

Research Paper

Meteors Do Not Break Exogenous Organic Molecules into High Yields of Diatomics

PETER JENNISKENS,¹ EMILY L. SCHALLER,² CHRISTOPHE O. LAUX,³
MICHAEL A. WILSON,⁴ GREG SCHMIDT,⁴ and RICK L. RAIRDEN⁵

ABSTRACT

Meteoroids that dominate the Earth's extraterrestrial mass influx (50–300 μm size range) may have contributed a unique blend of exogenous organic molecules at the time of the origin of life. Such meteoroids are so large that most of their mass is ablated in the Earth's atmosphere. In the process, organic molecules are decomposed and chemically altered to molecules differently from those delivered to the Earth's surface by smaller (<50 μm) micrometeorites and larger (>10 cm) meteorites. The question addressed here is whether the organic matter in these meteoroids is fully decomposed into atoms or diatomic compounds during ablation. If not, then the ablation products made available for prebiotic organic chemistry, and perhaps early biology, might have retained some memory of their astrophysical nature. To test this hypothesis we searched for CN emission in meteor spectra in an airborne experiment during the 2001 Leonid meteor storm. We found that the meteor's light-emitting air plasma, which included products of meteor ablation, contained less than 1 CN molecule for every 30 meteoric iron atoms. This contrasts sharply with the nitrogen/iron ratio of 1:1.2 in the solid matter of comet 1P/Halley. Unless the nitrogen content or the abundance of complex organic matter in the Leonid parent body, comet 55P/Tempel-Tuttle, differs from that in comet 1P/Halley, it appears that very little of that organic nitrogen decomposes into CN molecules during meteor ablation in the rarefied flow conditions that characterize the atmospheric entry of meteoroids \sim 50 μm –10 cm in size. We propose that the organics of such meteoroids survive instead as larger compounds. Key Words: Prebiotic chemistry—Origin of life—Meteors—Exogenous organics. *Astrobiology* 4, 67–79.

¹Center for the Study of Life in the Universe, SETI Institute, Mountain View, California.

²Dartmouth College, Hanover, New Hampshire.

³High Temperature Gasdynamics Laboratory, Mechanical Engineering Department, Stanford University, Stanford, California.

⁴NASA Ames Research Center, Moffett Field, California.

⁵Lockheed Martin Space Sciences Laboratory, Palo Alto, California.

INTRODUCTION

REFRACTORY ORGANIC CARBON in extraterrestrial materials is a likely source of prebiotic compounds for the origin of life (Oró, 1961; Chyba and Sagan, 1992, 1997; Delsemme, 1992). Organic carbon is abundant in the cometary grains probed by the GIOTTO and VEGA spacecraft (Kissel and Krueger, 1987; Jessberger and Kissel, 1991), making up some 23% by weight of the comet mass fraction and some 66% by weight of dust grains once the volatile compounds have evaporated (Greenberg, 2000). Primitive asteroids contain organic matter as well, up to 12% by weight based on the carbon content of interplanetary dust particles (IDPs) that are $\sim 10 \mu\text{m}$ in size (Keller *et al.*, 1995; Flynn *et al.*, 2000). Flynn *et al.* (2000) found from C-XANES and Fourier transform infrared spectroscopy that a substantial fraction of this carbon is organic. Most carbon-rich meteorites contain less than 3% by weight carbon, but these meteorites may not be representative of the most primitive C-type asteroids.

The organic carbon has high molecular mass and survives exposure to the vacuum of space even when approaching the Sun as close as Earth's orbit [$T_{\text{max}} \sim 250\text{--}300 \text{ K}$ (Levasseur-Regourd *et al.*, 2000)]. In order for this organic matter to have been delivered to an early Earth, it had to have survived impact with Earth's atmosphere. Of all infalling matter, it is believed that less than 8% by weight of carbon survives intact in micrometeorites with initial sizes 5–50 μm , but only in those that derive from prograde asteroidal orbits that approach Earth from behind (Anders, 1989). The remainder, and the bulk of the mass influx in the form of meteoroids, which includes all 50 μm –10 cm-sized meteoroids (Love and Brownlee 1993), is ablated in the upper atmosphere during a phase called a "meteor." In particular, we will use the term meteor here to refer to the physical condition of rarefied flow that pertains to the interaction with Earth's atmosphere of all meteoroids small enough (less than about 10 cm) not to form a shock wave. In that process, the organic molecules are chemically changed in a unique manner determined by the process of meteoroid ablation and subsequent chemistry in the air plasma in the meteoroid's wake (Jenniskens *et al.*, 2000a).

This paper investigates the possibility that organic matter carried to Earth via meteors is not necessarily broken down into atoms or diatomic

molecules and may survive in the form of larger molecules. On the primitive Earth, this surviving meteoritic material might have made an important contribution to the prebiotic organic matter. This idea comes at a time when other investigators are also proposing the survivability of extraterrestrial organic matter at relatively high temperatures. Brownlee *et al.* (2002) recently reported that refractory carbon in IDPs and micrometeorites survive relatively severe heating ($>1,200 \text{ K}$) when exposed to the beam of an electron microscope. In these experiments the organic matter was found to separate from the silicate melt as a solid carbon-rich material with embedded metal. It has not been established whether this amorphous carbonaceous material produced on heating is elemental or organic, although the latter is more likely. In addition, Glavin and Bada (1999) have demonstrated that several amino acids and nucleobases from the Murchison meteorite survive heating to $1,100^\circ\text{C}$ for several seconds at reduced pressures.

Indeed, micrometeorites are found to contain significant amounts of organic matter that have survived the heating process. Russell *et al.* (2002) even found the C-H stretch vibration band of organic matter in the debris left in the wake of a bright Leonid fireball. Based on measurements of organic matter in micrometeorites found in ocean sediments and Antarctic ice, Maurette and colleagues (Maurette, 1998; Maurette *et al.*, 2000; Toppani *et al.*, 2001) make the case that solid products from meteor ablation raining down to the surface may have contributed organic matter to the early Earth.

In contrast, our work pursues the idea that atmospheric chemistry is essential in creating useful prebiotic compounds. Jenniskens *et al.* (2000a) provided the first evidence that organic molecules may survive the meteor phase with the discovery that most light emission, and therefore most high temperature chemistry, occurs in a comparatively mild temperature ($\sim 4,300 \text{ K}$) air plasma in almost local thermodynamic equilibrium just behind the meteoroid (Boyd, 2000; Jenniskens *et al.*, 2000a). The product of that chemistry depends on the time available for reactions in the high temperature meteor plasma and the balance between oxygen and nitrogen insertion and polymerization versus carbon extraction and molecular breakup. Reactions with the ablated organic compounds that are too infrequent to occur with high probability in the allotted time are not

expected to reach equilibrium. After being chemically altered, the products will continue to react while settling to the Earth surface. Before addressing the latter, it is necessary to understand the products that derive from the meteor phase itself.

