1580 (sh), 1495 (m), 1450 (m), 1380 (w), 1320 (w), 1185 (w), 1160 (w), 1080 (w), 1030 (w), 1000 (sh), 740 (m), 700 (s), and 530 (br) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 270 (sh) and 485 nm (sh). Anal for $C_{112}H_{40}$: calcd C, 97.09 and H, 2.91; found C, 92.72, H, 3.26, and N, 0.00. $Ph_{10}C_{65}$: MW 1551.77; ^{1}H NMR (CD_2Cl_2) δ 8.4 to 6.8 (m, br, 50H); FAB MS 1553 to 1551 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1585 (sh), 1495 (m), 1450 (m), 1380 (w), 1320 (w), 1185 (w), 1160 (w), 1080 (w), 1030 (w), 1005 (w), 840 (w), 740 (m), 700 (s), and 535 (br) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 280 (sh) and 480 nm (sh). Anal for $C_{125}H_{50}$: calcd C, 96.75 and H, 3.25; found C, 94.97, H, 3.34, and N, 0.00. $Ph_{12}C_{66}$: MW 1717.992; ^{1}H NMR (CD_2Cl_2) δ 8.4 to 6.8 (m, br, 60H); ^{13}C NMR ($CDCl_3$) δ(all broad) 126.4, 127.4, 128.2, 129.1, 130.4, and 132.3 (all due to phenyl) and 140.0, 143.4, and 147.5 (fullerene); FAB MS 1718 to 1716 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1585 (sh), 1495 (m), 1450 (m), 1185 (w), 1160 (w), 1080 (w), 1030 (w), 1000 (w), 840 (w), 740 (m), 700 (s), and 530 (br) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 285 (sh) and 490 nm (sh); Anal for $C_{138}H_{60}$: calcd C, 96.48 and H, 3.52; found C, 96.08, H, 3.63, and N, 0.00.
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18. We thank the National Science Foundation for support through grants DMR-88-20933, DMR-91-11097, and CHE-89-08323, J. M. Hawkins for coordinates of the C_{60} osmylate, and E. Vogel for disclosing data in a personal communication.

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Evidence for Multiple Sources of Diamond from Primitive Chondrites

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Fine-grained diamonds, the most abundant form of circumstellar dust isolated from primitive meteorites, have elemental and isotopic characteristics that are dependent on the host meteorite type. Carbon isotopic compositions vary from −32 to −38 per mil, and nitrogen associated with the diamond changes in overall abundance by over a factor of four from 0.2 to 0.9 weight percent, between ordinary and CM2-type chondrites. Although the ratio of carbon to nitrogen evolves in a distinctive way during combustion of diamond separates, metamorphic degassing of nitrogen is not the main cause of the differences in nitrogen content. The data suggest that intrinsic differences must have been inherited by the diamonds at the time of their formation and that the diamonds were distributed heterogeneously in the solar nebula during condensation. However, the hypothesis that a distinct nitrogen carrier remains hidden within the diamond cannot be ruled out.

NANOMETER-SIZED DIAMONDS WERE first identified in acid-resistant residues from carbonaceous and enstatite chondrites by Lewis *et al.* in 1987 (*1*), and have since been isolated from all groups of primitive chondrites in amounts up to 940 ppm (*2, 3*). Although the diamond has a typical solar system–like carbon isotopic composition (*4, 5*), it has been recognized as a circumstellar grain from the anomalous isotopic signatures of the associated elements N (*6*) and Xe (*7*). Nitrogen is a more satisfactory tracer than Xe because it is normally substituted in the tetrahedral lattice of diamond and therefore must be cogenetic, whereas Xe is simply trapped. The amounts of Xe encountered are so small that only one diamond crystal in 3×10^6 actually contains a ^{132}Xe atom, whereas N is sufficiently abundant for each diamond to contain several atoms. To investigate the information that N can provide about the source and history of these putative circumstellar grains, we conducted a systematic study of diamonds from five separate classes of chondritic meteorites.

