

NITROGEN ABUNDANCE IN COMET HALLEY<sup>1</sup>

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## ABSTRACT

An inventory of nitrogen compounds observed in the coma of comet Halley is presented, and the elemental nitrogen abundance in the nucleus is derived. The dust fraction of the coma is found to contain virtually all (90%) of the elemental nitrogen. In the gas coma we find that  $\text{NH}_3$  and  $\text{CN}$  contain most of the nitrogen, and that  $(\text{N/O})_{\text{ice}} \sim 0.004$ , accounting for  $\sim 10\%$  of the nitrogen inventory in the comet. Molecular nitrogen accounts for only  $\sim 7\%$  of the nitrogen containing volatiles and less than 0.1% of the total volatile content of the comet. The elemental nitrogen abundance in the ice component of the nucleus is deficient by a factor  $\sim 75$  relative to the solar photosphere. For a mass ratio, dust/gas  $\sim 2$ , we find that the total (dust + gas) elemental nitrogen abundance in comet Halley is depleted by a factor  $\sim 6$  relative to the Sun. A correction to the nitrogen inventory for undetected species (e.g., ammonium salts and polymers) would reduce the nitrogen deficiency in the comet gases by a factor of  $\sim 2$  at most, and not significantly affect the total (gas + dust) nitrogen inventory in the comet. The fact that the dust component contains most of the nitrogen-bearing compounds in comet Halley means that the volatile and refractory solids in the nucleus had different evolutionary histories and probably did not result from a simple condensation sequence in the solar nebula.

If  $\text{N}_2$  were the most abundant nitrogen-containing species in the early protosolar cloud, then the depletion of nitrogen in the gas coma of the comet relative to the Sun can probably be explained by physical fractionation of  $\text{N}_2$  during the condensation process as originally suggested by Geiss, or by subsequent preferential diffusion of molecular nitrogen from the cometary ices, or by both. If, however, the low nitrogen abundance in comet Halley represents the actual N content of gas and dust in the comet-forming region, then the nucleus must be comprised of material with a different nucleosynthesis history from the rest of the solar system.

The elemental nitrogen deficiency in the comet ices indicates that the chemical partitioning of  $\text{N}_2$  into  $\text{NH}_3$  and other nitrogen compounds during the evolution of the solar nebula cannot account completely for the low abundance ratio,  $\text{N}_2/\text{NH}_3 \sim 0.1$ , observed in the comet. Moreover, the low and uniform ammonia/water abundance ratios among a small sample of comets indicates that comet nuclei were probably not subjected to significant episodic accretion of  $\text{NH}_3$ -rich material from the giant planet subnebulae. Rather, we suggest that the low  $\text{N}_2/\text{NH}_3$  ratio in comet Halley may be explained simply by physical fractionation or thermal diffusion, or both.

*Subject headings:* abundances — comets — molecular processes — stars: formation

## I. INTRODUCTION

The composition of cometary ices can provide direct information about the formation and evolution of the primordial solar nebula. A fundamental question in studies of planet formation regards the extent of chemical and physical processing which occurs in an accreting protoplanetary gas and dust disk. Comets are probably composed of a combination of preserved interstellar grains plus volatiles which condensed from gases in the primordial solar nebula 4.5 billion years ago (e.g., Whipple 1987; Greenberg 1982; Fegley 1990). New techniques used to study comet Halley have greatly improved our knowledge of the chemical composition of one comet. In 1986 March several spacecraft flew through the comet coma carrying experiments which sampled the coma dust and gas and telemetered the data to Earth. The Soviet *Vega* spacecraft (Sagdeev *et al.* 1986) passed sunward and within  $\sim 8500$  km of the nucleus carrying the PUMA 1 dust analyzer (Sagdeev *et al.* 1987; Jessberger and Kissel 1990), and the IKS-VEGA infrared spectrometer (e.g., Combes *et al.* 1986, 1988; Encrenaz and Knacke 1990). The

European Space Agency *Giotto* spacecraft (Reinhard 1986) passed within  $\sim 600$  km on the sunward side of the comet nucleus carrying two ion mass spectrometers (e.g., Balsiger *et al.* 1986; Krankowsky *et al.* 1986; Wegmann *et al.* 1987). The spacecraft data contributed an immense amount of new compositional information which complemented the ground-based spectroscopic results. Recent analyses of these comet Halley data indicate that the dust component of a comet coma consists of silicate ( $\sim 67\%$ ) and refractory organic material ( $\sim 33\%$ ) having elemental abundances of the rock-forming elements (except Fe and Si) roughly comparable to those found in primitive carbonaceous chondrites (Kissel and Krueger 1987; Jessberger, Christoforidis, and Kissel 1988; Anders and Grevesse 1989; Jessberger and Kissel 1990). On the other hand, significant enhancements in the light-element abundances (H, C, N, and O) were found in the comet dust compared with the CI chondrites (Jessberger and Kissel 1990).

Molecular abundance analyses of comet Halley indicate that the gas coma consisted mostly of  $\text{H}_2\text{O}$  ( $\sim 90\%$ ) with a mixture of  $\text{CO}$  ( $\sim 5\%$ ) and  $\text{CO}_2$  ( $\sim 3\%$ ), and other minor constituents such as  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{CO}$  (e.g., Krankowsky *et al.* 1986; Balsiger *et al.* 1987; Eberhardt *et al.* 1987; Mumma *et al.* 1986; Snyder, Palmer, and DePater 1989; Wyckoff, Tegler, and Engel 1991a). The relative abundances of most of the molecu-

<sup>1</sup> Observations obtained with the Kitt Peak and Cerro Tololo Inter-American Observatories, which are operated by the Association of Universities for Research in Astronomy, Inc., under contract with the National Science Foundation.

lar trace species have not yet been accurately determined in the ice components of either comet nuclei or interstellar grains. Of the above trace species only  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{CO}$  have been directly observed spectroscopically in comets (Feldman 1983; Weaver, Mumma, and Larson 1990; Snyder *et al.* 1989), although the ions of  $\text{N}_2$  and  $\text{CO}_2$  have long been observed in ground-based spectra (e.g., Wyckoff 1982). Only  $\text{CO}$  is known to vary significantly in abundance among comets (Feldman 1983).

