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THE VOLATILE COMPOSITION OF COMETS

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ABSTRACT

Comets may be our best probes of the physical and chemical conditions in the outer regions of the solar nebula during that crucial period when the planets formed. The volatile composition of cometary nuclei, in particular, can be used to decide whether comets are the product of a condensation sequence similar to that invoked to explain the compositions of the planets and asteroids, or if comets are simply agglomerations of interstellar grains which have been insignificantly modified by the events that shaped the other bodies in the solar system. Although cometary nuclei are not generally accessible to observation, observations of cometary comae can illuminate at least some of the mysteries of the nuclei provided one has a detailed knowledge of the excitation conditions in the coma and also has access to basic atomic and molecular data on the many species present in comets. This paper examines the status of our knowledge of the volatile composition of cometary nuclei and discusses how these data are obtained.

1. INTRODUCTION

The volatile composition of a comet is a sensitive indicator of its formation environment. In particular, the relative abundances of molecules in cometary nuclei can be used to infer the physical and chemical state of either the solar nebula or the interstellar cloud from which the nebula condensed. However, measuring the volatile inventory in comets is a demanding task that involves combining *in situ* spacecraft data with observations from ground-based, airborne, rocket, and Earth-orbiting observatories.

2. MOLECULES IN COMET NUCLEI

2.1 THE DOMINANT VOLATILE: H_2O

During the past two decades cometary observers built a strong circumstantial case for H_2O ice as the dominant volatile in nuclei. However, the apparition of comet Halley provided the first opportunity to observe the H_2O molecule *directly*. Infrared (IR) observations of Halley in December 1985 from the Kuiper Airborne Observatory (KAO) [1] revealed intense, solar-pumped fluorescent emission in the ν_3 band of H_2O near $\lambda \sim 2.65\mu$m. This same band was subsequently observed in Halley post-perihelion by the IR spectrometer on Vega (the IKS experiment) [2] and from the KAO [3,4]. Measurements by the neutral mass spectrometer (NMS) on Giotto demonstrated that H_2O comprised $\geq 80\%$ of the total volatile inventory of comet Halley [5].

Water is not particularly well-suited for constraining the formation conditions of comets because its sublimation temperature is relatively high ($T_{sub} \sim 150$ K), and H_2O is expected to be a relatively abundant molecule in the gas phase throughout much of the solar nebula. Thus, measuring the relative abundances of the more volatile *trace* species in cometary nuclei is required for establishing the connection between comets and interstellar grains and between comets and possible solar nebula condensates.

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2.2 MAJOR CARBON-BEARING SPECIES: CO, CH₄, CO₂, H₂CO

Carbon monoxide is ubiquitous in the interstellar medium and is also predicted to be the dominant carbon-bearing gas in non-equilibrium modelsof the solar nebula [6]. As illustrated in Table 1, CO may also be the second-most abundant volatile in cometary nuclei. Prior to Halley, CO had been observed definitely in only two comets: the CO fourth positive group at $\lambda \sim 1500$ Å was detected during sounding rocket observations of comet West (1976 VI) [7] and during IUE observations of comet Bradfield (1979 X) [8]. The derived CO abundance in comet West was huge ($\sim 30\%$ of theH_2O abundance). Similar observations were conducted on comet Halley [9], also showing a high CO/H_2O abundance ($\sim 17\%$ in this case). On the other hand, the UV observations of comet Bradfield yielded $CO/H_2O \sim 0.02$ [10]. Does the relative abundance of CO vary from comet to comet? The Giotto NMS measurements of CO in the coma of comet Halley provided some interesting insight into this question [11]. The NMS observations showed that only $\sim 7\%$ (or less) of the CO in the coma of Halley could be derived by sublimation from the nucleus. The rest of the CO in the coma is apparently produced from a distributed source, possibly due to the evaporation of organic mantles on cometary grains (the so-called CHON particles). Viewed from this new perspective, both the high CO abundances derived from UV observations of comets West and Halley, and the low CO abundance derived from the UV observation of comet Bradfield, are consistent. Whenever a large field-of-view (FOV) is used *and* the comet has a large dust production rate (the UV rocket observations of both West and Halley satisfied these conditions), a high abundance of CO will be observed in the coma due to extra CO production from grain evaporation. Whenever the FOV is small and/or the dust production rate is low, then the coma CO observation should be sampling something close to the "true" abundance in the nucleus (we are making a distinction here between the CO stored in the ice versus the presence of C-O bonds in complex hydrocarbons that may be coating cometary grains).