Diamonds were concentrated from each meteorite by acid treatments that destroy virtually all other forms of C in the meteorites, as described in (*8*). To avoid contamination from N in reagents used for the colloidal separation of diamond from spinels and silicon carbide, the ammonia suspension technique (*1, 3*) was not used. The extraction procedures that we adopted consisted of stepped combustion at very high resolution (temperature increments of 10°C); this procedure yielded release profiles showing that the N and C thought to be associated with diamond had been adequately resolved from other species (*9*). Most of the carbon isotopic values reported were obtained from diamond-rich samples in excess of 150 μg in mass and so could be measured with the use of a conventional dynamic mass spectrometer to a precision (±standard error) better than ±0.1 per mil (*10*). Nitrogen isotopic determinations on approximately 100-μg samples were made to a precision better than ±1 per mil with an instrument and method described in (*11*), so that nitrogen in the singly substituted state in diamond was converted to N_2 gas rather than condensable N-bearing species (*12*). Although the N abundance was measured absolutely, below we discuss primarily C/N ratios determined simultaneously on a single aliquot, because such an approach eliminates: (i) heterogenity problems involved in acquiring data for C from one aliquot and N from another; (ii) weighing errors on small specimens; and (iii) the difficulty of matching temperature scales.

The data (Fig. 1) show that the $\delta^{13}C$ values of diamond-rich fractions isolated

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from different meteorite groups are variable. The seven meteorites define three groups: (i) three CM2 samples (Cold Bokkeveld, Murchison, and ALH 83100,78) exhibited a similar and straightforward decline in $\delta^{13}C$ values to a minimum of −37.8, −38.2, and −38.8 per mil, respectively, as the diamond was lost; (ii) the CI specimen (Orgueil) reached the same nadir of −38.5 per mil but became isotopically light at a much earlier stage of the combustion; and (iii) replicates of the CV3 meteorite (Allende) were reminiscent of the trends for Orgueil but its $\delta^{13}C$ values are about 3 per mil heavier, whereas ordinary chondrites Inman (duplicated) and Tieschitz are almost identical to each other; none of this group shows $\delta^{13}C$ values lighter than −35 per mil, and the heaviest is Inman at −32 per mil. It has been proposed that the grain-size distribution of diamond is log normal (*13*); such a distribution suggests that the diamond grew in a single event and thus would not be expected to show differences in C isotopic composition with grain size and hence combustion temperature. A simplistic interpretation of that data is that there is some overlap in combustion between the diamond in the CV3 and ordinary chondrites and heavier C (graphite + silicon carbide) known to burn at higher temperature. However, this idea may be discounted because it is well established that type CM2 and CI1 meteorites are more prolific sources of ^{13}C-enriched high-temperature C (*14, 15*). We cannot dismiss the idea that the C isotopic profiles in Fig. 1 are the result of mixing between diamond and other components indigenous to the meteorites that have not been resolved by the chemical preparation procedure. However, one Allende sample was given a further treatment in $Cr_2O_7^{2-}$ and $HClO_4$ to check that all the amorphous C in the separate had been destroyed; analyses before and after showed that the C abundance did not change. If another C component is present it might be a different kind of diamond, or alternatively, Cλ (*16*), an isotopically light component of unknown stability in oxidizing acid, might have been partially released from spinel, its postulated host (*17*), in the treatments invoked.

We previously estimated the N content of diamonds in different meteorites by a variety of methods including (i) stepped combustion analysis of separate aliquots for C and N (*2, 6*); (ii) a pseudo-bulk procedure involving combustion in two steps followed by separation of the CO_2 and N_2 (*18*); and (iii) multiple-step combustion of a single sample with quantitation of both product gases at each stage. All these experiments showed that there was minor atmospheric contamination in the samples. The N abundance was then corrected for such a component with the assumption that mixing occurred between air at 0 per mil and indigenous N at an assumed value (−345 per mil). A compilation of all the data accumulated (Table 1) shows that the N concentration of diamond ranges from 2220 to 9220 ppm.