It is widely accepted that  $\text{N}_2$  is the dominant nitrogen-bearing compound in interstellar clouds (e.g., Mitchell 1984; Irvine and Knacke 1989), in spite of the fact that molecular nitrogen has not been spectroscopically detected in any astronomical source. However, observations of  $\text{H}^{15}\text{NN}^+$  do indicate that  $\text{N}_2/\text{CO} \sim 1$ , supporting the prediction of a high interstellar  $\text{N}_2$  abundance (Linke, Guélin, and Langer 1983). Solar nebula models predict that  $\text{N}_2$  would have remained the most abundant nitrogen compound in gas phase due to kinetic inhibition which would have quenched the chemical partitioning of  $\text{N}_2$  into other compounds (Lewis and Prinn 1980). Only in the environments of the giant protoplanet subnebulae (with relatively high pressures and low temperatures) would significant amounts of  $\text{N}_2$  have been converted into  $\text{NH}_3$  (Prinn and Fegley 1981, 1989). Simonelli *et al.* (1989) inferred from abundances derived for Pluto and Charon that the outer solar nebula was probably  $\text{CO}$ -rich, and argued based on Lewis and Prinn's (1980) model that  $\text{N}_2$  was likely to be the dominant nitrogen-containing compound. A similar argument regarding  $\text{N}_2$  in the solar nebula can be made from the  $\text{CO}$  abundance in comet Halley from which Encrenaz and Knacke (1990) have inferred a  $\text{CO}$ -rich solar nebula. Although  $\text{N}_2$  has not been directly detected by spectroscopy or unambiguously identified by mass spectrometry in a comet, both  $\text{N}_2^+$  and  $\text{NH}_2^+$  were observed spectroscopically in comet Halley, and used to derive  $\text{N}_2$  and  $\text{NH}_3$  abundances with reasonable accuracy for the first time in a comet. Based on a preliminary  $\text{N}_2/\text{NH}_3$  abundance ratio derived for comet Halley (Wyckoff and Theobald 1989), Prinn and Fegley (1989) suggested a mixed-component model for the nucleus composition, consisting of  $\sim 10\%$  giant planet subnebulae gases plus solar nebula volatiles.

The elemental abundances in both the dust and gas components of comet Halley have recently been considered in a variety of analyses (Jessberger *et al.* 1988; Encrenaz, d'Hendecourt, and Puget 1988; Jessberger and Kissel 1990; Delsemme 1988, 1990; Anders and Grevesse 1989; Encrenaz and Knacke 1990). The nitrogen abundance derived in some studies (Delsemme 1988, 1990) agreed within the observational uncertainties with the solar value. However, others (Geiss 1987; Encrenaz, d'Hendecourt and Puget 1988; Jessberger and Kissel 1990) have argued that nitrogen is significantly depleted in comet Halley. Here we rediscuss the elemental nitrogen abundance in the gas component of comet Halley based on recent results for  $\text{NH}_3$ ,  $\text{N}_2$ ,  $\text{NH}$ ,  $\text{HCN}$ , and  $\text{CN}$  (Schloerb *et al.* 1987; Bockelée-Morvan *et al.* 1986; Moreels *et al.* 1987; Wyckoff and Theobald 1989; Tegler 1989; Wyckoff, Tegler, and Engel 1991a; Wyckoff *et al.* 1991b; Ip *et al.* 1990). We find that the total (dust + gas) content of nitrogen in the coma is depleted by a factor  $\sim 6$  relative to the solar photosphere (at a  $2\sigma$  level of significance), and that nitrogen is deficient by a factor  $\sim 75$  in the coma volatiles (at a  $6\sigma$  level of significance). We find that nearly all of the elemental nitrogen (like carbon) is found in the dust component of the comet.

## II. OBSERVATIONS

### a) Nitrogen Inventory in the Volatile Component

The nitrogen-containing compounds observed spectroscopically in comet Halley were  $\text{NH}_2$  (Wyckoff *et al.* 1988),  $\text{HCN}$  (Schloerb *et al.* 1987),  $\text{N}_2^+$  (Wyckoff and Theobald 1989), and  $\text{NH}$  (Moreels *et al.* 1987; Wyckoff *et al.* 1991b). Atomic and molecular nitrogen as well as ammonia have never been directly detected in a comet. The nitrogen compounds which were potentially detectable by the *in situ* spacecraft ion mass spectrometer include  $\text{N}^+$ ,  $\text{NH}^+$ ,  $\text{NH}_2^+$ ,  $\text{NH}_3^+$ ,  $\text{NH}_4^+$ ,  $\text{HCN}^+$ ,  $\text{H}_2\text{CN}^+$ ,  $\text{N}_2\text{H}^+$ ,  $\text{CH}_4\text{N}^+$ ,  $\text{NO}^+$ ,  $\text{HNO}^+$  plus an assortment of heavier polyatomic nitrogen-containing species in trace amounts (Wegmann *et al.* 1987). However, due to mass redundancies, virtually no compounds detected by the *Giotto* mass spectrometers contribute uniquely to even the lowest  $m/q$  ion mass spectrometer channels. Hence the molecular and elemental abundances derived from the *in situ* data are highly model-dependent. An upper limit for the molecular nitrogen abundance,  $Q(\text{N}_2)/Q(\text{H}_2\text{O}) < 0.015$  was determined from the  $14\text{ amu } e^{-1}$  signal in the *Giotto* ion mass spectrometer (Balsiger *et al.* 1986). The signal in the  $28\text{ amu } e^{-1}$  channel of the neutral mass spectrometer was dominated by both  $\text{CO}$  and  $\text{N}_2$  for which Eberhardt *et al.* (1987) found  $Q(\text{N}_2)/Q(\text{H}_2\text{O}) < 0.1$ . A relatively large amount of  $\text{NH}_3$  ( $\sim 1\%$  to  $2\%$ ) was required to produce the  $\text{NH}_4^+$  detected by the *Giotto* mass spectrometer (Wegmann *et al.* 1987; Allen *et al.* 1987). However, we now know from ground-based observations (Tegler 1989; Wyckoff *et al.* 1991a, b; Allen *et al.* 1989) that the ammonia abundance in comet Halley was an order of magnitude less than that assumed in modeling the *Giotto* spacecraft results (Wegmann *et al.* 1987; Allen *et al.* 1987). The abundances of the dominant nitrogen-bearing compounds in comet Halley are summarized in Table 1 which has been compiled from production rates derived from ground-based spectroscopy and a reanalysis of the *in situ Giotto* mass spectrometer data by Ip *et al.* (1990).