Equilibrium condensation models of the solar nebula indicate that CH_4 should be the dominant carbon-bearing gas in the outer regions of the nebula. Indeed, for many years people often referred to comets as being composed of "water, methane, and ammonia" although the latter two molecules had never been observed in comets and the indirect evidence for their presence indicated that they were only trace constituents. Recent non-equilibrium chemical models of the solar nebula demonstrate that CH_4 should be extremely depleted relative to CO in the nebula, except near the sub-nebulae associated with the Giant planets [6].

Spectroscopic observations of the ν_3 band of methane near $\lambda \sim 3.3 \mu m$ have yielded the first direct evidence for the presence of CH_4 in comets. The R(1) line of this band was marginally detected in comet Halley [12] while an average over six R-branch lines in this band gave a tentative detection during KAO observations of comet Wilson (1986*l*) [13]. The interpretation of these results in terms of the CH_4 abundance is somewhat problematical. The derived abundance can vary significantly depending on the choice of the "effective" excitation temperature of the CH_4 molecules in the coma, especially if only one line is used. Some of this uncertainty is reflected in the range of values given in Table 1. We simply note that the above-referenced KAO observations of H_2O indicate that the appropriate excitation temperature of CH_4 is probably ~ 50 K implying that the CH_4 abundance is closer to 1% than 5%.

Strong evidence for the presence of CH_4 in the coma of comet Halley was also obtained by analysis of data taken by the ion mass spectrometer (IMS) on Giotto [21]. Using the CH_3^+ ion as a probe of the CH_4 abundance in the coma, and by comparing the observed

ion spectrum to a model spectrum containing all known important ion-molecule reactions, the IMS data indicate that $CH_4/H_2O \sim 0.02$. The uncertainty in this number is difficult to establish owing to the complexity of the modeling, but the nominal value reported is consistent with the results from the spectroscopic investigations.

Both the NMS experiment on Giotto and the IR spectrometer on Vega detected CO_2 in the coma of comet Halley and both measurements yield a CO_2 relative abundance of $\sim 3\%$ [5,15]. Assuming that the CO_2 observed in these experiments originated in the nucleus, the CO_2 abundance was approximately one-half of the CO abundance in Halley. UV observations of several comets indicate that the CO_2/H_2O abundance does not vary significantly from comet-to-comet (Feldman, private communication). If this is true, then CO_2 and CO may have comparable abundances in some comets (e.g., comet Bradfield [1979X]).

There was a tentative detection of H_2CO in Halley via IR fluorescence in a vibrational band near $\lambda \sim 3.5\mu m$ by the IKS experiment [15]. The derived abundance from the IKS is given in Table 1 as an upper limit. If the detection stands, it indicates that H_2CO is an important trace constituent in comets and may contribute significantly to the "extended" source of CO in the coma.

2.3 MAJOR NITROGEN-BEARING SPECIES: NH_3, N_2, HCN

There has only been one direct observation of NH_3 in a comet: a radio line was marginally detected in comet IRAS-Araki-Alcock (1983d) [16]. The derivation of an NH_3 abundance from these data is extremely model-dependent; the radio observers reported $NH_3/H_2O \sim 0.06$ while I have derived a ratio of ~ 0.003 from the same data.

Since $\geq 90\%$ of the photodissociation of NH_3 by solar UV radiation results in the production of NH_2, visible observations of the NH_2 molecule should provide reasonably accurate measurements of the NH_3 abundance. Observations of the NH_2 band at $\lambda \sim 5700$ Å in comet Halley gave $NH_3/H_2O = 0.003$ [17].