Because correction for the atmospheric contamination is model-dependent, we also considered the simultaneously acquired C and N data with no isotopic corrections. All the samples investigated showed a consistent pattern with heating in that the C/N rises steeply from low values (a N-rich component, $\delta^{15}N \approx 0$ per mil, that is presumably terrestrial atmospheric contamination) to a maximum then fell to an approximately level plateau. For diamonds from CI and CM2 chondrites the plateau was constant for 80% of the N released, whereas in diamond from Allende it was constant for less than 70% because the peak in the C/N ratio is considerably broader. If the N concentration in diamond is calculated on the basis of the plateau C/N ratio then the abundances given in Table 1 are obtained. These are generally higher (3770 to 12500 ppm) than abundances obtained by earlier methods, which included the C/N ratio peak in the early stages of the combustion.

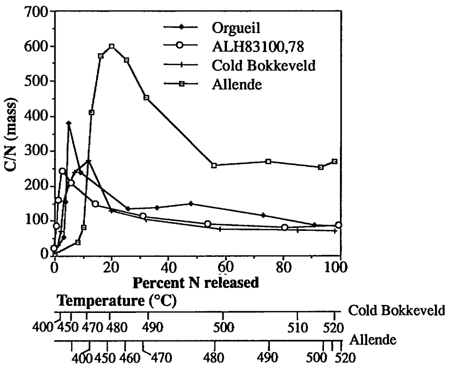

Fig. 2. Variation of C/N ratio as a function of the cumulative N released during the combustion of diamond samples from different meteorites over the temperature range 300° to 525°C. ALH 83100,78 and Orgueil approximate the Cold Bokkeveld scale. These temperature differences were reproducible and are not an artifact of the experiment, and so they also identify a difference between the diamonds from different meteorites.

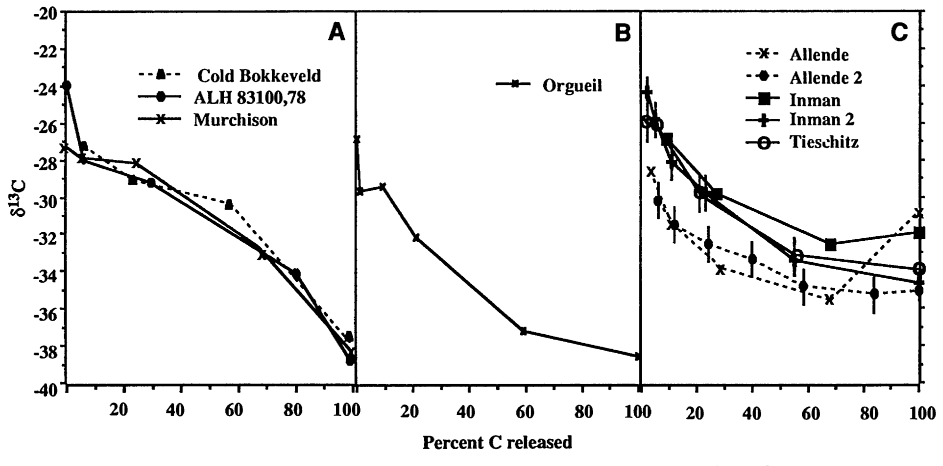

Fig. 1. Variation of C isotopic composition of CO_2 released during the combustion of diamond samples isolated from primitive chondrites of different classes; (**A**) CM2's, (**B**) Orgueil (CI1), and (**C**) Allende (CV3) and ordinary chondrites. The abscissa is the fraction of C released, which was controlled by increasing the temperature from 400° to 550°C. The standard error in isotopic measurement is ~0.1 per mil, except for Allende 2, Inman 2, and Tieschitz, which were analyzed using a less precise technique, with a standard error of 0.76 per mil (*14*). The final isotopic measurement in Allende 1 is thought to be affected by cocombustion of isotopically heavy graphite.