Meteors represent elusive physical conditions of rarefied high Mach number (up to 270) flow and non-equilibrium chemistry, which makes it difficult to simulate the conditions in the laboratory without a better understanding of the physical processes and fate of organic matter in real cases. The intense 1998–2002 Leonid storms have offered an opportunity to obtain data on these processes using modern instruments that would otherwise have only a small chance of detecting a meteor. If the physical conditions can be described quantitatively, then this will set boundaries to theoretical models that can provide insight into this elusive chemistry.

A key constraint for such models is the need to predict the production of the most abundant diatomic molecules created during decomposition of the complex organic matter. When complex organic matter is heated to high temperatures, or sputtered by fast ions or energetic photons, small molecular fragments and atoms are lost from the complex organic matter (such as H, O, H₂, O₂, OH, H₂O, CO, CO₂, CN, and CH₄) in a process called carbonization (Jenniskens and Russell, 1993; Fristrom, 1995, p. 318). Further heating (up to 700 K) leads to additional loss of H and H₂ in a process of polymerization, which is accompanied by the growth of aromatic ring structures. Prolonged heating in a confined environment leads to graphitization, which is the stacking of those rings into layers to form a crystal (e.g., Koidl *et al.*, 1989). Further temperature increase leads to decomposition by loss of H₂, CN, CH, C₂, HCN, NH₃, and C₂H. In this latter stage of decomposition, in the absence of rapid radiative cooling, after formation, hydrocarbon radicals higher than C₂ rapidly fission into lower-molecular-weight products, leaving only the thermally stable single and double bonded carbon radicals. Carbon atoms are also present, but at low abundance due to thermodynamic factors (Fristrom, 1995; Rairden *et al.*, 2000). Upon cooling, these lower-molecular-weight products can recondense into amorphous carbon to form soot.

We propose that the best chance of probing the fate of organic matter in the rarefied high Mach number flow of small meteoroids is to look for

the production of the CN radical. This radical is most easily detected because of a strong B → X transition of low excitation energy with a band head at 388 nm. CN is a product of reactions involving nitrogen embedded in the complex organic matter or interactions between the meteoric carbon atoms and atmospheric N₂. In general, nitrogen is closely associated with the organic matter in IDPs, in particular with polyaromatic hydrocarbons, and it is enriched in ¹⁵N (Keller *et al.*, 1995).

Early work by Cepplecha (1971) identified CN emissions in the –12 magnitude flare of a cometary meteoroid, but the identification is doubtful because of the many iron lines in the near-UV. Our first efforts at detecting the 388 nm band head of CN during the 1999 Leonid Multi-Instrument Aircraft Campaign (MAC) (Jenniskens and Butow, 1999; Jenniskens *et al.*, 2000b) focused on slit-less spectroscopy of meteors in first order in the same spectral region as observed by Cepplecha, using a UV-sensitive intensified charge coupled device (CCD) camera (Abe *et al.*, 2000; Rairden *et al.*, 2000). The 1999 Leonid storm was seen under good conditions, and the high meteor rates resulted in several bright spectra. Our most precisely measured spectrum set an upper limit of 1 CN molecule per 3 Fe atoms, only about a factor of 2 less than expected if all of the nitrogen in complex organic matter would have been released in the form of CN radicals (Rairden *et al.*, 2000).

In order to improve upon this result, we needed to resolve the underlying iron emission lines in the meteor spectrum. Here we report results from a high-resolution unintensified slit-less CCD spectrograph that obtained spectra with sufficient spectral resolution to separate the iron lines. From the new data, we conclude that CN production in meteors is not only low, but it is strongly inhibited.

METHODS

The two-stage thermoelectrically cooled slit-less CCD spectrograph for Meteor Astronomy and Astrobiology (“ASTRO”) was specially developed for the detection of small molecules in the optical spectra of relatively faint meteors. The design provides for a high spectral resolution with reasonable detection rates for meteors that are faint enough to have rarefied flow conditions

typical for even smaller (but too faint) $\sim 150 \mu\text{m}$ meteors. The instrument layout is shown in Fig. 1. An objective grating disperses the light of a meteor seen at some angle to the viewing direction, and a lens projects the spectrum on a cooled CCD detector. A typical result is shown in Fig. 2.

The detector, a Pixelvision camera with a two-stage thermoelectrically cooled $1,024 \times 1,024$ pixel back-illuminated SI003AB CCD with $24 \times 24 \mu\text{m}$ pixel size ($24.5 \times 24.5 \text{ mm}$ image region), was used in an unintensified mode to keep as high a spectral resolution as possible. The disadvantage of such an unintensified CCD detector is the relatively long readout time, which is 0.95 s for 1×4 binning. Exposure times needed to be kept to a minimum (0.1–0.8 s) so as not to have too many zero-order star images and star spectra overlap the meteor spectrum. Minimum exposure times

were also needed to prevent smearing of those star images from Earth's rotation and aircraft motion. Though the star background serves to calibrate the meteor intensity, once meteor intensity calibration was accomplished the star images were removed from the spectra by subtraction of a no-meteor image that was taken in the same viewing direction and with the same instrument setting only seconds after a meteor was detected. Noise residuals of the star images were removed by replacing the residue pixels with low-intensity pixels from neighboring rows. A 0.1 s exposure resulted in a maximum star magnitude that could be captured of +10.6. In general, the limiting magnitude for meteors was about +5.7 because of their higher angular velocity, and meteors brighter than magnitude +4 show the most intense first-order spectral lines. Our best spectra

