# Detection of Abundant Ethane and Methane, Along with Carbon Monoxide and Water, in Comet C/1996 B2 Hyakutake: Evidence for Interstellar Origin

Michael J. Mumma,* Michael A. DiSanti, Neil Dello Russo,
Marina Fomenkova, Karen Magee-Sauer, Charles D. Kaminski,
David X. Xie

The saturated hydrocarbons ethane ($C_2H_6$) and methane ($CH_4$) along with carbon monoxide (CO) and water ($H_2O$) were detected in comet C/1996 B2 Hyakutake with the use of high-resolution infrared spectroscopy at the NASA Infrared Telescope Facility on Mauna Kea, Hawaii. The inferred production rates of molecular gases from the icy, cometary nucleus (in molecules per second) are $6.4 \times 10^{26}$ for $C_2H_6$, $1.2 \times 10^{27}$ for $CH_4$, $9.8 \times 10^{27}$ for CO, and $1.7 \times 10^{29}$ for $H_2O$. An abundance of $C_2H_6$ comparable to that of $CH_4$ implies that ices in C/1996 B2 Hyakutake did not originate in a thermochemically equilibrated region of the solar nebula. The abundances are consistent with a kinetically controlled production process, but production of $C_2H_6$ by gas-phase ion molecule reactions in the natal cloud core is energetically forbidden. The high $C_2H_6/CH_4$ ratio is consistent with production of $C_2H_6$ in icy grain mantles in the natal cloud, either by photolysis of $CH_4$-rich ice or by hydrogen-addition reactions to acetylene condensed from the gas phase.

Cometary nuclei are the least modified solar system bodies remaining from the time of planetary formation. Their current compositions are thought to be representative of the materials from which they formed (*1*). The cometary nucleus is a solid body consisting of ices commingled with dust grains, and its detailed physical structure is a consequence of the accumulation process. The ices are most sensitive to thermal modification; indeed, they sublimate when warmed to even modest temperatures [~190 K for $H_2O$, but much lower (<100 K) for $C_2H_6$, $CH_4$, and CO]. The escaping vapors and entrained dust form the cometary coma, where the vapors eventually are destroyed mainly by photodissociation and photoionization by sunlight. Before complete destruction, these vapors can be identified in the coma by spectroscopic methods, and their abundances can be related to the production rates from the native ices (parent volatiles) in the nucleus. The native ices are thought to have originated either in the interstellar dense cloud core that preceded the solar system or at distances beyond Jupiter in the nebula surrounding the protosun. The ices trace chemical and physical conditions in the natal regions, and their identities and abundances are therefore key to understanding planetary and cometary formation. Because cometary impacts deliver volatiles to Earth and other planets even today—a recent example is the impact of comet Shoemaker-Levy 9 on Jupiter—cometary composition is also relevant to topics as diverse as the origin of Earth's oceans, the origin of organics, the origin of life, and the punctuated extinction of species. For these reasons, a central problem is the nature and composition of the cometary nucleus.

In recent years, it has become possible to detect some cometary parent volatiles remotely by infrared (IR) and submillimeter-wavelength spectroscopy. Examples include the detection of $H_2O$ (*2*), hydrogen cyanide (*3*), and formaldehyde ($H_2CO$) (*4*) in periodic comet 1P/Halley (Halley) and methyl alcohol ($CH_3OH$) (*5, 6*), hydrogen sulfide (*6*), and CO in comet Austin 1990 V (*7*). Since then, a new generation of highly sensitive cryogenic IR instruments, based on large format monolithic arrays of detectors, has become available. We observed comet C/1996 B2 Hyakutake (Hyakutake) with one of these advanced IR spectrometers.

We initially targeted $CH_3OH$, $CH_4$, and CO for our investigation, for reasons related to theories of the origin of cometary ices and to previous detections (*1*). These theories can be divided into two groups, according to the place of origin of the ices. In the interstellar origin models, ices form on grain surfaces in the natal cloud core and are carried into cometesimals without significant chemical modification. In the solar nebula models, the ices first vaporize in the nebula and later recondense onto grains that are then carried into cometesimals. The gases may be chemically modified while in the nebula (*8*), and if so, comets made in this way would have a composition different from those made from interstellar ice. Observations showed that the abundance of $CH_3OH$ relative to $H_2O$ in most comets is ~4 to 5%, consistent with that measured in icy grain mantles in dense interstellar cloud cores (*1, 5*). This agreement supports the view that many comets contain interstellar ices from the natal cloud core (*1*). However, the $CH_3OH$ abundances in two comets were lower, Levy 1990 XX at