Both NH_3 and CH_4 are required to explain the Giotto IMS data [14] (see the earlier discussion on CH_4). An NH_3 relative abundance of $\sim 1-2\%$ gives the best fit of the model to the data. However, the accuracy of this result has not yet been determined due to the complexity of the modeling, and the uniqueness of the interpretation has also been challenged [18].

The abundance of N_2 in comets is very difficult to establish with confidence. There are no known spectroscopic signatures of the neutral molecule and since its mass is coincident with that of CO, even *in situ* observations with mass spectrometers suffer from a confusion problem. Using the small difference in ionization potential between N_2 and CO, the Giotto NMS data were used to obtain $N_2/H_2O \leq 0.1$ [11].

The N_2^+ ion is observed in the visible spectra of comets near $\lambda \sim 3914$ Å. Since the ionization properties of N_2 and CO are similar, and since the CO/H_2O abundance can be determined by other means, the ratio of the intensities of the visible bands of N_2 and CO^+ can be used to infer the ratio of N_2/H_2O. Using this technique for the Halley observations yields $N_2/H_2O \leq 0.001$ (Feldman and Wyckoff, private communication).

Fluorescent emission from CN is usually the strongest feature in the visual spectra of comets. Most of the CN in the coma is probably produced by the photodissociation of HCN that has sublimated from the nucleus, although some may have been produced as a result of evaporation of organic-coated grains [19] or from photodissociation of more complex molecules [20]. The HCN molecule is detected via a rotational transition at radio frequencies, and the apparition of Halley witnessed the first systematic investigation of HCN in comets [21]. The derived abundance from these observations is $HCN/H_2O \sim 0.001$.

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2.4 MAJOR SULFUR-BEARING SPECIES: CS_2, S_2

Fluorescent emissions from CS and S are a prominent features in UV spectra of comets [22]. The most plausible parent for CS is the CS_2 molecule [23], although CS_2 has never been observed directly. Assuming that all of the CS observed in the coma comes from CS_2, then $CS_2/H_2O \sim 0.001$, i.e., CS_2 is a trace constituent of the nucleus.

UV observations of the "Earth-grazing" comet IRAS-Araki-Alcock (1983d) dramatically revealed the presence of S_2, a molecule which had never been observed previously in any astrophysical environment [24]. Since the S_2 discovery coincided with an "outburst" in cometary activity, and since the signal virtually disappeared during later observations, the presence of S_2 in IRAS-Araki-Alcock may not be typical. The abundance derived from the UV observations during the outburst is $S_2/H_2O \sim 0.001$.

The presence of the OCS molecule has been invoked to explain the spatial distribution of S atoms in the coma [25]. Although this hypothesis is speculative since OCS has never been detected in comets, it is also clear that if OCS is present it cannot be more than a trace constituent of the nucleus.

3. CONCLUSION

Table 1 summarizes the abundance data on cometary volatiles discussed in this paper. All values are expressed as volume abundances relative to H_2O. Although the ability to compile a table like this with reasonable confidence represents a significant improvement in our knowledge of the nature of cometary matter, several cautionary remarks must be made. First, the abundances of trace species have been measured in very few comets. Table 1 is heavily weighted toward results from Halley since the best data generally come from this comet. Systematic observations of trace species in both "new" and "old" comets are desperately needed to establish whether the results from Halley, and the handful of other comets mentioned here, are "typical" of comets as a class. Second, even when identifications of species are secure, the conversion from raw data into nucleus abundances frequently introduces significant uncertainties (factors of two or more are common). Finally, comets often exhibit dramatic temporal variability which may suggest that the observed composition is not constant in time (e.g., the case of S_2). Despite these present shortcomings, we are well on our way toward a more quantitative understanding of the link between comet compositions and cometary formation environments.

4. ACKNOWLEDGEMENTS

TABLE 1. VOLATILE ABUNDANCES
IN COMET NUCLEI

Molecule	Abundance
H_2O	1
CO	0.02 – 0.07
CH_4	0.01 – 0.05
CO_2	~0.03
H_2CO	≤0.05
NH_3	0.003 – 0.02
N_2	≤0.001
CS_2	≤0.001
S_2	≤0.001
HCN	~0.001

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