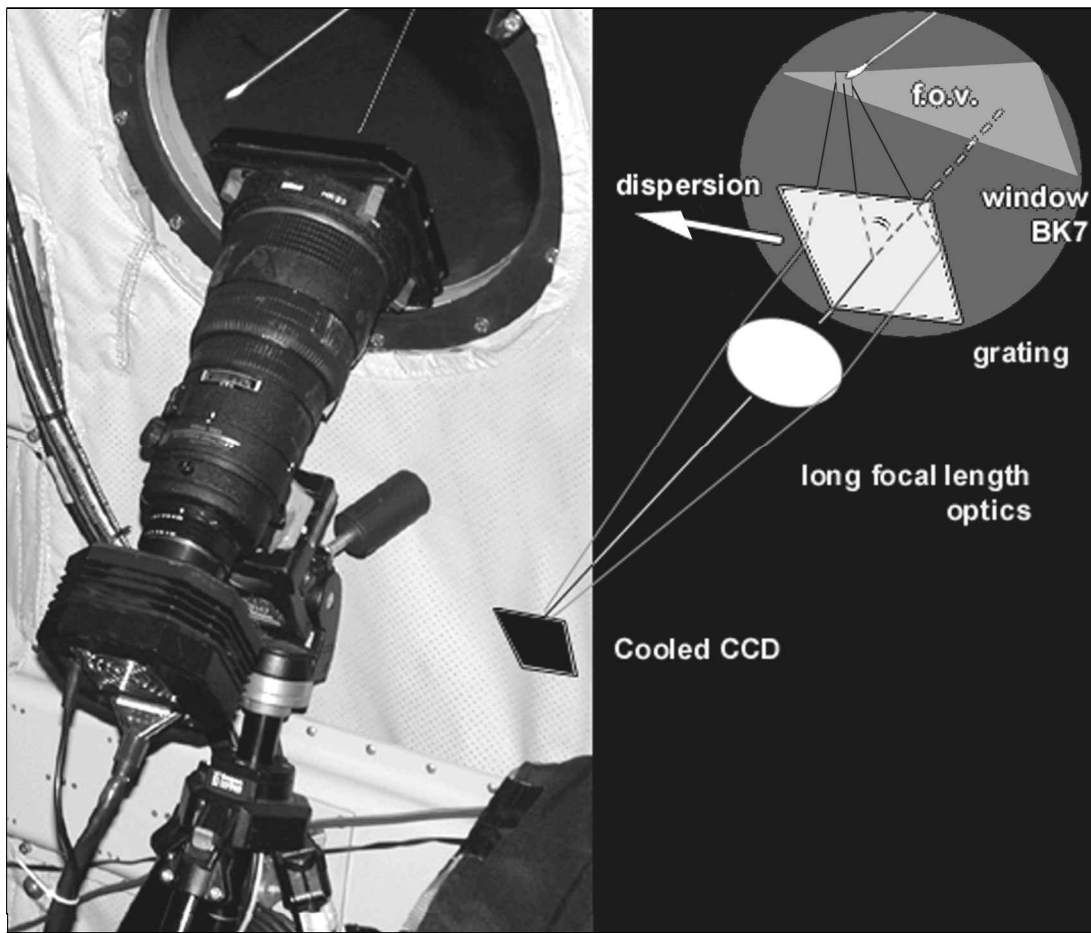


FIG. 1. Instrument setup on “FISTA” and a schematic of the instrumental layout. The instrument consists of a cooled CCD detector, optical system, and grating. The field of view of the instrument is only 5° narrow, but stretches in the dispersion direction of the grating for the full range of unvignetted viewing. The camera is typically positioned at an angle of 20° to the aircraft's optical window.

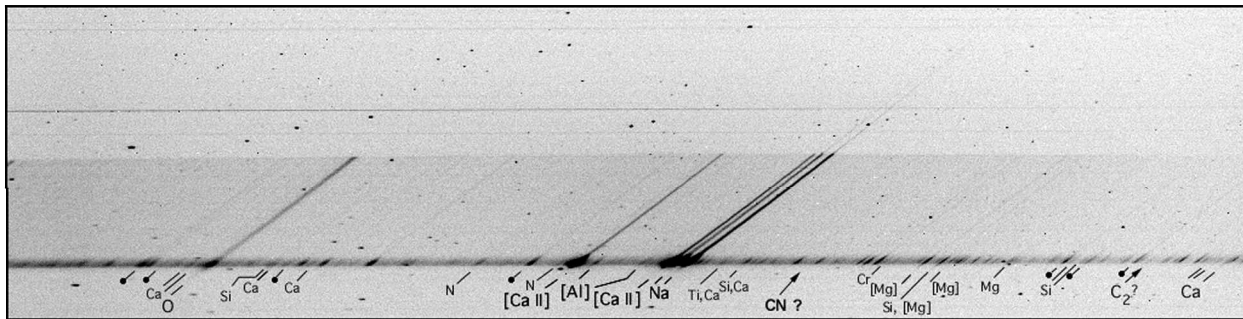


FIG. 2. Second order spectrum of the 09:05:58 UT, November 18, 2001, Leonid meteor. Lines other than those caused by iron are marked. Brackets indicate emission lines in the overlapping third order.

probed -2 magnitude meteors at altitudes of 90–120 km, which corresponds to about 1 cm size meteoroids in the case of Leonid entry speeds of 72 km/s. These are about 5 magnitudes fainter (a factor of 100 in mass less) than those studied from traditional photographic spectroscopy techniques. This is small enough to have the required rarefied flow field that characterizes meteor conditions for the bulk of meteoroid mass influx (Jenniskens *et al.*, 2000a).

The AF-S Nikkor f2.8/300D IF-ED 300-mm telephoto lens collection optics determined the field of view (5°) and the short wavelength cutoff of sensitivity, which extended down to about 360 nm. The grating dispersion was chosen in order to be able to capture any section of the zero, first, and full second order spectrum (Fig. 1). Second order refers to the integer wavelength difference of 2 for diffractions from two neighboring grating grooves. Based on this, we chose an 11×11 -cm plane transmission grating #35-54-20-660 with aluminum coating on 12-mm BK7 substrate manufactured by Richardson Grating Laboratory (Rochester, NY). We did not use an order separation filter, a holder for which is provided by the telephoto lens. Without such an order separation filter, the near-UV part of the third order spectrum is also captured, which overlaps the second order spectrum above 540 nm ($3 \times 360 \text{ nm} = 2 \times 540 \text{ nm}$). Grating and detector were positioned such that the dispersion occurred along the rows of the CCD. We measured a dispersion of 540 \AA/mm and blaze wavelength of 698 nm (34°). This configuration provided a full second order spectrum out to about 925 nm. The factory grating specifications suggested a good sensitivity out to 1.1 \mu m , but we found that the grating efficiency fell off rapidly above 850 nm. Figure 3 shows the response curves for the camera cali-

brated for various orders, which were measured by using an approximate point source (an optical fiber manufactured by Ocean Optics) illuminated with a mercury-argon lamp (wavelength calibration) and a tungsten lamp (absolute intensity calibration). The measured efficiencies have been scaled to the product of the factory response curve for the transmission grating, the transmission of the camera lens, and the CCD quantum efficiency (dashed line, Fig. 3).

The response curve shown in Fig. 3 does not include the effects of (a) vignetting (or flatfielding) or (b) the geometric correction (a simple cosine function with angle of incidence) for the orientation of the grating relative to the direction of the meteor. By measuring the response of the instrument to a homogeneously illuminated flat

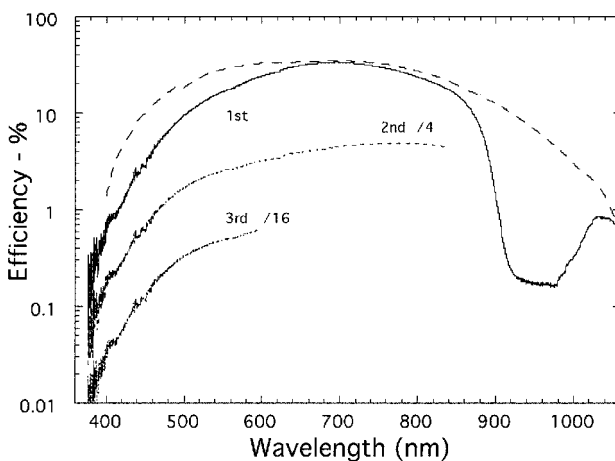


FIG. 3. Measured spectral response curves for first (1st), second (2nd), and third (3rd) order. The second and third orders are scaled down for comparison. The dashed line shows the theoretical response for the combined factory given grating efficiency, CCD quantum efficiency, and camera optics transparency.

surface we found that vignetting varied as a function of row and pixel position. This allowed us to determine the flatfielding intensity calibration correction factor (f) for a given position of the spectrum on the CCD. Two examples are shown in Fig. 4, each representing the mean over a band of CCD rows.