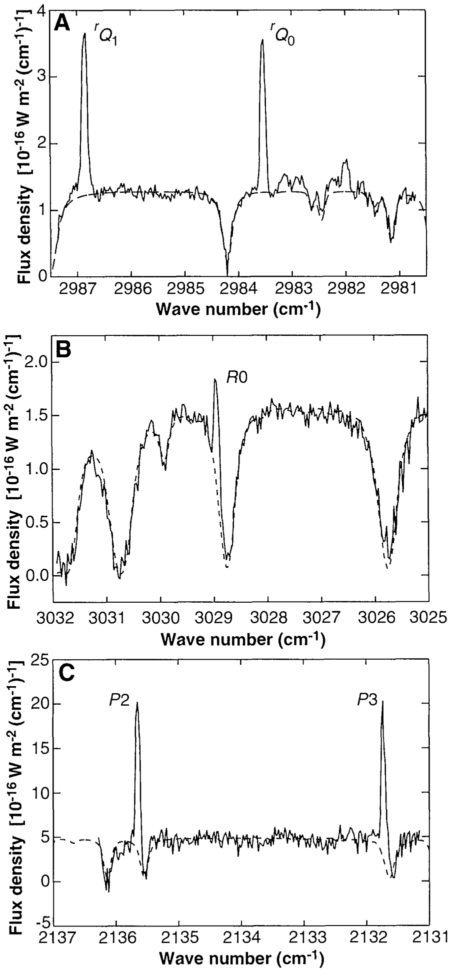

**Fig. 1.** Flux calibrated spectra of Hyakutake (solid lines), as observed through the terrestrial atmosphere. (**A**) The $^rQ_0$ and $^rQ_1$ branches of the $C_2H_6$ $\nu_7$ band. (**B**) The *R*0 line of the $CH_4$ $\nu_3$ band. (**C**) The *P*2 and *P*3 lines of the CO 1-0 vibrational band. Synthetic spectra of atmospheric transmittance for conditions appropriate to Mauna Kea are also shown (dashed lines). The telluric lines are seen in absorption against the cometary continuum, and their cometary counterparts are Doppler shifted to higher frequencies by the comet's motion relative to the observer.

M. J. Mumma, N. Dello Russo, D. X. Xie, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA.
M. A. DiSanti, NASA Goddard Space Flight Center and Department of Physics, Catholic University of America, Washington, DC 20064, USA.
M. Fomenkova, Center for Astrophysics and Space Sciences, University of California, La Jolla, CA 92093-0111, USA.
K. Magee-Sauer, Department of Chemistry and Physics, Rowan College of New Jersey, Glassboro, NJ 08028, USA.
C. D. Kaminski, NASA Infrared Telescope Facility, Hilo, HI 96720, USA.

---

*To whom correspondence should be addressed. E-mail: mmumma@lepvax.gsfc.nasa.gov

~0.5% and Halley at ~1.5%, suggesting that ices in those comets may have experienced a different origin and evolution.

We detected IR emission from $C_2H_6$, $CH_4$, CO, and $H_2O$ in Hyakutake, using the CSHELL cryogenic grating spectrometer (*9*) at the NASA Infrared Telescope Facility on Mauna Kea (*10, 11*). Emission lines of these molecules were measured to distances of ±1000 km from the center of the nucleus, with ~30-km resolution. The emission lines were strongly peaked at the nucleus, as expected for parent volatiles released from the nucleus. CO also showed evidence for a distributed source. The most surprising of these detections was that of $C_2H_6$, which has not been detected in the interstellar medium or comets but was found in Hyakutake with an abundance comparable to that of $CH_4$.

Ethane cannot be detected at ultraviolet (UV) wavelengths because its higher electronic states are predissociated; hence, they do not fluoresce (*12*). It cannot be detected at radio wavelengths because it is homopolar and has no allowed rotational transitions. Ethane has strong IR vibrational transitions [$\nu_7$ near 3.35 μm, $\nu_5$ near 3.43 μm, $\nu_8$ near 6.79 μm, $\nu_6$ near 7.25 μm, and $\nu_9$ near 12.2 μm (*13, 14*)], and these could permit its detection under favorable circumstances.

The ${}^{r}Q_0$ (2983.4 $cm^{-1}$) and ${}^{r}Q_1$ (2986.8 $cm^{-1}$) branches of the $C_2H_6$ $\nu_7$ band were serendipitously detected on universal time (UT) 24.5 March (Fig. 1A), during a search for emission in the $\nu_2$ and $\nu_9$ bands of $CH_3OH$. Inspection of an atmospheric spectral atlas (*15*) revealed weak features at the rest frequencies of the Doppler-shifted cometary emissions, and a search of a molecular line listing (*16*) suggested that $C_2H_6$ was a likely candidate for the cometary emitter. A laboratory spectrum of $C_2H_6$ at 130 K was taken in response to this discovery (Fig. 2), and we then searched for two other branches on the basis of measured laboratory line positions and intensities (*17*). We detected the ${}^{r}Q_4$ (2996.8 $cm^{-1}$) and ${}^{r}Q_5$ (3000.3 $cm^{-1}$) branches in Hyakutake on UT 2.0 April. All four Q branches were found in emission from the comet at the correct Doppler-shifted frequencies, confirming the identification of $C_2H_6$.

The dominant excitation mechanism for IR vibrational emission from cometary parent volatiles is solar IR fluorescence (*18, 19*). If only a few individual lines are measured, it is necessary to know or to invoke the rotational distribution and the fluorescence efficiency in order to infer the total population of the molecular species from the observed lines. Ethane is a symmetric top molecule and $\nu_7$ is a perpendicular band, consisting of a series of ${}^{r}Q_K$ branches (with $\Delta K = +1$), a series of ${}^{p}Q_K$ branches (with $\Delta K = -1$), and *P* and *R* branches for each ($K_l \Delta K = \pm 1$) (*13*). The upper level for ${}^{r}Q_0$ has $K = 1$; hence, it can be pumped from $C_2H_6$ molecules in the $K = 0$ and $K = 2$ ladders of the ground vibrational level, whereas the upper level for the ${}^{r}Q_1$ transition has $K = 2$ and can be pumped from molecules in ladders with $K = 1$ and $K = 3$. The total pump rate into an upper level $K_u$ thus responds to the sum of the populations in the ground vibrational levels with $K_l = K_u \pm 1$.