The mean ammonia/water abundance ratio (by number) determined for four comets (Wyckoff *et al.* 1991a), including comet Halley, indicated  $Q(\text{NH}_3)/Q(\text{H}_2\text{O}) = 0.0013 \pm 0.0006$ . The abundances were found to be the same within the observational errors for the four comets. Furthermore, the pre- and post-perihelion ammonia abundances derived for comet Halley (Tegler 1989; Wyckoff *et al.* 1991a) indicated no significant variation at different depths in the nucleus (over scales of  $\sim 6\text{ m}$ ; Keller *et al.* 1987). Hence the nucleus was chemically homogeneous over this depth scale. Earlier determinations of the ammonia abundance ratios in comets were derived using the Haser (1957) model and incorrect photodissociation scale-lengths and/or fluorescence efficiencies (A'Hearn, Hanisch, and Thurber 1980; Wyckoff *et al.* 1988). Tegler (1989) has shown from the observed distribution of  $\text{NH}_2$  in the coma that the dominant source of  $\text{NH}_2$  is  $\text{NH}_3$ . The vectorial model (Festou 1981) and improved fluorescence efficiencies were used to derive the ammonia production rates by Wyckoff, Tegler, and Engel (1991a) who demonstrated that different models (Haser, vectorial, or collisional Monte Carlo) give results which agree within  $\pm 20\%$  provided the correct photodissociation lifetimes are used. An analysis (Wyckoff *et al.* 1991b) of the spatial distributions of  $\text{NH}$  and  $\text{NH}_2$  in comets Halley and Thiele demonstrated that virtually all of both species are produced by

TABLE 1  
ABUNDANCES OF NITROGEN COMPOUNDS IN VOLATILES

$X_i$	$\frac{Q(X_i)^a}{Q(H_2O)}$	References
$N_2^b$ .....	$\sim 0.0002$	1, 2
$NH_3^c$ .....	$0.002 \pm 0.001$	3, 4
$NH_2$ .....	$0.002 \pm 0.001$	3, 4
$NH$ .....	$0.002 \pm 0.001$	5
$HCN$ .....	$\left\{ \begin{array}{l} < 0.0002 \\ 0.001 \pm 0.0005 \end{array} \right.$	6, 7, 8
$CN$ .....	$0.001 \pm 0.0005$	9
$C_2N_2$ .....	$< 0.0001$	6
$CH_3CN$ .....	$< 0.0001$	6
$NH_4HCO_3$ .....	$< 0.002^d$	10
$NH_4COONH_2$ .....	$< 0.002^d$	10
$HC_3N$ .....	$< 0.0002$	10
$OCN^-$ .....	$\leq 0.0002$	11
$C \equiv N (4.45 \mu m)$ .....	$< 0.01$	12
.....	.....	13

<sup>a</sup> Ratio of production rates, species  $X_i/H_2O$ , by number.

<sup>b</sup> Not observed directly, but derived from  $N_2^+$  observations.

<sup>c</sup> Not observed directly, but derived from  $NH$  and  $NH_2$  observations.

<sup>d</sup> Not observed, but predicted by Lewis and Prinn (1980).

REFERENCES.—(1) Wyckoff and Theobald 1989; (2) this work; (3) Tegler 1989; (4) Wyckoff, Tegler, and Engel 1991a; (5) Wyckoff *et al.* 1991b; (6) Ip *et al.* 1990; (7) Schloerb *et al.* 1987; (8) Bockelée-Morvan *et al.* 1987; (9) Wyckoff *et al.* 1988; (10) Lewis and Prinn 1980; (11) Bockelée-Morvan *et al.* 1986; (12) Grim and Greenberg 1987; Encrenaz and Knacke 1990; (13) Encrenaz and Knacke 1990.

the UV photolysis sequence,



A multistep Monte Carlo model indicates that the computed branching ratios and photodissociation rates are consistent with the observed  $NH$  and  $NH_2$  spatial distributions and an ultimate and common origin for both species in  $NH_3$ . Thus in accounting for the elemental nitrogen in a comet either  $NH_2$  or  $NH$  should be counted, since both derive from the same source. Here we use the  $NH_2/H_2O$  ratio derived by Wyckoff, Tegler, and Engel (1991a).

The revised molecular nitrogen abundance given in Table 1 was determined from the same spectrum used previously (Wyckoff and Theobald 1989), but with an improved  $N_2^+$  fluorescence efficiency [ $B-X(0-0)$  band,  $g = 0.07$  photon  $s^{-1}$ ; Lutz 1989]. We have also revised the photolysis rates for  $N_2$  and  $CO$ . The photoionization rates for  $N_2$  and  $CO$  were calculated with the ultraviolet solar flux obtained from the *Solar Mesosphere Explorer* satellite on the date of the comet observation (G. Rottman 1989, private communication), and the photoabsorption cross sections were taken from references in Berkowitz (1979) and Gallagher *et al.* (1988). The  $N_2/CO$  abundance ratio was estimated from the observed column density ratio,  $N(N_2^+)/N(CO^+)$  determined from the tail spectrum of comet Halley where the  $B-X N_2^+(0-0)$  and  $A-X CO^+(3-0)$  band fluxes were measured in the 3915 Å region. We therefore assumed that photoionization was the dominant production mechanism for both species, and that the main loss mechanism for both was dissociative recombination (Schmidt *et al.* 1988). We found that the fractions of photoabsorptions resulting in photoionization (i.e., the ionization branching ratios) were 45% and 50% for  $N_2$  and  $CO$ , respectively. An abundance ratio,  $CO/H_2O = 0.1$  (Balsiger *et al.* 1986) was used in deriving

the revised value of the  $N_2/H_2O$  abundance ratio given in Table 1. The new nitrogen/ammonia ratio in comet Halley is  $Q(N_2)/Q(NH_3) \sim 0.1$  for which we estimate an accuracy of a factor of  $\sim 5$ .