The position of the meteor on the sky and the choice of focus determined what part of the spectrum was recorded. Together with its encasing, the camera left an effective hunting ground of a strip of sky 5° wide and up to 88.6° from the forward direction (Fig. 1). The wavelength scale was close to linear over the full range, which spanned about 13,600 pixels:

$$\lambda \text{ (nm)} = 15.737 + 0.13382 \times \text{pixel} \quad (1)$$

A small 2 nm residual, described by the following second order polynomial, remained:

$$\lambda \text{ (observed - calculated) (nm)} = 10.638 - 0.0030227 \text{ pix} + 1.8322\text{e-}7 \times \text{pix} \times \text{pix} \quad (2)$$

For each individual spectrum, the scale was also nearly linear, and the pixel position of higher-order lines was simply a multiple of the pixel position at first order.

The highest possible resolution was obtained only when the meteor moved nearly perpendicular to the dispersion direction. A 4-pixel binning

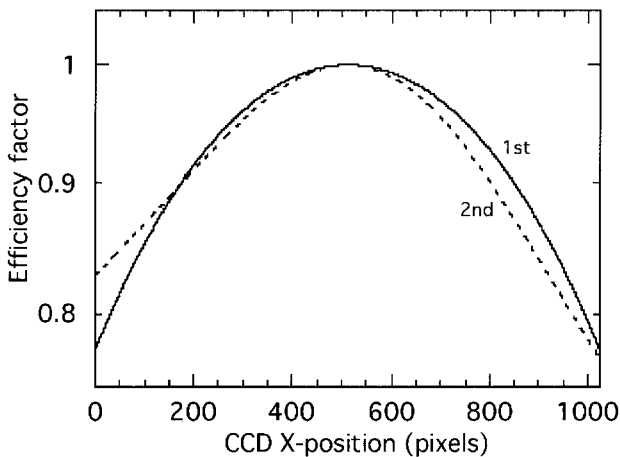


FIG. 4. Examples of vignetting in the camera for two different positions of the spectrum on the CCD. The first example applies to a band near the upper edge of the CCD frame. The second example is that valid for the position of the spectrum in Fig. 2.

was applied perpendicular to the dispersion direction to shorten the readout time, but this also decreased the resolution if the meteor did not move perpendicular to the dispersion direction. Unfortunately, the meteor orientation varies as a function of the angle on the sky and the left/right position relative to the viewing direction in the field of view. Under optimal conditions the full width at half-maximum (FWHM) spectral resolution in third order was as low as 1.8 \AA , which outperforms photographic spectral analysis techniques by a factor of 3.

RESULTS

The instrument was deployed during the intense 2001 Leonid meteor storm over the continental United States onboard the USAF/418th FLTS-operated NKC-135 "FISTA" research aircraft during the 2001 Leonid MAC mission at the time of the intense November 18th 10:40 universal time (UT) Leonid storm peak (Jenniskens and Russell, 2003).

Figure 2 shows our best result, a Leonid with a brief terminal flare, which appeared in a west-northwestern direction while flying over Little Rock, AR, at 09:05:58 UT, November 18 (92.97W , $+34.80\text{N}$, 37,000 ft). No meteor trajectory information is available from a stereoscopic perspective, because this was a single-plane mission, but the typical altitude at which such meteors end is $93 \pm 5 \text{ km}$ (Jenniskens *et al.*, 1998; Betlem *et al.*, 2000). While most of the spectrum consists of second order lines of sodium, third order lines of ionized calcium are readily identified and very strong. The region shortward of the sodium lines is dominated by intrinsically bright third order iron lines, which were detected despite the factor of 50 lower instrumental sensitivity for third order lines (Fig. 3).

The spectrum shown in Fig. 3 is slightly out of focus at one side of the CCD because of a small misalignment of the optics and CCD plane. As a result, the spectral resolution increases from a FWHM = 1.3 \AA at 370 nm to about 2.4 \AA at 410 nm. This does not affect the analysis of the data other than to require line profile integration prior to comparing relative intensities. The sodium emissions detected above this main portion of the spectrum on the CCD frame are due to the persistent afterglow or recombination line emission from sodium atoms released at a time prior to the

start of the exposure. No correction was made for this (small) contribution to the main spectrum.

After summing all relevant rows, we found that emission lines were on top of a continuum emission, identified as the First Positive Band of N_2 , observed in second order (Fig. 5). No known second or third order molecular band from atmospheric emissions, other than that of CN, was expected in the region around the CN band head. After correction for second order instrument response (Fig. 3), we fit the N_2 band contour to the whole spectrum. The N_2 band contour defined the background level. A small correction for instrument response to the remaining iron lines was made by subtracting the N_2 band contour and correcting the resulting spectrum in a manner appropriate for the third order response (Fig. 3).

The CN molecular band

Once instrument and background corrections were made we focused our attention on the third order spectrum around 388 nm (Fig. 6). The new third order spectrum resolved the weaker iron lines considerably as compared with our earlier first order spectra (Rairden *et al.*, 2000). The expected Fe line emission spectrum, shown as a dashed line in Fig. 6, was calculated for excitation temperatures of 4,300 and 4,500 K, using all neutral iron lines in the NIST Atomic Spectra Database Version 2.0 (NIST Standard Reference Database #78). A comparison of the observed and calculated emission lines established their iden-

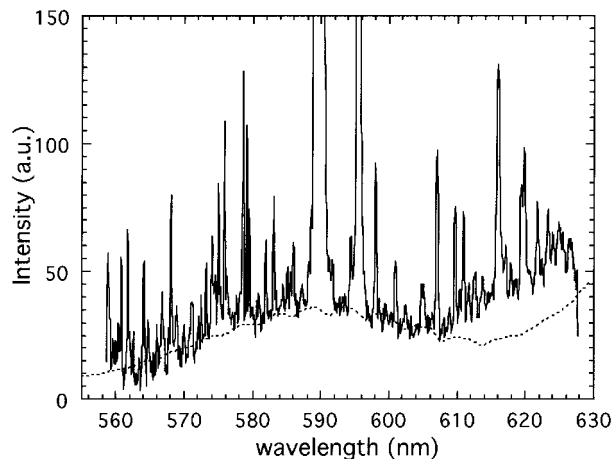


FIG. 5. Extracted spectrum of Fig. 2, after correction for instrument response and vignetting. The dashed line shows the contribution from the first positive band of N_2 in second order.