Although the N concentration showed a factor of 4 variation (6 if data from Tieschitz obtained by the two-component mixing model are considered), the N isotopic composition measured by a number of procedures remained relatively constant. For example, the mean value, without any corrections made, for the minimum $\delta^{15}N$ value seen in 21 experiments involving eight individual meteorites was −343 ± 16 per mil (1σ errors). Diamonds from Cold Bokkeveld and Allende have the same minimum $\delta^{15}N$ value even though they represent opposite ends of the concentration spectrum. However, as can be seen in Fig. 3, the isotopic composition of the N liberated by stepped combustion of the Allende residue (if atmospheric contamination is considered the same for both meteorites) is heavier than that released by diamonds from Cold Bokkeveld at the same stage of the extraction. The higher $\delta^{15}N$ value in the early stages of the combustion could be interpreted as isotopic fractionation and preferential loss, by degassing, of ^{14}N-enriched molecular N, possibly as a result of a metamorphic overprint.

Table 1. N concentration in diamond (in parts per million, by mass). Results from the two-component mixing model are mean values from "*n*" experiments (numbers in parentheses) on the same residue (1σ errors) for both multi- and two-step combustion. Concentrations from plateau values are calculated from the mean C/N ratio over the plateau region.

Meteorite (type)	From two-component mixing model	Plateau C/N ratio	Concentrations from C/N plateau values (ppm)
Orgueil (CI)	7560 ± 450 (2)	141 ± 5	7090 ± 240
Cold Bokkeveld (CM2)	8350 ± 1290 (5)	81 ± 14	12500 ± 2000
Murchison (CM2)	8190 ± 2090 (4)		
ALH 83100 (CM2)	9220 ± 1030 (2)	92 ± 10	11000 ± 1300
Allende (CV3)	3020 ± 1070 (11)	265 ± 11	3770 ± 150
Inman (L/LL3.4)	3000 ± 820 (3)		
Tieschitz (:/H.3.6)	2200 ± 510 (3)		
Indarch (EH4)	4210 ± 560 (2)		

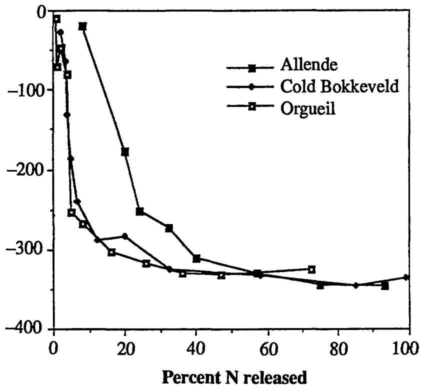

Fig. 3. Isotopic compositions of N as function of N released during combustion of diamond samples. The error in the $\delta^{15}N$ value is smaller than the size of the data points. The final measurement for Orgueil was lost.

The data confirm earlier suspicions (*2, 12, 18*) that the nanometer-sized diamonds extracted from chondritic meteorites are distinguishable. The isotopic composition of C, the fundamental element of diamond, and the concentration of N, the most significant associated anomalous element, are variable among different meteorite classes. This variability might have been expected, because other interstellar materials (SiC and graphite), which can be studied at the individual grain level by ion microprobe (*19*), are derived from multiple sources. However, Xe data suggested that nanometer-sized diamonds were either of a common composition or too well mixed to allow resolution of different populations. Huss (*3*), for example, suggested that fine-grained diamond has such a remarkably uniform Xe(HL) content [^{132}Xe content ± SE estimated at 25 × 10^{-8} ± 3 × 10^{-8} cm^3 g^{-1} (*20*)] and isotopic composition ^{124}Xe/^{132}Xe and ^{136}Xe/^{132}Xe ratios of 0.00774 ± 0.00008 and 0.642 ± 0.007, respectively) that these values can be used to calculate the abundance of diamond in a given meteorite, from the analysis of minimally processed acid residues (*21*). Schelhaas *et al.* (*22*) have shown that the relative abundance of Xe(H) to Xe(L) is constant for ordinary chondrites and that this fixed value is indistinguishable from the same measurement made for Allende. It is clearly important to resolve the conflict between the C/N and Xe stories, and we consider first the possibility that a metamorphic effect might be responsible.