The measured strength of the $C_2H_6$ $\nu_7$ band is $12.31 \times 10^6$ cm $mol^{-1}$ (or 538 $cm^{-2}$ $atm^{-1}$), in agreement with ab initio intensity calculations (*14*). The fluorescence efficiency for the entire band derived from this strength is $4.3 \times 10^{-23}$ W $molecule^{-1}$. A simplified analysis of the fluorescence pumping efficiency can be given as follows. For $K_l \neq 0$, the pump is equally divided between transitions with $\Delta K = +1$ and those with $\Delta K = -1$; hence, the pump for $K_u = 2$ is $(2.15 \times 10^{-23}$ W $molecule^{-1})(n_1 + n_3)$, where $n_1$ and $n_3$ are the populations in $K = 1$ and $K = 3$ of the ground vibrational level. For $K_l = 0$, only $\Delta K = +1$ is possible, so the total pump out of that level is half as large, but it all goes into only one upper level, so again the pump for $K_u = 1$ is $(2.15 \times 10^{-23}$ W $molecule^{-1})(n_0 + n_2)$. The downward branching ratios follow the standard expression for *P*, *Q*, and *R* branches, except that two sets are permitted ($\Delta K = \pm 1$). Hence, each ${}^{r}Q_K$ branch in emission takes one-quarter of the total pump fluorescence efficiency from the sum of molecules with $K_l = K_u \pm 1$. The fluorescence efficiency $g_1$ is then $5.4 \times 10^{-24}$ W $molecule^{-1}$, for each Q branch.

From the ${}^{r}Q_0$ branch, we derived the $C_2H_6$ production rate (*20*) for the sum of the $K = 0$ and $K = 2$ ladders, and the production rate for the sum of the $K = 1$ and $K = 3$ ladders was obtained from the ${}^{r}Q_1$ branch (Table 1). The summed production rate for $C_2H_6$ in the ladders $K = 0$ to 3 is then $6.4 \times 10^{26}$ molecules $s^{-1}$ on UT 24.5 March. From our measured $H_2O$ lines, we estimated the rotational temperature for $H_2O$ within our aperture to be ~70 K. Rotational relaxation should be slower for homopolar species than for strongly polar species such as $H_2O$; hence, $C_2H_6$ may have a rotational temperature between 70 K and the temperature at which $H_2O$ ice sublimates rapidly from the nucleus, ~190 K. The detection of emission from the ${}^{r}Q_4$ and ${}^{r}Q_5$ branches on UT 2.0 April demonstrated that significant populations existed in ladders above $K = 3$. Our laboratory spectrum (Fig. 2) showed that only one-third of the $C_2H_6$ molecules resided in the four ladders $K = 0$ to 3 at 130 K, so the production rate for cometary $C_2H_6$ could be as much as $\sim 2 \times 10^{27}$ molecules $s^{-1}$ if the rotational temperature approaches 130 K. Even if the ${}^{r}Q_0$ and ${}^{r}Q_1$ branches sampled most of the rotational distribution on UT 24.5 March, $C_2H_6$ is still a surprisingly abundant parent volatile in Hyakutake.

Methane has been detected in vapor and ice phases in dense interstellar clouds (*21*). Like $C_2H_6$, $CH_4$ cannot be detected by UV or radio astronomical methods. It does have two strong IR vibrational bands ($\nu_3$ at 3.3 μm and $\nu_4$ at 7.7 μm), and these have been the subject of theoretical modeling and observational searches in comets. An IR spectroscopic search at 3.3 μm from the Kuiper Airborne Observatory showed an upper limit of ~4% for the production rate of $CH_4$ relative to that of $H_2O$ in Halley (*22*), but a ground-based search for the *R*1 and *P*2 lines (*23*) reported an upper limit of 0.2 to 1.2%, the range depending on the assumed rotational temperature (50 to 200 K). A $CH_4$ abundance of ~2% was derived from ion mass spectrometer data taken on the Giotto fly-

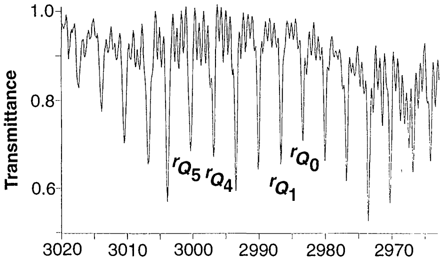

**Fig. 2.** Laboratory spectrum of $C_2H_6$ at 130 K.

**Table 1.** Spectral lines observed in C/1996 B2 Hyakutake and inferred parent volatile production rates.

| Molecule | Band | Line | Frequency ($cm^{-1}$) | Line flux ($10^{-16}$ W $m^{-2}$) | Q ($10^{26}$ molecules $s^{-1}$) | Continuum ($10^{-16}$ W $m^{-2}$ $cm^{-1}$) |
|---|---|---|---|---|---|---|
| $H_2O$ | 111-100 | $2_{02}$-$3_{03}$ | 5084 | 0.06 | 1700 | 1.2 |
| $CH_4$ | $\nu_3$ | *R*0 | 3028 | 0.26 | 12 | 1.6 |
| $C_2H_6$ | $\nu_7$ | ${}^{r}Q_0$ | 2983 | 0.27 | 2.8* | 1.3 |
|  |  | ${}^{r}Q_1$ | 2987 | 0.35 | 3.6† | 1.3 |
| CO | 1-0 | *P*2 | 2136 | 2.1 | 82‡ | 4.9 |
|  |  | *P*3 | 2132 | 2.8 | 115‡ | 4.9 |

*Sum of the production rate in the $K = 0$ and $K = 2$ ladders. †Sum of the production rate in the $K = 1$ and $K = 3$ ladders. ‡This is the total production rate for CO on the basis of the flux of this line alone.

through of Halley (*24*). However, the mass spectrum could also be explained by including fractionation fragments of polymeric $H_2CO$ instead of $CH_4$, and this approach simultaneously reproduced the spatial distribution of the extended source of CO found in Halley (*25*). A provisional detection (~7%) was reported in the dynamically new comet Wilson 1987 VII, but the detection at 3.3 μm was only $3\sigma$ above the noise level (*26*). A sensitive high-resolution search at 3.3 μm in comet Levy 1990 XX provided an upper limit of ~0.2% (*27*) for the production rate of $CH_4$ relative to $H_2O$.