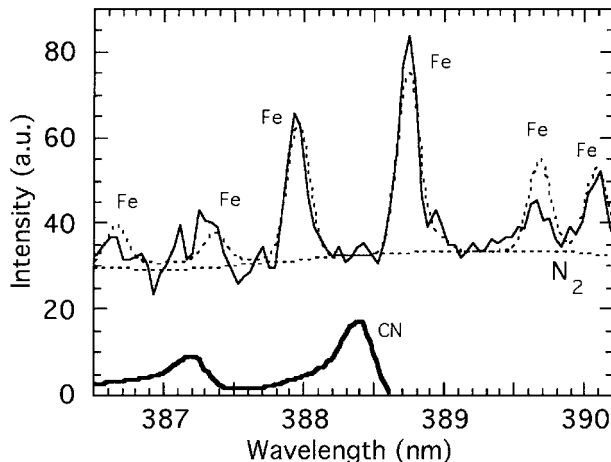


FIG. 6. Detail of Fig. 5, showing the position of the CN band and the iron lines in third order. A model spectrum at 4,300 K of iron atom line emission is shown by a dashed line. The continuum background is the band contour of N_2 in second order. The thick line is a theoretical profile of the CN band for air plasma at 4,300 K and instrumental broadening FWHM = 1.8 Å.

tity and showed that weak iron lines did not contribute to the background continuum. It should be noted that second order iron lines are present elsewhere in the spectrum.

As indicated in Fig. 6 two iron lines bracket the position of the CN molecular band. Because of the absence of any additional faint line emissions in this region, an upper limit on the CN abundance could be established. Though the CN band might have in fact been detected as a small bump, it is at the noise level of the spectrum.

The relative abundance of CN molecules versus iron atoms was calculated using the NEQAIR2 model of heated air in thermodynamic equilibrium (Laux, 1993; Park *et al.*, 1997). The CN band profile for a resolution of 1.8 Å FWHM is shown in Fig. 6. The band head at 388.44 nm is unresolved, with its width reflecting the instrument profile. With I_{CN} equal to the total integrated emission intensity of CN in the range 375–393 nm, and I_{Fe} equal to the total integrated emission intensity of all third order Fe lines in the range 381.3–386.7 nm, we calculated for $T = 4,500$ K that $I_{Fe}/n_{Fe} = 3.24 \times 10^{-16}$ W/sr and $I_{CN}/n_{CN} = 5.58 \times 10^{-17}$ W/sr, where n_{Fe} is the total concentration of Fe atoms in cm^{-3} and n_{CN} is the total concentration of CN molecules/ cm^3 . For $T = 4,300$ K, $I_{Fe}/n_{Fe} = 2.13 \times 10^{-16}$ W/sr and $I_{CN}/n_{CN} = 3.93 \times 10^{-17}$ W/sr. To calculate these values we assumed that the emitting levels were in

Boltzmann equilibrium with the ground state of Fe and CN at the given temperature. These are concentrations per total Fe atoms and total CN molecules (that is, not per molecule of CN in the excited electronic B state).

From these calculations, we found that the ratio of the total number of atoms of CN and Fe in the meteor plasma was $n_{\text{CN}}/n_{\text{Fe}} \leq 0.017$ for an excitation temperature of 4,500 K (or ≤ 0.019 for an excitation temperature of 4,300 K). The largest uncertainty was caused by the position of the background level. However, given the good fit of the N_2 band contour to the overall spectrum shortward of 590 nm (Fig. 5), a conservative error of less than 50% places the upper limit at $n_{\text{CN}}/n_{\text{Fe}} \leq 0.03$.

An even more precise upper limit was derived from a Geminid spectrum obtained during the 2001 Geminid shower with the same instrument deployed from a ground site at Fremont Peak Observatory, California (Fig. 7). For that spectrum, we calculated for an excitation temperature of 4,500 K that $n_{\text{CN}}/n_{\text{Fe}} \leq 0.011$ (or 0.012 at 4,300 K). However, Geminid meteoroids frequently approach the Sun to within 0.14 AU, which heats the meteoroids every 1.6 years to at least $T = 510$ K (the temperature of small zodiacal cloud meteoroids) and possibly as high as 1,800 K if the larger meteoroids are more like a black body (Levasseur-Regourd *et al.*, 2000). This is hot enough to change their morphology into more compact objects and can result in the loss of some or all of the organic matter.

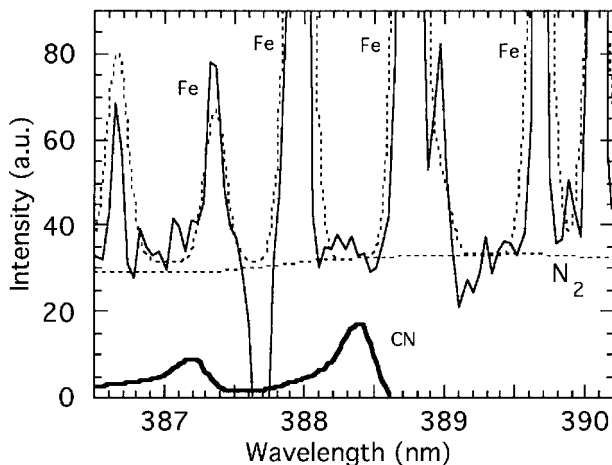


FIG. 7. Detail of the 08:41:27 UT Geminid meteor spectrum observed on December 13, 2001, with symbols and lines the same as in Fig. 6.

The more intense Geminid spectrum confirms that no weak second or third order atomic lines of any kind are present at the position of the CN band. Hence, we conclude that the meteor plasma responsible for most of the Leonid meteor's emission contains ≤ 1 CN molecule per 30 Fe atoms. This result improves by more than a factor of 10 the upper limit of 1 CN per 3 Fe atoms found earlier by Rairden *et al.* (2000). These numbers are significantly less than expected. If all of the nitrogen in the complex organic matter of the comet dust was decomposed in the form of CN molecules, this would give $n_{\text{CN}}/n_{\text{Fe}} = 0.79 \pm 0.02$, based on the observed nitrogen abundance of complex organic matter in small dust grains of comet 1P/Halley (Delsemme, 1991). The observed abundance is a factor of 26 lower.

CN can also be formed by reactions in the meteor air plasma involving CO_2 and N_2 in the ambient atmosphere. Though CN formation via such aerothermochemistry is not well understood, in the case of thermodynamic equilibrium there would not be enough CN made from this mechanism to be detectable. The calculated CN abundance for a 4,300 K air plasma in local thermodynamic equilibrium at 95 km altitude equals 1.0×10^5 molecules of CN/cm³. The -2 magnitude Leonid meteor studied here has a mass of about 0.44 g, of which 0.033 g is iron (Delsemme, 1991). That iron is ablated and distributed over a path length of about 17 km (Betlem *et al.*, 2000), in a cylindrical volume of at least a 2-m radius (Boyd, 2000), which indicates a mean density of $n_{\text{Fe}} = 2 \times 10^9$ atoms/cm³ and an expected $n_{\text{CN}}/n_{\text{Fe}}$ of about 5×10^{-5} , a factor of 6 less than our detection limit.

DISCUSSION

There are several reasons why the abundance of CN in the meteor plasma can be a factor of 26 lower than expected from the decomposition of meteoric organic matter during ablation: (1) the abundance of organic matter in the dust of 55P/Tempel-Tuttle is not known; (2) the abundance of nitrogen in that organic matter is unknown; (3) the fate of organic matter in the interplanetary medium due to space weathering is not known; (4) the organic matter could have been lost at higher altitude (earlier in flight) than where the measurement was made; (5) the process of ablation could favor the release of ni-

trogen in atomic form or in the form of some other small molecules; or (6) the nitrogen could survive in the form of larger organic compounds that are not detected. The latter possibility could provide a new pathway towards prebiotic compounds. We will now consider the significance and implication of these arguments one by one.