At face value, N abundance seems to be higher in lower petrologic-type meteorites. This relation suggests that degassing has taken place in the higher petrological types. It would be extremely difficult, however, to conceive of circumstances in which the nitrogen concentration could vary metamorphically by a factor of up to six (from Tieschitz to Cold Bokkeveld) without affecting the Xe concentration or, more likely, its isotopic composition and abundance relative to Ne.

Huss (*3*) suggested that diamond is destroyed rather than degassed in meteorite parent bodies during metamorphism to account for an apparent relation between petrologic grade and diamond abundance without change in Xe(HL) concentration, Xe isotope systematics, and the Xe/Ne ratio. The C isotope differences for the samples we studied are in the right sense to provide evidence of partial loss in that petrologic type 3 samples are enriched in ^{13}C compared to type 1 or 2. However, the diamond population would need to consist of a mix of ^{12}C-rich grains together with their ^{13}C-rich counterparts so that it was the former that were being preferentially destroyed to give the measured ratios. Such a mix could account for why diamond, an interstellar material, has a remarkably solar system–like δ^{13}C value.

The best evidence for N loss by degassing is the shift in δ^{15}N values and the increased C/N ratio of the first 30% of the gas liberated by Allende diamonds compared to diamonds from Orgueil and Cold Bokkeveld (see Figs. 2 and 3). However, modeling of the C/N ratios during combustion suggests that although degassing has taken place, it is not the major cause of N concentration differences. The CI1 and CM2s appear have lost 5 to 10% of their N by degassing and the CV3 Allende 20%; an effect superimposed on an initial N concentration difference of a factor of 3 (*23*).

Because metamorphism does not readily account for the observations, the differences in C and N are most likely primordial in origin. If Xe(HL) can be shown to be as constant for the CM2 and CI1 meteorites as it is for the higher petrologic types, then a logical conclusion would be that the diamonds acquired their Xe after the more fundamental characteristics involving C and N were fixed. This process would require that the implantation of noble gas constituents took place at a time when diamonds of different C isotopic composition and N abundance were already mixed. Clayton (*24*) envisaged that Xe(H) and Xe(L) were produced in the He and Ne burning shells of a type II supernova and bathed the C that had solidified from the He level in the isotopically anomalous gas. We have no information about how such an environment would produce diamonds of variable C to N ratio, unless the He level was stratified.

A particular difficulty of Clayton's model is the solar system–like δ^{13}C values of the diamond. Only one diamond crystal in about 3 million carries a ^{132}Xe atom; with this minimal compliment of noble gas there may be a tiny subpopulation of Xe-bearing diamond from a highly specific stellar source admixed into copious Xe-free mineral, which may itself be from a mixture of sources, not all necessarily presolar, and these diamonds may have been heterogeneously distributed in the solar nebula. Under such circumstances it becomes difficult to account for the consistency of N isotopic values. Perhaps the simplest explanation is that the N is not carried in the diamond at all but inhabits a mineral yet to be discovered—possibly a nitride or even a carbon nitride (*25*). Although our attempts to decouple C and N in diamond from primitive meteorites by chemical and physical methods have so far been to no avail, such an idea would make concentrations of up to 1.25 weight percent N (at least a factor of three higher than that of terrestrial diamonds) easier to accept.