We targeted the $\nu_3$ band of $CH_4$ near 3.3 μm for our search. The parent volatiles (for example, $H_2O$, $CH_3OH$, and $H_2S$) are known to be relaxed to rotational temperatures of ~50 K in the inner coma (*2, 5, 6, 28*), and $CH_4$ should also be relaxed. We searched for spectral lines that originate on low-lying rotational-vibrational levels having energies $<2kT$ (where $k$ is Boltzmann's constant and $T$ is the effective rotational temperature). Five spectral lines are needed to determine the populations of $CH_4$ in the five lowest energy levels (*22*). The *R*0 line (3028.75 $cm^{-1}$) of the $CH_4$ $\nu_3$ band was detected on UT 23.4 March 1996 and again on UT 24.5 March (Fig. 1B and Table 1). The *R*1 line (3038.50 $cm^{-1}$) was detected on UT 24.5 March, and the *P*2 line (2999.02 $cm^{-1}$) was detected on UT 2.0 April. On UT 12.2 April, we detected all five lines. The detection of multiple lines—all at the correct Doppler shift and with the expected intensity ratios—confirmed the identification of $CH_4$.

We adopted a rotational temperature of 50 K for $CH_4$, and we used $g_1 = 1.2 \times 10^{-24}$ W molecule$^{-1}$ (*27*) for the *R*0 line. If the rotational temperature were >50 K, our production rate (Table 1) would be higher. The effective gas kinetic temperature is thought to be ~200 K near the surface of the nucleus, dropping to ~20 K at 100 km, as adiabatic expansion cools the outflowing gas. Because our effective aperture diameter at Hyakutake is only ~100 km, we expect the temperature to be between 200 and 20 K.

Carbon monoxide can be present as a native ice in the nucleus, but it can also be produced in the coma by dissociation of other species such as $H_2CO$ and $CO_2$ (*1*). In Halley, about half of the CO found was released directly from the nucleus, the remainder being attributed to the distributed source (*29*). There is considerable interest in separately identifying the direct and distributed sources of CO, and this can be done with high–angular resolution measurements using ground-based telescopes at IR wavelengths (*7, 8, 30*).

The *P*2 and *P*3 lines of the 1-0 vibrational band of CO were detected in Hyakutake on UT 23.4 and 24.5 March (Fig. 1C). On UT 24.5 March, we surveyed eight lines in the *P* and *R* branches near 4.67 μm, representing solar pumping from rotational levels $J = 0$ to 6 of the ground vibrational level. Fluorescence efficiencies have been determined for two observing geometries, representing field-of-view diameters of 4 arc sec and 1 arc min (*30*). We used fluorescence efficiencies from the 4–arc sec model to derive CO production rates from the observed line fluxes. The 4–arc sec model is better suited for analysis of our data because it weights the near-nucleus population more heavily and is thus more appropriate for our observing conditions. The mean CO production rate was $9.8 \times 10^{27}$ molecules $s^{-1}$, derived from *P*2 and *P*3 (Table 1).

The principal parent volatile in comets is $H_2O$, and chemical implications of the minor constituents are best interpreted in the context of their abundances relative to $H_2O$. Ground-based detection of extraterrestrial $H_2O$ is normally impossible because of severe extinction by terrestrial $H_2O$, so we used a method that avoids this problem (*31*). Using this approach, 13 emission lines of $H_2O$ in the 111-100 vibrational band were detected in Hyakutake on UT 23.4 March. On UT 24.5 March, three of the cometary lines ($2_{02}$-$3_{03}$, $2_{11}$-$3_{12}$, and $2_{12}$-$3_{13}$) were measured again, and a $H_2O$ production rate of $1.7 \times 10^{29}$ molecules $s^{-1}$ was obtained. A provisional rotational temperature of ~70 K was found, but a more accurate value must await analysis of the full set of $H_2O$ lines. The $H_2O$ production rates retrieved from observations of OH on UT 24.5 March agree with our production rate (*32*). We will use our value for the $H_2O$ production rate when referring to mixing ratios in the cometary nucleus.

The abundances of $C_2H_6$, $CH_4$, CO, and $H_2O$ in Hyakutake were in the proportions $C_2H_6$:$CH_4$:CO:$H_2O$ = 0.4:0.7:5.8:100. The nucleus of Hyakutake exhibits a volatile carbon chemistry that differs from that of $CH_3OH$-rich ($C_2H_6$-poor) comets. This diversity may reflect variations in the processing of icy grain mantles in the solar nebula with distance from the protosun (temperature UV flux, and H atom density) and exposure time being controlling factors. We note that the $C_2H_6$:$CH_4$ ratio in Hyakutake exceeds the values found for three carbonaceous chondrite meteorites [$C_2H_6$:$CH_4$ $\leq 10^{-3}$ in Orgueil, Cold Bokkeveld, and Murray (*33*)] but is consistent with that found in a fourth [$C_2H_6$:$CH_4$ ~1 in Murchison (*34*)]. The close agreement of the $C_2H_6$:$CH_4$ ratio in Hyakutake and the Murchison meteorite suggests that their volatiles may have had a common origin.

The abundances of homologous hydrocarbons provide a test of cometary origin. $CH_4$ is the first and simplest member of the saturated hydrocarbon homologous series $C_nH_{2n+2}$; the abundance ratios of successive members can reveal whether their formation was controlled by kinetics (such as in gas-phase ion-molecule reactions), by thermodynamic processes, or by processing of icy grain mantles (for example, by photolysis or by H atom addition reactions).