The discrepancy between the  $HCN$  abundances determined from radio observations (Schloerb *et al.* 1987; Bockelée-Morvan *et al.* 1986) and a reanalysis of spacecraft data (Ip *et al.* 1990) listed in Table 1 may be ascribed to differences in models or to time variations in the gas production rate which propagate to incorrect relative abundances for species with significantly different photodissociation lifetimes (Ip *et al.* 1990). The  $CN$  abundance given in Table 1 is well determined, and may derive predominantly from  $HCN$  if the radio production rates are correct (Schloerb *et al.* 1987). However, both the optical  $CN$  jets (A'Hearn *et al.* 1986; Cosmovici *et al.* 1986) and the *Vega* spacecraft spectrometry (Moreels *et al.* 1987) indicate that more than one source for  $CN$  existed in the coma of comet Halley. A question still remains, however, about the relative contributions of the different sources to the observed  $CN$ . Evidently the spatial distribution of  $CN$  indicates that it is a secondary product and does not arise directly from the nucleus (Encrenaz and Knacke 1990). If the Ip *et al.* (1990) analysis is correct, the  $HCN$  contributes only a small fraction of the  $CN$  observed in the visible spectrum of comet Halley in which case the  $CN$  arises predominantly from an unobserved source. In assessing the nitrogen inventory we note that  $HCN$  photodissociates predominantly into  $CN$  (Schmidt *et al.* 1988). Thus the abundance of  $CN$  accounts for  $HCN$  plus any additional significant  $CN$ -bearing parent species. If other abundant  $CN$  parents dissociate predominantly into  $CN$  on time scales  $\leq 10^6$  s, the  $CN$  production rate accounts for most of the  $CN$  compounds in the gas coma. Grim and Greenberg (1987) have suggested that a spectral feature measured in laboratory interstellar ice simulations at 4.6  $\mu m$  (Allamandola and Sandford 1990) is attributable to the cyanate ion,  $OCN^-$ , which could have sufficient abundance in the icy grain mantles to account for the  $CN$  observed in comets. Encrenaz and Knacke (1990) have suggested that the feature marginally present at 4.45  $\mu m$  in the spectrum of comet Halley is attributable to the  $C \equiv N$  stretch mode in small grains. Whatever the source of the observed  $CN$ , its abundance in Table 1 can be used to account for the nitrogen inventory of this radical and its parents in the comet. Here we assume that the production rate of  $CN$  can be used to account for the bulk of the  $CN$ -bearing molecules, and estimate that our error in making this assumption is less than a factor  $\sim 2$ .

Other possible nitrogen-containing molecules include  $N_2H_4$ ,  $CH_3CN$ ,  $C_2N_2$ , ammonium salts, and cyanide polymers (Encrenaz and Knacke 1990; Delsemme and Combi 1983; Lewis and Prinn 1980; Matthews and Ludicky 1986), though none of these species has been observed in comets. Delsemme and Combi (1983) suggested that  $N_2H_4$  (hydrazine) is the dominant source of  $NH_2$ . Also, single bond attachments of  $NH_2$  to hydrocarbons have been suggested as a significant source of the  $NH_2$  molecules. However, Tegler (1989) has shown that any species with a photodissociation lifetime  $\geq 8000$  s (e.g.,  $N_2H_4$  and  $CHON$  volatiles) would be inconsistent with the parent of  $NH_2$ . From this analysis of the spatial distribution of  $NH_2$  in the coma of comet Halley, Tegler (1989) concluded that  $NH_3$  is the dominant parent of  $NH_2$ . Solar nebula chemistry models (e.g., Lewis and Prinn 1980) also fail to predict sufficient amounts of  $N_2H_4$  relative to  $NH_3$  to account for the  $NH_2$  observations (Wyckoff *et al.* 1991a, b).

Both the observed spatial distribution of  $\text{NH}_2$  and the production rates of  $\text{NH}$  and  $\text{NH}_2$  demonstrate convincingly that  $\text{NH}_2$  in comets must derive directly and predominantly from the photodissociation of  $\text{NH}_3$ . Ip *et al.* (1990) have shown that  $\text{CH}_3\text{CN} + \text{C}_2\text{N}_2$  comprise less than 0.01% of the coma gases.

Also unaccounted for in Table 1 are those nitrogen-containing diatomic and polyatomic molecules which do not strongly fluoresce in the UV, optical, and infrared spectral regions, as well as large molecules (20–50 Å in size) observable in the submillimeter region, such as carbonaceous particles and cyanide polymers. However, we note that the most abundant ice and gas phase nitrogen-bearing compounds observed in star-forming regions are represented in Table 1 (Blake *et al.* 1987; Tielens and Allamandola 1987). Lewis and Prinn (1980) predicted that the ammonium salts,  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{COONH}_2$ , would be present in trace amounts in the solar nebula (utilizing  $\lesssim 1\%$  of the available C and N). Using the abundance predictions for ammonium salts in solar nebula models (Lewis and Prinn 1980; Prinn and Fegley 1989), we estimate that these unobserved nitrogen carriers in the gas coma of comet Halley could contribute at most an additional 50% to the nitrogen inventory in cometary ices (if the ammonium salts utilized  $\sim 1\%$  of the available C). For a dust/gas ratio  $\sim 2$  (Jessberger and Kissel 1990), this amount of undetected nitrogen compounds would increase the total (gas + dust) N inventory in comet Halley by only 4%. Here we therefore assume that the nitrogen compounds listed in Table 1 represent most of the nitrogen inventory in the coma gas of comet Halley. We note that an error as large as a factor  $\sim 10$  underestimating the amount of N in the volatiles would result in an error in the total (gas + dust) N inventory of ( $< 50\%$ ). Thus we assume that the bulk of the nitrogen-bearing compounds in the volatiles of comet Halley are carried by the most abundant nitrogen compounds observed, namely,  $\text{CN}$ ,  $\text{N}_2^+$ ,  $\text{NH}$ , and  $\text{NH}_2$ . Since it has been shown that both  $\text{NH}_2$  and  $\text{NH}$  are photodissociation products of  $\text{NH}_3$  (Wyckoff *et al.* 1991b), we conclude from Table 1 that ammonia is then the dominant nitrogen-bearing species in the gas coma of comet Halley, and that the CN-containing compounds also contribute a significant fraction to the nitrogen inventory. Surprisingly, the contribution by  $\text{N}_2$  to the nitrogen volatile inventory is very small ( $\sim 7\%$ ). We estimate that the inventory of nitrogen compounds in Table 1 is complete to an estimated uncertainty of a factor of 2. The nitrogen/oxygen abundance ratio derived for the volatile component of the nucleus from Table 1 is given in Table 2 where we have assumed that  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CO}_2$ , and  $\text{OCS}$  contain all of the oxygen in the gas coma. From the compilation of Encrenaz and Knacke (1990) we find that the oxygen-bearing molecular fraction (by number) in the gas

coma is 97.9%. From the data in Table 1 we assume that  $\text{NH}_3$ ,  $\text{N}_2$ , and the CN carrier contain all of the nitrogen in the gas coma, amounting to a fractional abundance of 0.4%. The ratio of these two percentages is then the N/O ratio in the gas coma of comet Halley given in Table 2. The remainder of the gas coma is assumed to consist of  $\text{CH}_4$  (1.6%) (Encrenaz and Knacke 1990) and  $\text{CS}$  (0.1%) (Feldman *et al.* 1987). No corrections for the undetected nitrogen compounds have been included in the abundances given in Table 2.