Since the abundance of organic matter in the dust of 55P/Tempel-Tuttle is not known, it is possible that there was little or no organic matter in the Leonid particles to begin with. Consequently, the absence of nitrogen-bearing organic matter in the Leonid meteoroids may have resulted in our inability to detect CN. The only other measurement that could have detected nitrogen-bearing organic matter in the dust (as opposed to molecules in the gas phase) is *in situ* mass spectroscopy. The Leonid parent comet has not been visited. In the coma of comet 1P/Halley, nitrogen-bearing organic matter was detected in particles (the CHON particles) analyzed by the mass spectrometers on the GIOTTO and VEGA spacecraft. Because comet Halley is not the parent of the Leonid stream, it is recommended that future work focus on the meteoroids of the Orionid and eta-Aquarid streams that do originate from comet Halley. Though bright meteors from these showers are much more difficult to observe, much the same result would be expected. The Leonid parent comet is remarkable only because it passes so close to Earth's orbit. Most importantly, since 55P/Tempel-Tuttle is in a Halley-type orbit and it should originate from the Oort cloud just as 1P/Halley, there is no reason to expect that it is less rich in organic matter.

For the same reason, there is no reason to expect that the nitrogen content or composition of the organic matter would differ from that of 1P/Halley. Halley dust is as rich in nitrogen than primitive meteorites. Though the nitrogen content in the organic matter of comet Halley has been questioned because of calibration problems with the detectors, there is no reason to expect there to be more nitrogen in the less primitive meteorites. The heating and irradiation that alter the organics in meteorites tend to evolve the organic matter towards materials less rich in nitrogen and oxygen (Jenniskens *et al.*, 1993).

It is unknown how the organic content changes with dust grain size and exposure to the planetary medium; hence the fate of the organic matter in the interplanetary medium is not known. However, we know when the observed Leonids

were ejected from the parent comet: in 1767. The 09:05:58 UT Leonid meteoroid never came closer to the Sun than 0.976 AU and remained in the interplanetary medium only for 225 years (seven orbits), most of that time far from the Sun.

Might the organic matter have been lost in the Earth's atmosphere early in the trajectory at higher altitudes, when the meteoroid first warmed up to above the evaporation and decomposition temperature of $T \sim 700$ K? This scenario was proposed by Elford *et al.* (1997), who observed that radar meteors are initially detected at heights up to ~ 140 km. They concluded that a more volatile component than stony minerals must be ablating at those heights. The specific case of fast Leonids was discussed by Steel (1998), who calculated the altitude of evaporation for a range of small organic compounds with relatively low sublimation temperatures, finding ablation heights in excess of 140 km for some compounds. However, the light curve of bright Leonid fireballs above 136 km was found to be very flat and starting at about 200 km (Spurný *et al.*, 2000a,b), which is inconsistent with the light curves calculated by Elford *et al.* (1997) and Steel (1998). At 200 km, the grains are not warm enough to evaporate the organic compounds that survived the vacuum of space.

Indeed, the Leonid studied here shows no sign of *differential ablation* of minerals in order of their volatility. The elements Na, Fe, Mg, and Ca are lost in the same proportion (Fig. 2), except for the last wisp of matter after the catastrophic fragmentation during the terminal flare (a topic of future work). Sodium is at least partially found in more volatile minerals than those containing magnesium and iron. Though some smaller Leonid meteoroids are known to lose sodium early in their trajectory, this is only found in fragile cometary shower meteoroids small enough to expose the minerals efficiently to the impinging air flow (Borovička *et al.*, 1999). Sodium may be contained in the larger Leonids at lower altitudes because of the limited time available for inward diffusion of heat and outward diffusion of molecules. Although the organic and mineral components are separate entities, they are intimately mixed down to very small size scales in comet Halley dust, and the diffusion of those volatile compounds out of the grains (if at all possible) will take time. Such considerations are not included in the model of Steel (1998). Hence, the organic matter is not lost early in flight.

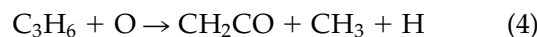
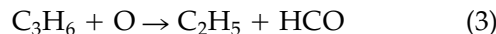
The low CN abundance in the air plasma of the 09:05:58 UT Leonid meteoroid cannot be understood by merely allowing some fraction of nitrogen to escape as N, NH, N₂, NH₃, NH₂, NCO, NO, HNO, or HCN, *etc.* The configuration of N in the complex organic matter of meteoroids is not known. However, from meteorite and micrometeorite studies (where much organic matter has been altered by aqueous alteration processes), we know that a significant fraction of the nitrogen is contained in the organic framework (see references in Keller *et al.*, 1995; Greenberg, 2000). Aqueous alteration tends to move nitrogen from the organic framework to functional groups such as -NH. In cometary matter, no aqueous alteration has occurred. So, if N is in the framework in meteorite organics, it should also exist in the organic framework of cometary matter. Coal-bound nitrogen also resides principally in heterocyclic ring moieties, mostly five-membered pyrrolic rings and six-membered pyridinic rings (Smith *et al.*, 1994; Zhang, 2001). In pyrolysis studies of tar such nitrogen is observed to escape, predominantly in the form of HCN and NH₃ (Chen and Niksa, 1992; Nelson *et al.*, 1992; Ledesma *et al.*, 1998). Ammonia is a product of amino compounds. At the low pressure and high temperature conditions in meteor plasma, CN radicals rather than HCN are stable, and ammonia will break apart. Small hydrocarbon radicals higher than CN are so excited by their formation that they rapidly fission into lower products, leaving only the thermally stable single and double carbon radicals, unless prevented by rapid radiative cooling. Carbon atoms are present too, but at lower abundance because of thermodynamic considerations. The carbon atoms react with N₂ to form CN. At 4,400 K, CN and N₂ are only partially dissociated, while O₂ and CO (and CO₂) are fully dissociated, leading to high abundances of CN if the plasma is in local thermodynamic equilibrium (Jenniskens *et al.*, 2000a). Only if oxygen plays a role in extracting the nitrogen *after* ablation, then NO_x compounds are expected to dominate. Hence, CN should be a significant product of the ablation of organic matter, unless the organic matter is released as larger compounds.

We conclude that the most likely explanation for the lack of CN molecules in the meteor plasma is that meteoric organic matter is lost in the form of a large range of relatively complex molecules, or perhaps as an amorphous carbon solid with embedded metal as proposed by Brownlee *et al.*

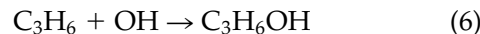
(2002). Until now, no evidence has been found of such meteoric soot particles in the Earth environment, and it remains unknown how well the heating conditions in the electron microscope used in the experiment by Brownlee *et al.* (2002) mimic the actual physical conditions during meteoroid ablation.