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9. Stepped combustion of diamonds separated with the use of the ammonia technique of (*1*) give identical C release profiles, over the appropriate temperature range, to residues for which the separation was not performed; these data demonstrate the efficacy of our method.
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$$\delta^{13}C = \frac{(^{13}C/^{12}C)\text{sample} - (^{13}C/^{12}C)\text{std}}{(^{13}C/^{12}C)\text{std}} \times 1000$$

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Reduced Antarctic Ozone Depletions in a Model with Hydrocarbon Injections

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Motivated by increased losses of Antarctic stratospheric ozone and by improved understanding of the mechanism, a concept is suggested for action to arrest this ozone loss: injecting the alkanes ethane or propane (E or P) into the Antarctic stratosphere. A numerical model of chemical processes was used to explore the concept. The model results suggest that annual injections of about 50,000 tons of E or P could suppress ozone loss, but there are some scenarios where smaller E or P injections could increase ozone depletion. Further, key uncertainties must be resolved, including initial concentrations of nitrogen-oxide species in austral spring, and several poorly defined physical and chemical processes must be quantified. There would also be major difficulties in delivering and distributing the needed alkanes.

LARGE LOSSES OF ATMOSPHERIC ozone are occurring over Antarctica each austral spring (*1, 2*). Ozone losses have also been observed (*3*) at middle and higher latitudes in both hemispheres for the period 1979 to 1990. South of 60°S the ozone loss rate was more than 0.5% per year; a reasonable interpretation is that mixing of ozone-poor air from the Antarctic stratosphere is causing this wider impact (*3*). Episodes of reduced ozone have also been observed over Australia and New Zealand (*4*). There are also indications that the size and severity of the Antarctic ozone hole could increase (*5*) and that the hole will form each year for the next 100 years even if CFC releases are controlled (*6*).

The threat of expanded future impacts of the Antarctic ozone hole leads one to search for measures that could prevent them. Here we explore a concept for mitigating ozone-hole formation. It is based on recent gains in scientific understanding of the processes responsible for ozone loss in the polar winter stratosphere, including increased knowledge of polar stratospheric clouds [PSCs (*7*)].

We explore whether injections of certain hydrocarbons into the lower stratosphere during an optimal time period each year could prevent ozone-destroying reactions in the austral spring. The annual sequence of physical and chemical events that occur during the formation of the ozone hole includes a several week period during which stratospheric Cl atoms are activated for ozone attack. Our idea is to immobilize this active chlorine through the rapid reaction of Cl atoms with simple alkanes like propane, as in

$$Cl + C_3H_8 \rightarrow HCl + C_3H_7 \qquad (1)$$

Because the concentrations of active chlorine are as large as 2 parts per billion (ppb by volume) of the local atmosphere during the period of ozone destruction, we expect that it would be necessary to raise the concentration of propane (or ethane) artificially to at least 2 ppb. In this report we test this idea with a model of Antarctic ozone-layer chemistry. Before presenting results of the model calculations we must describe the processes that we are simulating.

The formation of PSCs is now known to be essential to the formation of the ozone hole over Antarctica (*7*). PSCs cause dehydration and denitrification of polar air and activate inert chlorine species (HCl and $ClONO_2$) into photolytically unstable chlorine species (Cl_2, $ClNO_2$, and HOCl) that are transformed by sunlight into ozone-reactive species (Cl and ClO). The morphological properties of polar stratospheric clouds are well-defined by satellite observations (*8*) and by optical and physical evidence; there are two broad categories. Type I PSCs consist of an aerosol haze of micrometer-sized nitric acid ice particles composed of HNO_3 and H_2O in roughly a molar ratio of 1:3, respectively (*9*). Type II PSCs are composed of larger (>10 μm) water-ice crystals.

Type I PSCs begin to form at temperatures near 195 K, generally late in the austral fall, when the southern polar vortex has formed and cooling within the vortex has occurred in the absence of strong solar or longwave heating. These PSCs continue to form well into the austral spring. Type II PSCs condense at lower temperatures (≤187 K), at the frost point of water vapor in the polar stratosphere. Type II clouds therefore appear later in the winter season and dissipate earlier in the spring than type I clouds. Type I haze dominates during the early part of the Antarctic winter season, but the proportion of type II clouds increases as cooling progresses. Type II particles cause dehydration, and both type I and type II clouds appear to cause denitrification of the polar vortex. Chlorine activation seems to

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