Homologic analyses have been applied to monocarboxylic acids ($H_{2n-1}C_{n-1}COOH$) isolated from the matrix of Murchison. The abundances of successive homologs of these acids decrease by ~60 to 70% for each additional carbon, revealing the influence of a kinetically controlled process (*35*). Ion-molecule reactions are important in dense interstellar clouds (*36*) and lead to nearly equal abundances for successive homologs. However, production of $C_2H_6$ and higher homologs of $CH_4$ is energetically forbidden at low temperatures because all of the relevant reactions are endothermic (*37*). Hence, these homologs are not expected if comets contain ices formed in this way.

Thermodynamic processes were probably important in high-density, high-temperature regions of the solar nebula (*8, 38, 39*). In thermochemical equilibrium models, the abundances of the higher homologs decrease for each $CH_2$ group added. The $C_2H_6$:$CH_4$ ratio was $<10^{-3}$ in equilibrium models with 1000 K and 1-atm total pressure, while it was 0.014 in models with 500 K and 1-atm pressure (*39*). For lower pressures, the $C_2H_6$:$CH_4$ ratio was much smaller, typically $<10^{-5}$. Equilibrium models for the jovian subnebula also predict $C_2H_6$:$CH_4$ $<10^{-3}$ (*8*). The presence of $C_2H_6$ with an abundance comparable to $CH_4$ in Hyakutake is not consistent with production by thermochemical equilibrium processes in the solar nebula or in a giant planet subnebula.

Aliphatic hydrocarbons are easily formed by radiation processing of just about any higher order organic mixture (*40*). Ethane is readily made in interstellar ice analogs in the laboratory—for example, by photolysis either of mixed $H_2O$-$CH_4$ ices (*41*) or of pure $CH_4$ ice (*42*). Photolysis also breaks bonds in $H_2O$ and other comixed ices, leading to production of many compounds of C, H, O, N, S, and other elements in laboratory simulations (*43*). This possible origin may be tested once abundances are known for the full suite of organic compounds detected in Hyakutake.

Ethane can also be a product of H atom addition reactions on grain surfaces in interstellar dense cloud cores (*44*). Acetylene ($C_2H_2$) is readily produced by gas-phase ion-molecule chemistry there and, after condensing onto grain surfaces, can undergo hydrogenation until becoming saturated (thereby forming $C_2H_6$). A detection of $C_2H_2$ has been reported in Hyakutake, at an abundance of 0.1 to 0.4% relative to $H_2O$ (*45*).

The mixing ratio for CO reported here is ~5.8% relative to $H_2O$, and this is a measure of the direct (native) source, primarily. In Halley, about half of the total CO was produced from a distributed source with a scale length of about $10^4$ km; dissociation of $H_2CO$ was suggested (*46*). If a similar distributed source exists in Hyakutake, it would be discriminated against in our production rate because of the small aperture used in our reductions (but would still contribute some of the measured flux). CO has also been detected in Hyakutake through fluorescence of its $A^1\Pi$ -$X^1\Sigma^+$ electronic transition in the UV, and a production rate of ~5% relative to $H_2O$ was reported (*47*). Like our IR results, the UV detections are most sensitive to native CO because of the small instrumental field-of-view of the International Ultraviolet Explorer (IUE) and the Hubble Space Telescope (HST). On the other hand, CO rotational transitions (detected at radio wavelengths) suggest a production rate ~20 to 30% relative to $H_2O$ (*48, 49*). These observations feature much larger instrumental field-of-views and so are sensitive to the sum of the native and distributed sources for CO. Therefore, most of the CO found in Hyakutake seems to be associated with a distributed source, whereas the mainly native CO reported here represents only about 20% of the total CO produced from Hyakutake. The relative abundance for $CH_3OH$ is reported to be ~0.3 to 2% relative to $H_2O$, from radio observations (*49*), and our IR measurements independently confirm that it is depleted relative to most other comets.

The presence of abundant $C_2H_6$ and $CH_4$, a relatively low abundance for $CH_3OH$, a modest amount of native CO, and a higher production rate of CO from a distributed source are all consistent, if H addition reactions significantly modified a $H_2O$-$CO$-$CH_4$-$C_2H_2$ ice. If H atom addition reactions did hydrogenate some of the $C_2H_2$ originally deposited on icy grain mantles, the reaction was not complete. The ratio of $C_2H_6$:$C_2H_2$ is in the range 1 to 10 in Hyakutake, suggesting that the conversion of $C_2H_2$ to $C_2H_6$ could have proceeded with an efficiency ranging from 50 to 90%. CO would also have been hydrogenated, first forming the formyl radical (HCO), then $H_2CO$, then $CH_3OH$, with the final products being $CH_4$ and $H_2O$. Note that $CH_4$ may also condense directly from the gas phase in the interstellar medium, and thus the origin of the $CH_4$ we observe is unclear. If the distributed source of CO comes mainly from polymeric $H_2CO$, the implied conversion efficiency of CO to $H_2CO$ would be ~80%. With only ~0.3 to 2% $CH_3OH$ and ~1% $CH_4$, however, the hydrogenation reaction would seem to have stopped with $H_2CO$, possibly because the $H_2CO$ was rapidly incorporated into polymers or because $CH_3OH$ formation is inhibited at low temperatures (10 to 20 K) (*50*). Although hydrogenation on grain surfaces seems plausible, it is also possible that the unusual carbon chemistry observed in Hyakutake is the result of radiation processing of ices in the dense cloud core.