#### b) Nitrogen Inventory in the Dust Component

The data from dust analyzers aboard the *Vega* spacecraft (Sagdeev *et al.* 1987) have been analyzed to determine the elemental abundances of the dust particles sampled during transit of the coma of comet Halley in 1986 March. Results of the analyses Kissel and Krueger 1987; Jessberger *et al.* 1988) indicate that two-thirds of the particles sampled represent silicates, and the remaining one-third of the dust component consists of particles containing predominantly the light elements, C, N, O, H, hence the name CHON particles. Here we use the results of the analysis of the CHON particles by Jessberger and Kissel (1990), who found  $(\text{N/O})_{\text{dust}} = 0.047$  by number. This compares with the interstellar value,  $(\text{N/O})_{\text{dust}} = 0.14$  derived by Encrenaz, d'Hendecourt, and Puget (1988). As all of the particles were reduced to elemental constituents upon impact with the dust analyzer, the elemental nitrogen inventory is complete for the dust analysis (Jessberger *et al.* 1988; Jessberger and Kissel 1990).

#### c) Total (Dust + Gas) Nitrogen Abundance

The logarithmic value of the nitrogen abundance given in Table 2 was derived assuming a ratio by mass, dust/gas = 1.8 (McDonnell *et al.* 1987; Jessberger and Kissel 1990). We note that the elemental abundances adopted above to determine the total nitrogen abundance in Table 2 correspond to ratios,  $(\text{O/C})_{\text{gas}} \sim 6$  and  $(\text{H/O})_{\text{gas}} \sim 2$ , which agree with the same light elemental abundance ratios measured in comet Halley by the *Giotto* mass spectrometers (Krankowsky *et al.* 1986; Balsiger *et al.* 1986). The total (dust + gas) N/O ratio given in Table 2 is less than the dust N/O ratio because the elemental abundances are distributed differently between the dust and gas components of the coma. We find  $\sim 55\%$  of the total oxygen content of the comet in the gas coma, and  $\sim 10\%$  of the total nitrogen inventory in the gas.

### III. DISCUSSION

In Table 2 we present the ratio of the elemental abundances, N/O, in comet Halley together with the solar abundance from the compilation by Anders and Grevesse (1989). We also give

TABLE 2  
NITROGEN ABUNDANCE IN COMET HALLEY<sup>a</sup>

Element	Comet (Gas) <sup>b</sup>	Comet (Dust) <sup>c</sup>	Comet (Dust + Gas) <sup>d</sup>	Sun <sup>e</sup>
log N .....	6.18 ± 0.3	7.20 ± 0.12	7.24 ± 0.4	8.05 ± 0.04
N/O .....	0.004	0.047	0.023	0.132

<sup>a</sup> Abundance ratios given by number and elemental logarithmic abundances normalized to  $\text{Mg} = 7.58$ , following Anders and Grevesse (1989) and using the dust abundances and dust/gas ratio of Jessberger and Kissel (1990).

<sup>b</sup> This work.

<sup>c</sup> Jessberger and Kissel 1990.

<sup>d</sup> Dust/gas = 1.8 assumed.

<sup>e</sup> Anders and Grevesse 1989.

the logarithmic nitrogen abundances in Table 2 normalized to the logarithmic Mg abundance (7.58) following Anders and Grevesse (1989) and using the comet dust abundances of Jessberger and Kissel (1990). The results indicate that the comet nitrogen-containing volatiles are depleted by a factor  $\sim 75$  compared with the solar photosphere. The total elemental nitrogen abundance in the combined gas and dust components is depleted by a factor  $\sim 6$  relative to the Sun, which is significant at the  $2\sigma$  level, where an error of a factor  $\sim 2$  for the dust/gas ratio has been included in the uncertainty. In Figure 1 we show our combined gas plus dust nitrogen abundance in comet Halley relative to the solar photosphere abundance, where the solar abundances were taken from Anders and Grevesse (1989) and the comet dust elemental abundances from Jessberger and Kissel (1990). The gas elemental abundances in comet Halley were taken from Krankowsky *et al.* (1986), Balsiger *et al.* (1986), Feldman *et al.* (1987), Wegmann *et al.* 1987, Encrenaz and Knacke (1990), and Wyckoff, Tegler, and Engel (1991a). For comparison, the abundances of the light elements H, C, N, O, and S, and the rock-forming elements Mg, Si, and Fe are also presented in Figure 1. Except for the volatiles, the CI carbonaceous chondrites have been considered to have the most primitive solar system abundances. The CI chondrite elemental abundances (Jessberger and Kissel 1990) are also plotted in Figure 1. The figure shows that both H and N are significantly depleted in comet Halley relative to the Sun. Anders and Grevesse (1989) have previously discussed the depletion of H and the marginally low Fe/Si ratio in comet Halley. They point out that if the Fe/Si ratio is significantly different from the Sun and all other solar system objects, then comet Halley cannot be comprised of pristine interstellar material. The sulfur abundance for the gas component of the

comet was derived from production rates of OCS (Encrenaz and Knacke 1990) and CS (Feldman *et al.* 1987), the only two sulfur compounds detected in comet Halley, and should probably be considered a lower limit due to incompleteness of the sulfur inventory.

It is noteworthy in Figure 1 that none of the cometary elemental abundances significantly exceeds that of the Sun, and that none is less than the CI chondrite. This is strong evidence that comet Halley formed from solar nebula material, and that the nucleus is significantly less processed (more primitive) than CI chondrites. That the nitrogen depletion in the comet gas coincides with the deficient N abundance in the chondrites is probably fortuitous and can probably be explained by different mechanisms, since the comet and the chondrites must have formed and evolved in significantly different environments.