If the organic matter survives as large molecules, this implies that bonds are prevented from breaking by rapid radiative cooling or because heat is carried away by collisional fragments that transfer much of the kinetic energy to the ambient air. The latter mechanism is the more likely one and comes about because of conservation of momentum in a collision. The result is that the lower mass fragment will carry most of the kinetic energy, and it will carry proportionally more kinetic energy as the mass of the main residue increases. This is an indirect form of the collisional cooling that facilitates laser desorption, a technique widely used in the laboratory to study high-molecular-mass polyaromatic hydrocarbons in the gas phase and for detecting complex organic compounds in meteorites.

Once released from the surface, a single collision will cause the molecule to slow down and lag behind relative to the meteoroid. The molecule then is slowed to thermal speeds in another ~10 collisions and remains in the warm wake of the meteor for ~50 collisions. Only about 3% of air collisions with atoms are inelastic (Öpik, 1958). For collisions with molecules, that percentage is higher, but only a fraction of collisions will result in chemical reactions. Typical reactions that occur in the burning of propene, for example, are (*e.g.*, Marinov *et al.*, 1996):



Hydrogen can react in an early Earth-like atmosphere with CO₂ to form OH radicals, which continue to attack the organic matter via reactions such as:



Radical attack can also lead to the growth of carbon chains by polymerization reactions in the rare case that organic compounds meet. Hence, the result of chemistry in the meteor plasma is

likely a product of relatively high molecular mass that is enriched in oxygen (and nitrogen). Such compounds are much more interesting for prebiotic chemistry than the very-high-molecular-mass, functional group-poor compounds found in (micro-) meteorites.

CONCLUSIONS

We conclude that complex organic matter in meteoroids does not fully decompose into diatomic constituents or atoms during the most intense phase of meteor ablation, and that meteoric organics are most likely lost in the form of large molecular fragments cooled by radiative cooling and the loss of hot molecular fragments. The product of chemical interactions in the air plasma in the meteoroid's wake is most likely a large variety of molecules and radicals that are chemically altered, functional group-enriched, molecular fragments and condensation products.

This result marks an alternative route to prebiotic molecules from organic matter contributed to the Earth by particles at the peak of the mass-frequency distribution of infalling matter. At the time of the origin of life, there would have been typically as much extraterrestrial matter impacting Earth in the form of dust as in the form of large asteroids and comets (Ceplecha, 1992), if they arrived on elliptic orbits to have time to deposit debris. Moreover, the organic content of those meteoroids should have been similar to that of the impacting parent bodies, with the exception of the volatile compounds lost during dust ejection. This makes the product of meteor ablation and subsequent chemistry potentially the dominant source of complex organic molecules on the early Earth at the time of the origin of life.

ACKNOWLEDGMENTS

We thank George Flynn and an anonymous referee for discussions that helped improve this paper. The cooled CCD slit-less spectrograph was developed with support of the NASA Ames Research Center's Director's Discretionary Fund during preparation of the Leonid MAC missions. We thank Mike Koop (California Meteor Society) and Gary Palmer for technical support at various stages in this project. The 2001 Leonid MAC mission was sponsored by NASA's Astrobiology

ASTID and Planetary Astronomy programs. The 2001 mission was executed by the USAF 418th Flight Test Squadron of Edwards AFB in California, with logistic support from the SETI Institute.

ABBREVIATIONS

CCD, charge coupled device; FWHM, full width at half-maximum; IDP, interplanetary dust particle; MAC, Multi-Instrument Aircraft Campaign; UT, universal time.

REFERENCES

- Abe, S., Yano, H., Ebizuka, N., and Watanabe, J.-I. (2000) First results of high-definition TV spectroscopic observations of the 1999 Leonid meteor shower. *Earth Moon Planets* 82-83, 369-377.
- Anders, E. (1989) Pre-biotic organic matter from comets and asteroids. *Nature* 342, 255-257.
- Betlem, H., Jenniskens, P., Spurny, P., Docters van Leeuwen, G., Miskotte, K., Ter Kuile, C.R., Zerubin, P., and Angelos, C. (2000) Precise trajectories and orbits of meteoroids from the 1999 Leonid meteor storm. *Earth Moon Planets* 82-83, 277-284.
- Borovička, J., Stork, R., and Bocek, J. (1999) First results from video spectroscopy of 1998 Leonid meteors. *Meteoritics Planet. Sci.* 34, 987-994.
- Boyd, I.D. (2000) Computation of atmospheric entry flow about a Leonid meteoroid. *Earth Moon Planets* 82-83, 93-108.
- Brownlee, D.E., Joswiak, D.J., Kress, M.E., Taylor, S., and Bradley, J. (2002) Survival of carbon in moderately to strongly heated IDPs and micrometeorites [abstract 1786]. In *33rd Lunar and Planetary Science Conference*, LPI Contribution No. 1109, Lunar and Planetary Institute, Houston.
- Ceplecha, Z. (1971) Spectral data on terminal flare and wake of double-station meteor No. 38421 (Ondrejov, April 21, 1963). *Bull. Astron. Inst. Czech.* 22, 219-304.
- Ceplecha, Z. (1992) Earth influx of interplanetary bodies. *Astron. Astrophys.* 263, 361-366.
- Chen, J.C. and Niksa, S. (1992) Coal devolatilization during rapid transient heating 1. Primary devolatilization. *Energy Fuels* 6, 254-264.
- Chyba, C.F. and Sagan, C. (1992) Endogenous production, exogenous delivery and impact shock synthesis of organic molecules: An inventory for the origins of life. *Nature* 355, 125-132.
- Chyba, C.F. and Sagan, C. (1997) Comets as a source of prebiotic organic molecules for the early Earth. In *Comets and the Origin and Evolution of Life*, edited by P.J. Thomas, C.F. Chyba, and C.P. McKay, Springer Verlag, New York, pp. 147-173.
- Delsemme, A.H. (1991) Nature and history of the organic compounds in comets: an astrophysical view. In *Astro-*