## REFERENCES AND NOTES

1. M. J. Mumma, P. R. Weissman, S. A. Stern, in *Protostars and Planets*, *III*, E. H. Levy and J. I. Lunine, Eds. (Univ. of Arizona Press, Tucson, 1993). pp. 1177–1252.
2. M. J. Mumma, H. A. Weaver, H. P. Larson, D.S. Davis, M. Williams, *Science* **232**, 1523 (1986).
3. F. P. Schloerb, W. M. Kinzel, D. A Swade, W. M. Irvine, *Astrophys. J.* **310**, L55 (1986).
4. M. Combes *et al.*, *Icarus* **76**, 404 (1988); M. J. Mumma and D.C. Reuter, *Astrophys. J.* **344**, 940 (1989); L. E. Snyder, P. Palmer, I. de Pater, *Astron. J.* **97**, 246 (1989).
5. S. Hoban, M. J. Mumma, D. C. Reuter, M. DiSanti, R. R. Joyce, *Icarus* **93**, 122 (1991).
6. D. Bockelèe-Morvan *et al.*, *Nature* **350**, 318 (1991).
7. M. DiSanti, M. Mumma, J. Lacy, R. Parmar, *Icarus* **96**, 151 (1992).
8. B. Fegley, Jr. and Prinn, R. G., in *The Formation and Evolution of Planetary Systems*, H. A. Weaver and L. Danly, Eds. (Cambridge Univ. Press, Cambridge, 1989), pp. 171–205; R. G. Prinn and B. Fegley Jr., in *The Origin and Evolution of Planetary and Satellite Atmospheres*, S. K. Atreya, J. B. Pollack, and M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1989), pp. 78–136.
9. T. P. Greene, A. T. Tokunaga, D. W. Toomey, J. S. Carr, in *Proc. Spie* **1946**, 311 (1993).
10. M. J. Mumma *et al.*, *IAU Circular 6366* (1996); M. A. DiSanti *et al.*, *IAU Circular 6374* (1996).
11. The geocentric Doppler shift was $-30$ km $s^{-1}$ on UT 23.5 March and $-15$ km $s^{-1}$ on UT 24.5 March, sufficient to shift the cometary emissions away from the corresponding terrestrial absorption lines. For each observation, we integrated for 120 s per frame for the observations of $H_2O$, $CH_4$, and $C_2H_6$, but only 30 s per frame for CO owing to the higher background thermal emission at 4.6 μm. For each grating setting, we acquired two frames with the CSHELL spectrometer entrance slit centered on the nucleus, *A*) and two with it displaced by 5 arc min to the west, *B*), in a sequence *ABBA*. Calibration was achieved by observations of the IR flux standard star BS 4550.
12. G. Herzberg, *Molecular Spectra and Molecular Structure III: Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1966).
13. G. Herzberg, *Molecular Spectra and Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1945).
14. J. H. Lii and N. L. Allinger, *J. Comput. Chem.* **13**, 1138 (1992).
15. W. Livingston and L. Wallace, *NSO Tech. Rep. 91-001* (National Solar Observatory, Tucson, AZ, 1991).
16. L. S. Rothman *et al.*, *J. Quant. Spectrosc. Radiat. Transfer* **48**, 469 (1992); A. Goldman, M. Dang-Nhu, and J. P. Bouanich, *ibid.* **41**, 17 (1989).
17. N. Dello Russo and M. J. Mumma, in preparation.
18. H. A. Weaver and M. J. Mumma, *Astrophys. J.* **276**, 782 (1984); *ibid.* **285**, 872 (1984).
19. J. Crovisier and T. Encrenaz, *Astron. Astrophys.* **126**, 170 (1983).
20. The production rate $Q$ (molecules $s^{-1}$) can be evaluated from: $Q = (F/g_1)(8\pi v\Delta R2/\theta)$ where $F$ is the line flux outside Earth's atmosphere, $g_1$ is the fluorescence efficiency at 1 AU heliocentric distance, $\Delta$ is the geocentric distance, $R$ is the heliocentric distance of the comet, and $\theta$ is the aperture diameter. The outflow velocity $v$ is taken to be 800 m $s^{-1}$, the value obtained for Halley at a distance of 500 km from the nucleus [P. Lämmerzahl *et al.*, *Astron. Astrophys.* **187**, 169 (1987)]. We take this value to be characteristic of outflow in Hyakutake, since the total molecular production rates and the heliocentric distances were comparable for Halley during the Giotto flythrough and for Hyakutake during our observations. The geocentric distance was 0.106 AU and $R$ was 1.06 AU on UT 24.5 March. We evaluate production rates from the flux measured in a rectangular aperture 1 arc sec by 1.4 arc sec, centered on the nucleus, which corresponds to an effective aperture diameter $\theta$ of 1.33 arc sec. $Q$ may then be written as $(F/g_1)$*5.55 × $10^{19}$.
21. J. H. Lacy *et al.*, *Astrophys. J.* **376**, 556 (1991).
22. S. Drapatz, H. P. Larson, D. S. Davis, *Astron. Astrophys.* **187**, 497 (1987).
23. K. Kawara, B. Gregory, T. Yamamoto, H. Shibai, *ibid.* **207**, 174 (1988).
24. M. Allen *et al.*, *ibid.* **187**, 502 (1987); R. Wegmann, H. U. Schmidt, W. F. Huebner, D. C. Boice, *ibid.* p. 339.
25. D. C. Boice, W. F. Huebner, M. J. Sablik, I. Konno, *Geophys. Res. Lett.* **17**, 1813 (1990).
26. H. P. Larson, H. A. Weaver, M. J. Mumma, S. Drapatz, *Astrophys. J.* **338**, 1106 (1989).
27. T. Y. Brooke, A. T. Tokunaga, H. A. Weaver, G. Chin, T. R. Geballe, *ibid.* **372**, L113 (1991).
28. D. Bockelèe-Morvan and J. Crovisier, *Astron. Astrophys.* **187**, 425 (1987); D. Bockelèe-Morvan, R. Padman, J. K. Davies, J. Crovisier, *Planet. Space Sci.* **42**, 655 (1994).
29. P. Eberhardt *et al.*, *Astron. Astrophys.* **187**, 481 (1987).
30. G. Chin and H. A. Weaver, *Astrophys. J.* **285**, 858 (1984).
31. M. J. Mumma, M. A. DiSanti, A. Tokunaga, E. E. Roettger, *Bull. Am. Astron. Soc.* **27**, 1144 (1995). Cometary $H_2O$ molecules are excited into the 111 state from the 000 vibrational level by sunlight and then cascade into the 100 state with ~12% efficiency, emitting fluorescent photons with wavelengths near 2 μm. The emitted photons are not absorbed by telluric $H_2O$ vapor because only $H_2O$ molecules in the 100 vibrational level can absorb those photons, but even at 300 K, fewer than $10^{-8}$ of the total $H_2O$ molecules occupy this level (the proportion is even smaller at temperatures typical of Earth's troposphere above Mauna Kea, 280 to 220 K). The cometary $H_2O$ emission band falls in a spectral region where a weak band of atmospheric $CO_2$ also occurs, but the $H_2O$ lines we observed were not affected by accidental extinction.
32. Ground-based results from D. Schleicher, D. Osip, S. Lederer, *IAU Circular 6372* (1996); IUE results from M. Festou, P. D. Feldman, R. Gonzalez, P. M. Rodriguez, *IAU Circular 6355* (1996), as revised by M. A'Hearn, private communication.
33. M. H. Studier, R. Hyatsu, E. Anders, *Science* **149**, 1455 (1965).
34. G. Yuen, N. Blair, D. J. Des Marais, S. Chang, *Nature* **307**, 252 (1984).
35. J. G. Lawless and G. U. Yuen, *ibid.* **282**, 396 (1979); J. R. Cronin, S. Pizzarello, D. P. Cruikshank, in *Meteorites and the Early Solar System*, J. F. Kerridge and M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1988), pp. 819–857.
36. E. F. Van Dishoeck, G. A. Blake, B. T. Draine, J. I. Lunine, in *Protostars and Planets III*, E. H. Levy and J. I. Lunine, Eds. (Univ. Arizona Press, Tucson, 1993), pp. 163–241.
37. E. Herbst, N. G. Adams, D. Smith, *Astrophys. J.* **269**, 329 (1983).
38. M. O. Dayhoff, E. R. Lippincott, R. V. Eck, *Science* **164**, 1461 (1964).
39. R. V. Eck, E. R. Lippincott, M. O. Dayhoff, Y. T. Pratt, *ibid.* **153**, 628 (1966).
40. A. Charlesby, *Atomic Radiation and Polymers* (Pergamon, New York, 1960).
41. L. J. Stief, V. J. DeCarlo, J. J. Hillman, *J. Chem. Phys.* **43**, 2490 (1965).
42. P. A. Gerakines, W. A. Schutte, P. Ehrenfreund, *Astron. Astrophys.*, in press.
43. L. J. Allamandola, S. A. Sandford, G. J. Valero, *Icarus* **76**, 225 (1988); W. A. Schutte and J. M. Greenberg, *Astron. Astrophys.* **244**, 190 (1991); M. H. Moore and R. L. Hudson, *Astrophys. J.* **401**, 353 (1992).
44. A. G. G. M. Tielens and L. J. Allamandola, in *Interstellar Processes*, D. J. Hollenbach and H. A. Thron-