Thus we find that the dust contains the bulk ( $\sim 90\%$ ) of the elemental nitrogen and the gas component of the coma contains  $\sim 10\%$  of the nitrogen. A similar imbalance in the distribution between the dust and gas components in comet Halley was found for carbon,  $\sim 80\%$  dust and  $\sim 20\%$  gas (Encrenaz and Knacke 1990). Estimates of a few percent have been made (e.g., Encrenaz, d'Hendecourt, and Puget 1988) for the amount of comet material contained in large molecules (e.g., polymers) which would have escaped detection in the *in situ* dust and mass spectrometer experiments, as well as by remote spectroscopic techniques. In addition, the nitrogen-containing carbonates,  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{COOH}_2$  could have condensed in small amounts ( $\lesssim 1\%$ ) from the solar nebula gas (Lewis and Prinn 1980). Thus some nitrogen could be hidden by processing into undetected polymers (e.g., Matthews and Ludnick 1986; Grim and Greenberg 1990) or condensed into complex compounds which do not fluoresce with solar radiation, and could not be unambiguously identified with the ion mass spectrometer which sampled the coma gases of comet Halley. If we apply a factor of 2 incompleteness correction factor to the volatile nitrogen abundance, the ice component depletion factor relative to the Sun is  $\sim 40$ , and the total (dust + gas) nitrogen deficiency for dust/gas  $\sim 2$  changes by only 10%. Thus the nitrogen deficiency in comet Halley appears firmly established, independent of any correction factor as large as 2 for undetected nitrogen compounds.

The N/O ratio for the comet gases in Table 2 is  $\sim 3$ –5 times smaller than that found by Geiss (1987),  $\sim 3$  times smaller than the N/O ratio adopted by Encrenaz, d'Hendecourt, and Puget (1988), and 25 times smaller than that derived by Delsemme (1988, 1989). The elemental nitrogen abundance in comet Halley is different from these previous determinations primarily due to the revision of the ammonia and molecular nitrogen abundances given here and elsewhere (Wyckoff, Tegler, and Engel 1991a; Wyckoff and Theobald 1989).

The difference between the nitrogen abundance derived for the volatile and dust components is sufficiently large to indicate differences in formation conditions for the two cometary components. Any existing interstellar grains were probably exposed to a variety of conditions during the collapse of the protosolar cloud. Calculations indicate that accretion heating by drag friction and grain-grain collisions should have heated the grains sufficiently ( $T \gtrsim 150$  K) to have vaporized any ice mantles on preexisting grains (Lunine 1989; Bar-Nunn and Kleinfeld 1989; Engel, Lunine, and Lewis 1990). Recent infrared spectroscopy may provide direct evidence for annealing ( $T \gtrsim 800$  K) of dust grains observed in comet comae (e.g., Hanner 1990). If this is a general characteristic of dust grains in

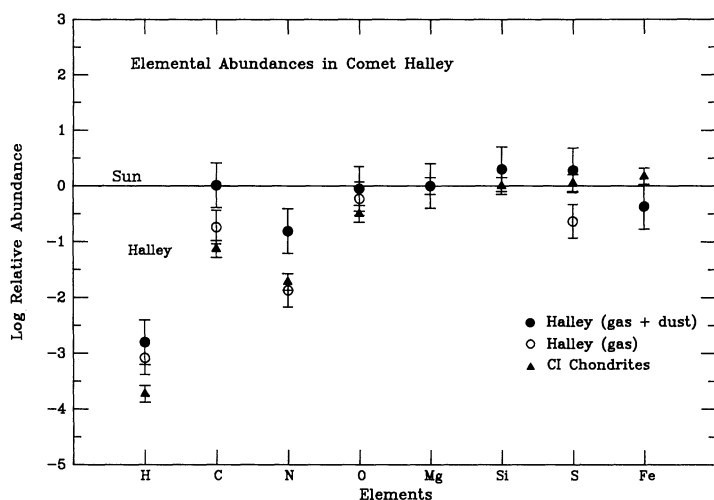


FIG. 1.—Elemental abundances of selected light elements in the gas and the combined gas-plus-dust components of comet Halley coma relative to solar photospheric abundances, normalized to Mg. A dust/gas mass ratio  $\sim 2$  was used. Abundances of CI carbonaceous chondrites shown for comparison. Solar data from Anders and Grevesse (1989); Halley nitrogen abundance from this work; other cometary abundances from Balsiger *et al.* (1986), Krankowsky *et al.* (1986), Feldman *et al.* (1987), Wegmann *et al.* (1987), Encrenaz, d'Hendecourt, and Puget (1988) (Case 4:  $3.2$ – $3.5\ \mu\text{m}$  emitter assumed entirely of solid origin) Jessberger and Kissel (1990), Encrenaz and Knacke (1990). Nitrogen is depleted by a factor  $\sim 6$  in the gas + dust component of comet and  $\sim 75$  in the gas component relative to the Sun. Error bars for comet abundances include an uncertainty of a factor  $\sim 2$  in the abundances and an uncertainty of a factor  $\sim 2$  in the dust/gas ratio.

comets, then the interstellar grain ice mantles would not have survived the early protosun phase, and the volatiles observed in comets would have condensed entirely from solar nebula gases, in which case the dust and gas components of the comet nucleus would have had significantly different evolutionary histories. On the other hand, the recent discovery of presolar circumstellar grains in primitive carbonaceous chondrites (e.g., Anders 1988) indicates that some ( $\lesssim 1\%$ ) of the bulk meteorite material survived processing in the solar nebula at heliocentric distances as close as  $r \sim 4$  AU to the protosun. Thus it is reasonable to expect a larger mass fraction of the solar nebula which condensed into comet nuclei at  $r > 10$  AU to have survived as interstellar grains. Indeed, Greenberg (1982) has claimed that comet nuclei consist largely of unaltered interstellar grains (Greenberg and Hage 1990). If the comet volatiles consist mostly of preserved interstellar ice mantles, then processing by cosmic rays and UV radiation would have affected the ice abundances, and may account for  $S_2$  observed in a comet (A'Hearn and Feldman 1985). Below we discuss the origin of the ice composition in comet Halley, assuming the ices arose predominantly from solar nebula condensates.