- physics and Space Science Library, Vol. 167: Comets in the Post-Halley Era, Vol. 1*, edited by R.L. Newburn, M. Neugebauer, and J.H. Rahe, Kluwer, Dordrecht, The Netherlands, pp. 377–428.
- Delsemme, A.H. (1992) Cometary origin of carbon, nitrogen and water on the Earth. *Origins Life* 21, 279–298.
- Eldford, W.G., Steel, D.I., and Taylor, A.D. (1997) Implications for meteoroid chemistry from the height distribution of radar meteors. *Adv. Space Res.* 20, 1501–1504.
- Flynn, G.J., Keller, L.P., Jacobsen, C., Wirick, S., and Miller, M.A. (2000) Organic carbon in interplanetary dust particles. In *ASP Conference Series, Vol. 213: A New Era in Bioastronomy*, Astronomical Society of the Pacific Press, San Francisco, pp. 191–194.
- Fristrom, R.M. (1995) *Flame Structure and Processes*, Oxford University Press, New York.
- Glavin, D.P. and Bada, J.L. (1999) The sublimation and survival of amino acids and nucleobases in the Murchison meteorite during a simulated atmospheric heating event [abstract 1085]. In *30th Lunar and Planetary Science Conference*, LPI Contribution No. 964, Lunar and Planetary Institute, Houston.
- Greenberg, J.M. (2000) From comets to meteors. *Earth Moon Planets* 82–83, 313–324.
- Jenniskens, P. and Butow, S.J. (1999) The 1998 Leonid multi-instrument aircraft campaign—an early review. *Meteoritics Planet. Sci.* 34, 933–943.
- Jenniskens, P. and Russell, R.W. (2003) The 2001 Leonid Multi-Instrument Aircraft Campaign—an early review. *ISAS Rep. SP* 15, 3–15.
- Jenniskens, P., Baratta, G.A., Kouchi, A., de Groot, M.S., Greenberg, J.M., and Strazzulla, G. (1993) Carbon dust formation on interstellar grains. *Astron. Astrophys.* 273, 583–600.
- Jenniskens, P., de Lignie, M., Betlem, H., Borovicka, J., Laux, C.O., Packan, D., and Krüger, C.H. (1998) Preparing for the 1998/99 Leonid Storms. *Earth Moon Planets* 80, 311–341.
- Jenniskens, P., Wilson, M.A., Packan, D., Laux, C.O., Boyd, I.D., Popova, O.P., and Fonda, M. (2000a) Meteors: A delivery mechanism of organic matter to the early Earth. *Earth Moon Planets* 82–83, 57–70.
- Jenniskens, P., Butow, S.J., and Fonda, M. (2000b) The 1999 Leonid Multi-Instrument Aircraft Campaign—an early review. *Earth Moon Planets* 82–83, 1–26.
- Jessberger, E.K. and Kissel, J. (1991) Chemical properties of cometary dust and a note on carbon isotopes. In *Astrophysics and Space Science Library, Vol. 167: Comets in the Post-Halley Era, Vol. 2*, edited by R.L. Newburn, M. Neugebauer, and J.H. Rahe, Kluwer, Dordrecht, The Netherlands, pp. 1075–1092.
- Keller, L.P., Thomas, K.L., Bradley, J.P., and McKay, D.S. (1995) Nitrogen in interplanetary dust particles. *Meteoritics* 30, 526–527.
- Kissel, J. and Krueger, F.R. (1987) The organic component in dust from comet Halley as measured by the PUMA mass spectrometer onboard Vega 1. *Nature* 326, 755–760.
- Koidl, P., Wild, Ch., Dischler, B., Wagner, J., and Ramsteiner, M. (1989) Plasma deposition, properties and structure of amorphous hydrogenated carbon films. *Materials Science Forum* 52–53, 41–70.
- Laux, C.O. (1993) Optical diagnostics and radiative emission of high temperature air plasmas [Ph.D. Dissertation], HTGL Report T288, Stanford University, Stanford, CA.
- Ledesma, E.B., Li, C.Z., Nelson, P.F., and Mackie, J.C. (1998) Release of HCN, NH₃, and HNCO from the thermal gas-phase cracking of coal pyrolysis tars. *Energy Fuels* 12, 536–541.
- Levasseur-Regourd, A.C., Mann, I., Dumont, R., and Hanner, M.S. (2000) Optical and thermal properties of interplanetary dust. In *Interplanetary Dust*, edited by E. Gruen, B.Å.S. Gustafson, S. Dermott, and H. Fechtig, Springer Verlag, Berlin, pp. 57–94.
- Love, S.G. and Brownlee, D.E. (1993) A direct measurement of the terrestrial mass accretion rate of cosmic dust. *Science* 262, 550–553.
- Marinov, N.M., Pitz, W.J., Westbrook, C.K., Castaldi, M.J., and Senkan, S.M. (1996) Modeling of aromatic and polycyclic aromatic hydrocarbon formation in premixed methane and ethane flames. *Combust. Sci. Technol.* 116–117, 211–287.
- Maurette, M. (1998) Carbonaceous micrometeorites and the origin of life. *Origins Life Evol. Biosphere* 28, 385–412.
- Maurette, M., Duprat, J., Engrand, C., Gounelle, M., Kurat, G., Matrajt, G., and Toppani, A. (2000) Accretion of neon, organics, CO₂, nitrogen and water from large interplanetary dust particles on the early Earth. *Planet. Space Sci.* 48, 1117–1137.
- Nelson, P.F., Buchley, A.N., and Kelly, M.D. (1992) Functional forms of nitrogen in coals and the release of coal nitrogen as NO_x precursors (HCN and NH₃). In *24th Symposium on Combustion*, The Combustion Institute, Pittsburgh, pp. 1259–1267.
- Öpik, E. (1958) *Physics of Meteor Flight in the Atmosphere*, Interscience Publishers, New York.
- Oró, J. (1961) Comets and the formation of biochemical compounds on the primitive Earth. *Nature* 190, 389–390.
- Park, C.S., Newfield, M.E., Fletcher, D.G., Gökçen, T., and Sharma, S.P. (1997) *Spectroscopic Emission Measurements Within the Blunt-Body Shock Layer in an Arc-Jet Flow*, AIAA 97–0990, American Institute of Aeronautics and Astronautics, Reston, VA.
- Rairden, R.L., Jenniskens, P., and Laux, C.O. (2000) Search for organic matter in Leonid meteoroids. *Earth Moon Planets* 82–83, 71–80.
- Russell, R.W., Rossano, G.S., Chatelain, M.A., Lynch, D.K., Tessensohn, T.K., Abendroth, E., Kim, D., and Jenniskens, P. (2002) Mid-infrared spectroscopy of persistent Leonid trains. *Earth Moon Planets* 82–83, 429–438.
- Smith, K.L., Smoot, L.D., Fletcher, T.H., and Pugmire, R.J. (1994) *The Structure and Reaction Processes of Coal*, Plenum Press, New York.
- Spurný, P., Betlem, H., van't Leven, J., and Jenniskens, P. (2000a) Atmospheric behavior and extreme beginning heights of the thirteen brightest photographic Leonid

- meteors from the ground-based expedition to China. *Meteoritics Planet. Sci.* 35, 243–249.
- Spurný, P., Betlem, H., Jobse, K., Koten, P., and van't Leven, J. (2000b) New type of radiation of bright Leonid meteors above 130 km. *Meteoritics Planet. Sci.* 35, 1109–1115.
- Steel, D. (1998) The Leonid Meteors: Compositions and consequences. *Astron. Geophys.* 39, 24–26.
- Toppani, A., Libourel, G., Engrand, C., and Maurette, M. (2001) Experimental simulation of atmospheric entry of micrometeorites. *Meteoritics Planet. Sci.* 36, 1377–1396.
- Zhang, H. (2001) Nitrogen evolution and soot formation during secondary coal pyrolysis [Ph.D. Thesis], Department of Chemical Engineering, Brigham Young University, Salt Lake City, UT.

Address reprint requests to:

P. Jenniskens

Center for the Study of Life in the Universe

SETI Institute

2035 Landings Drive

Mountain View, CA 94043

E-mail: pjenniskens@mail.arc.nasa.gov