son, Eds. (Reidel, Dordrecht, 1987), pp. 397–470; S. B. Charnley, M. E. Kress, A. G. G. M. Tielens, T. J. Millar, *Astrophys. J.* **448**, 232 (1995).

45. A. T. Tokunaga, T. Y. Brooke, H. A. Weaver, J. Crovisier, D. Bockelee-Morvan, *IAU Circular 6378* (1996).
46. R. Meier, P. Eberhardt, D. Krankowsky, and R. R. Hodges, *Astron. Astrophys.* **277**, 677 (1993).
47. CO was detected from IUE, P. D. Feldman, M. Festou, P. M. Rodriguez, R. Gonzalez, *IAU Circular 6370* (1996); CO was detected from HST, H. A. Weaver *et al.*, *IAU Circular 6374* (1996).
48. M. Senay, H. Matthews, D. Jewitt, *IAU Circular 6335* (1996).
49. M. Womack, M. C. Festou, and S. A. Stern, *IAU Circular 6345*; H. E. Matthews *et al.*, *IAU Circular 6353* (1996).
50. K. Hiraoka *et al.*, *Chem. Phys. Lett.*, **229**, 408 (1994).

51. This work was supported by the Planetary Astronomy Program of the Research Programs Division, National Aeronautics and Space Administration under RTOP 196-41-54 to M.J.M. and M.A.D., N.D.R. and D.X.X. acknowledge support as Resident Research Associates from the National Research Council. K.M.S. acknowledges support from the NASA JOVE Program, and from the NASA Planetary Atmospheres Program under grant NAGW-461 to R. E. Johnson (Univ. of Virginia). M.F. acknowledges support under the NSF Visiting Professorship for Women Program. D. K. Yeomans provided updated ephemerides for Hyakutake. M.J.M. thanks S. B. Charnley and T. J. Millar for insightful discussions regarding interstellar chemistry, and D. C. Reuter for review. We thank R. Joseph for approving our target of opportunity request, and we thank the IRTF staff for their operational support.