Models of the early solar nebula predict that CO and  $N_2$  dominated the solar nebula gas (Lewis and Prinn 1980), while molecular cloud models indicate that these same stable compounds dominate as a result of cosmic abundances and ion-molecule chemistry (Mitchell 1984; Yamamoto 1985). Thus distinguishing characteristics between presolar ices and solar nebula condensates are expected to be subtle (Prinn and Fegley 1989). Assuming revised solar abundances (Anders and Grevesse 1989) for C, O, and N in the comet-forming regions of the solar nebula, that 60% of the O was in CO (Fegley and Prinn 1989, adjusted for revised solar  $O/C = 0.4$ ) and all of the N was in  $N_2$  we estimate that  $CO/N_2 \sim 10$  in the solar nebula. Thus to account for the observed ratio,  $CO/N_2 \sim 200$ , in the gas coma of comet Halley, assuming the comet ices condensed entirely from a CO and  $N_2$  dominated solar nebula, i.e., an unaltered interstellar cloud composition, a mechanism is required for depleting  $N_2$  relative to CO by a factor  $\sim 20$ . A model including solar nebula chemistry (Fegley and Prinn 1989) predicts maximum abundance ratios,  $NH_3/H_2O \sim 0.002$  and  $NH_3/N_2 \sim 0.006$  using a CO and  $N_2$  dominated solar nebula model in which  $N_2$  is partially converted into  $NH_3$  over the lifetime of the solar nebula  $\sim 10^6$  yr, facilitated by Fe grain catalysis. If  $NH_3$  were completely condensed in comet nuclei, then a comparison of the chemically processed model ratios with the observed ratios (Table 1) indicates that the  $NH_3$  abundance in Halley is within the model prediction and that  $N_2$  is depleted in the comet by a factor  $\sim 1500$  compared with  $NH_3$ . Recall from Table 2 that the observed elemental nitrogen deficiency in the gas coma of comet Halley is a factor  $\sim 75$  less than the solar nitrogen abundance.

Thus the abundances of  $N_2$ ,  $NH_3$ , and CO in comet Halley are inconsistent with both the pristine interstellar and the chemically processed solar nebula models as Prinn and Fegley (1989), Lunine (1989), and Engel *et al.* (1990) have previously concluded. If the initial chemical composition of the solar nebula were solar throughout, then both the nitrogen deficiency and the observed molecular ratios can probably be understood by a combination of the following: (1) chemical partitioning in the solar nebula (Lewis and Prinn 1980), (2) a relatively long time scale for enclathration of  $N_2$  (Prinn and Fegley 1988, 1989, Fegley 1988), and (3) chemical differentiation subsequent to condensation (Houppis, Ip, and Mendis

1985). On the other hand, the material from which the comet formed may not have had solar composition. In this case, the disparate elemental nitrogen abundance could be explained if the comet composition derived from gas having a different nucleosynthesis history from that of the Sun. Each of these possibilities is discussed below.

1. The  $N_2$  gas in the outer solar nebula was chemically partitioned into other compounds. Solar nebula models dominated by  $N_2$  and CO predict that nitrogen-containing carbonates,  $NH_4HCO_3$  and  $NH_4COONH_2$ , would be produced in small amounts as discussed above (Lewis and Prinn 1980; Prinn and Fegley 1989), where we estimated that the maximum amount of nitrogen which could be distributed into these undetected nitrogen compounds would have been  $\sim 50\%$  of the nitrogen inventory of the ice component of the comet nucleus, assuming unfractionated condensation. Ammonium salts could therefore account for a significant fraction of the elemental nitrogen in comet Halley. However, as noted above, the same solar nebula model (Prinn and Fegley 1989) predicts that the maximum amount of  $N_2$  which could have been converted into  $NH_3$  is a factor  $\sim 1500$  less than the observed ratio (Table 1). A more accurate model is needed to more fully assess the thermochemical partitioning and kinetic inhibition effects on nitrogen compounds in the solar nebula. On the other hand, additional mechanisms for partitioning the nitrogen compounds in the solar nebula could have prevailed. Prinn and Fegley (1988, 1989) have suggested that the giant planet subnebulae regions could efficiently convert  $N_2$  into  $NH_3$ . Both shocks in the collapsing presolar nebula (Lunine 1989) and lightning discharges (Prinn and Fegley 1989) could, through shock chemistry, have converted  $N_2$  into HCN and other compounds. Lunine (1989) and Fegley (1990) have suggested that the fact that  $NH_3 \sim HCN$  in comet Halley could be indicative of the importance of shock chemistry. Although a variety of chemical processes could have redistributed the  $N_2$  into other nitrogen-bearing compounds, including undetected species, the elemental nitrogen deficiency observed in comet Halley cannot be explained simply by chemical repartitioning the molecular nitrogen into unobservable compounds.

2. The  $N_2$  was excluded from the condensation process by physical fractionation, as suggested previously (Geiss 1987; Lunine 1989; Ip 1989). The low-temperature ( $T \lesssim 160$  K) gas-grain chemistry model for an  $N_2$  and CO rich solar nebula of Prinn and Fegley (1989) predicts a condensation sequence for the nitrogen compounds. At low pressures both  $H_2O$  and the ammonium salts,  $NH_4HCO_3$  and  $NH_4COONH_2$ , would condense into solids at comparable temperatures,  $T \lesssim 150$  K, while  $N_2$  could condense as a clathrate ( $N_2 \cdot 6H_2O$ ) at  $T \lesssim 55$  K, and directly as pure  $N_2$  ice at  $T \lesssim 20$  K (Fegley 1988; Prinn and Fegley 1989). However, the entrapment of  $N_2$  in a clathrate hydrate is predicted to be kinetically inhibited and a very inefficient process relative to other species such as CO and  $CH_4$  over the limited lifetime and the low pressure conditions of the solar nebula (Lunine and Stevenson 1985; Fegley 1988; Prinn and Fegley 1989). Also  $N_2 \cdot 6H_2O$  is relatively unstable compared with  $CO \cdot 6H_2O$  (Prinn and Fegley 1989). For these reasons the solar nebula conditions for  $N_2$  clathrate formation were probably relatively unfavorable compared with other condensates (Lunine and Stevenson 1985; Lunine 1989; Prinn and Fegley 1989). Direct condensation of  $N_2$  and CO ices would have required temperatures lower than expected for comet formation (e.g., Bar-Nun and Kleinfeld 1989).