8 April 1996; accepted 3 May 1996

---

# Type II Supernova Matter in a Silicon Carbide Grain from the Murchison Meteorite

Peter Hoppe, Roger Strebel, Peter Eberhardt, Sachiko Amari,*
Roy S. Lewis

**The circumstellar silicon carbide (SiC) grain X57 from the Murchison meteorite contains large amounts of radiogenic calcium-44 (20 times its solar system abundance) and has an anomalous silicon isotopic composition, different from other circumstellar SiC grains. Its inferred initial $^{44}$Ti/Si and $^{44}$Ti/$^{48}$Ti ratios are $1.6 \times 10^{-4}$ and 0.37. In addition, it contains radiogenic magnesium-26; the inferred initial $^{26}$Al/$^{27}$Al ratio is 0.11. The isotopic and elemental data of X57 can be explained by selective mixing of matter from different zones of a typical type II supernova of 25 solar masses during its explosion. The high $^{44}$Ti/Si ratio requires contributions from the innermost nickel zone of the supernova to the SiC condensation site, as similarly suggested by astronomical observations.**

Meteorites contain refractory dust grains that are believed to be of circumstellar origin (*1*). These grains provide information about stellar nucleosynthesis, stellar evolution and mixing of material in the interior of stars, physical and chemical conditions in stellar atmospheres during grain formation, and the inventory of stars that contributed dust to the protosolar nebula. After formation in the atmospheres of stars and passage through the interstellar medium, these dust grains went into the ancestral molecular cloud from which our solar system formed. Refractory dust grains survived the formation of the solar system inside small planetary bodies and comets, and they are carried to Earth by meteorites.

Identified circumstellar grains include SiC, diamond, graphite, corundum ($Al_2O_3$), spinel ($MgAl_2O_4$), silicon nitride ($Si_3N_4$), and carbides of Ti, Zr, and Mo (*1*). One class of SiC grains, the X grains, constitute approximately 1% of all SiC grains separated from meteorites (*2*, *3*). The X grains are characterized by strong isotopic enrichments relative to their solar system abundances of $^{28}$Si (up to threefold), $^{15}$N (up to 20-fold), and in many grains, $^{12}$C (up to 80-fold). They also show large excesses of $^{26}$Mg and, in some cases, also of $^{44}$Ca and $^{49}$Ti. These excesses are believed to be a result of the in situ decay after grain formation of the radionuclides $^{26}$Al (half-life $T_{1/2}$ = 716,000 years), $^{44}$Ti ($T_{1/2}$ = 47 years), and $^{49}$V ($T_{1/2}$ = 330 days). Corresponding initial $^{26}$Al/$^{27}$Al and $^{44}$Ti/$^{48}$Ti ratios range up to 0.61 and 0.16, respectively.

On the basis of their enrichments in $^{28}$Si and the presence of $^{44}$Ti at the time of grain formation, type II supernovae have been suggested as the most likely stellar sources of the X grains (*2*). These supernova stars are believed to consist of a Ni core surrounded by concentric layers that experienced different stages of nuclear burning (*4*–*6*) (Fig. 1). The isotopic signatures of the X grains suggest deep and inhomogeneous mixing of matter in the supernova ejecta. When the X grain data are quantitatively compared with model predictions for the ejecta of typical type II supernovae (*5*, *6*), some discrepancies do exist. In particular, the large $^{15}$N excesses, high initial $^{26}$Al/$^{27}$Al ratios, and enrichments of $^{29}$Si relative to $^{30}$Si cannot be satisfactorily explained. These differences point to deficiencies in the understanding of current type II supernova models or to an alternate origin [for example, type I supernovae (*2*)] of the X grains.

To provide constraints for supernova models from X grain data, we analyzed more than 6000 individual SiC grains separated from the Murchison meteorite by ion imaging with the University of Bern ion microprobe. Grains from fractions KJD and KJE having sizes around 1 μm (*7*) were dispersed on gold foils. Digitized isotopic images of $^{12}C^-$, $^{28}Si^-$, and $^{30}Si^-$ ions emitted from the SiC grains under bombardment with $Cs^+$ ions were acquired with a CCD (charge-coupled device) camera, and X grains were found by searching for grains with low $^{30}$Si/$^{28}$Si ratios (Fig. 2). The 43 X grains we identified were subsequently analyzed with high mass resolution for the isotopic compositions of C, N, Mg-Al, Si, and Ca-Ti. Because the grains are small, only a limited number of these elements could be analyzed on each grain.

The isotopic data of most X grains agree with those obtained previously, and the same general problems are encountered when the grain data are compared with predictions from current type II supernova models. An exception is X57, which has a distinct Si isotopic signature and a comparatively low $^{26}$Al/$^{27}$Al ratio. Besides the generally observed $^{28}$Si enrichment, it has an excess of $^{30}$Si over $^{29}$Si, falling well below the array formed by the majority of the X grains in a three-isotope representation (Fig. 3). Magnesium in X57 is monoisotopic $^{26}$Mg, and the inferred initial $^{26}$Al/$^{27}$Al ratio is 0.11 (Table 1). In addition, X57 has a

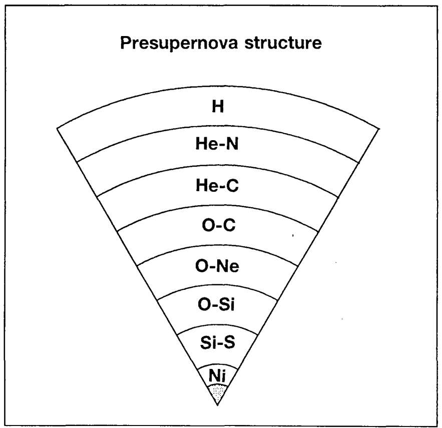

**Fig. 1.** Schematic section through a $25M_{\odot}$ type II supernova. Zones are designated according to their most abundant elements. The spatial extent of the zones is not accurately indicated. The shaded area represents the supernova remnant. [Adapted from (5)]

P. Hoppe, R. Strebel, P. Eberhardt, Physikalisches Institut, Universität Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland.
S. Amari and R. S. Lewis, Enrico Fermi Institute, University of Chicago, Chicago, IL 60637, USA.

---

*Present address: McDonnell Center for the Space Sciences and Physics Department, Washington University, St. Louis, MO 63130, USA.