Thus models and laboratory experiments indicate that the

assimilation of  $N_2$  into condensates would have required a time scale which exceeded the solar nebula lifetime,  $\sim 10^6$  yr. It is therefore very likely that there was a preferential accumulation of  $N_2$  gas as condensation proceeded for other gases in the solar nebula, with the solar bipolar outflow eventually sweeping the remaining  $N_2$ -rich gas from the solar system, accounting for the deficiency of both the elemental and molecular nitrogen. We suggest that the reasons for the abundance ratio,  $N_2/CO$  being  $\sim 20$  times less than expected in a CO and  $N_2$  rich solar nebula, and most of the elemental N and C being contained in the dust not the ice component of the comet nucleus, are due at least in part to the relative efficiency with which each molecule (1) bonds with other species (Geiss 1987), and (2) fractionates upon condensation (Bar-Nunn and Kleinfeld 1989; Lunine 1989; Ip 1989). In regard to the first point we note that more than half of the CO observed in the comet coma comes from a more complex compound as indicated by the distributed CO source in comet Halley (Balsiger *et al.* 1987).

3. The  $N_2$  compounds condensed and were incorporated into the comet nuclei, but have since diffused, chemically differentiating the comet nucleus (Houppis, Mendis, and Ip 1985). The low vapor pressure of  $N_2$  would favor its preferential diffusion relative to all other molecular compounds except  $H_2$ , producing a chemically differentiated nucleus. Diffusion could have occurred from the ice mantles of grains as a result of heating or grain-grain collisions prior to their coagulation into comet nuclei, or from the comet nuclei as a result of heating due to successive close approaches to the Sun (or the warm giant protoplanets), or both. Internal heating of comet nuclei by radioactive elements could also have promoted diffusion of the most volatile condensates. If the  $N_2$  in comet nuclei were depleted by selective thermal diffusion, then, depending on their individual thermal histories, comet nuclei should be chemically differentiated by different amounts. We would therefore expect the  $N_2$  abundance to vary significantly from comet to comet, with individual nuclei eventually evolving toward  $H_2O$ -domination as suggested by Houppis, Mendis, and Ip (1985). The  $N_2^+$  emission bands are highly variable in strength from comet to comet, but no systematic study of the  $N_2$  abundances in a sample of comets has yet been made. We note that CO is the only volatile known to vary in abundance significantly among comets (Feldman 1983). Like  $N_2$ , CO has one of the lowest vapor pressures for cosmically abundant volatiles. Thus the CO abundance variations among comets could be indicative of the effects of thermal diffusion. If this is the dominant cause of the CO abundance variations among comet nuclei, then one would expect a correlated variation in the  $N_2$  abundance. Because of the greater tendency of CO to bond with other species the amplitude of its abundance variations would probably be smaller than that for  $N_2$ .

If the explanation for the deficient nitrogen abundance in the comet cannot be found in some combination of chemical partitioning, physical fractionation, or selective diffusion, then the comet must have formed in an environment consisting of material with a nucleosynthesis history different from the protosolar nebula. We note that the carbon isotope ratio in comet Halley has been found to be significantly different from the rest of the solar system (Wyckoff *et al.* 1989). Thus both the nitrogen depletion and the low  $^{12}C/^{13}C$  abundance ratio could indicate that the comet either formed far from the Sun (but in the same protocluster) or was captured after the solar system formed.

#### IV. CONCLUSIONS

We conclude that chemical partitioning of nitrogen compounds into unobservable species is highly unlikely to account entirely for the nitrogen deficiency observed in comet Halley. The more important cause for the nitrogen deficiency in the comet coma relative to the Sun can probably be found in the low vapor pressure of  $N_2$  which led to its exclusion when gases condensed into solid phase in the cooling solar nebula. The bipolar outflow from the protosun then swept away the  $N_2$ -rich gases remaining after  $\sim 10^6$  yr. That  $N_2$  which did condense into comet nuclei (as pure  $N_2$  ice or as a clathrate,  $N_2 \cdot 6H_2O$ ) would have been preferentially lost due to thermal diffusion as a result of successive solar passages (Houppis, Mendis, and Ip 1985) or other heating effects. Both physical fractionation and differential thermal diffusion are thus plausible mechanisms which would have occurred to all comet nuclei and could account both for the low  $N_2$  and for the low elemental nitrogen abundances (Table 2) in comet Halley.

For fractionation to be significant requires that  $N_2$  clathrate formation occurred at a slower rate than the condensation rates of other species, leaving an  $N_2$  enriched gaseous residue to be swept away. Fractionation would have affected all comet nuclei equally if the solar nebula were chemically homogeneous (and all comets formed under similar conditions of temperature and pressure). The effectiveness of chemical differentiation by thermal effects would depend on the individual comet orbit and nucleus characteristics (e.g., injection epoch, orbital elements and their variations with time, nucleus radius, porosity, and chemical composition). Selective thermal diffusion of  $N_2$  would be expected to produce a distribution of heterogeneous chemical compositions among comet nuclei. The observed  $N_2/H_2O$  ratio in a sample of comets could provide a sensitive test of the relative importance of the two mechanisms (physical fractionation vs. chemical differentiation) in depleting  $N_2$ . Since the ammonia abundances in comets (Wyckoff, Tegler, and Engel 1991a) are within the expected predictions of current solar nebula models (e.g., Prinn and Fegley 1989), we conclude that it is the  $N_2$  deficiency that gives rise to the small  $N_2/NH_3$  ratio in the comet compared with solar nebula models, and not an  $NH_3$  enrichment which has been proposed by Prinn and Fegley (1989) and Engel *et al.* (1990).

In the subnebulae of the giant protoplanets, models indicate temperatures and pressures sufficient for conversion of  $N_2$  into  $NH_3$  (Fegley and Prinn 1989). Based on the  $N_2/NH_3$  ratio determined for comet Halley (Wyckoff and Theobald 1989), Prinn and Fegley (1989) suggested that the nucleus is comprised of a small fraction of protoplanetary subnebula  $NH_3$ -rich condensates which are somehow mixed with CO-rich solar nebula condensates. However, as noted above, the large depletion of the cometary elemental nitrogen relative to the Sun cannot be explained simply by conversion of  $N_2$  into  $NH_3$ . Accretion of protoplanet subnebulae gases by episodic exposure to  $NH_3$ -rich material (Prinn and Fegley 1989) might produce observable inhomogeneities in the  $NH_3$  abundances on scales of meters (for individual comets) to AU (for a statistical sample of comets). Although the data are scant, such inhomogeneities have not been observed (Wyckoff, Tegler and Engel 1991a).

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