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Comets: Chemistry and Chemical Evolution

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Summary. Lasting commitment to cosmic chemistry and an awareness of the fascinating role of comets in that study was a consequence of an association with Harold Urey early in my astronomical career. Urey's influence on cometary research spread as colleagues with whom I was associated, in turn, developed their own programs in cometary chemistry. One phase of the Chicago research shows that Whipple's icy nucleus would be below about 250 K. This property, combined with their small internal pressure, means cometary interiors remain essentially unchanged during their lifetime. Observations of cometary spectra indicate that they are rich in simple organic species. Experiments on comet-like ice mixture suggests that the extensive array of interstellar molecules also may be found in comets. The capture of cometary debris by the earth or the impact of comets would have been an early source of biochemically significant molecules. Recent hypotheses on radiogenic heating and melting of water ice in the central zone of nuclei do not seem consistent with recent observations or ideas of structure. Thus comets are not a likely place for life to develop.

Key words: Comets – Cometary molecules – Chemical evolution – Origin of life

I. Introduction

Comets are a fertile field for cosmic chemistry and lately there have been considerations of a possible role in biochemical evolution. As with many other scientific fields in which chemistry is important, Harold C Urey had a considerable influence on cometary research. I will begin with a brief survey of how Urey's insights affected subsequent research and for which I have direct knowledge.

In the mid-fifties I was a research associate in Urey's laboratory in the University of Chicago. My interest was the chemistry of interstellar grains. At that time the prevailing grain model (Oort and Van de Hulst 1946; Field 1975) was a condensed mixture of the abundant volatile molecules, assumed to be water, ammonia and methane with a small fraction of metal silicates. On a sub-micron scale these resemble the icy comet nucleus proposed by Whipple (1950). This model is now generally accepted as outlining the basic structure and composition (Whipple and Huebner 1976; Donn and Rahe 1982; Delsemme 1982) of cometary nuclei.

It was during the course of investigating the condensation of irradiated gases and behavior of trapped radicals in ice mixtures that Urey read Whitney's (1955) paper on the outbursts of Comet Schwassmann-Wachmann I. It occurred to him that the work in several laboratories on chemical energy from radicals trapped in inert matrices may well be applicable to cometary outbursts. There were two consequences of Urey's idea. One was a series of papers on possible consequences of chemical energy for comets (Donn and Urey 1956), and meteorites (Urey and Donn 1956) and a revised, more general hypothesis (Donn and Urey 1957). Variations of these ideas has been proposed by Clayton (1980) to form meteoritic chondrules.

The investigation of the icy nucleus showed that because of evaporation, the temperature of the nucleus would remain below about 250 K to within 0.1 AU of the sun. Consequently, comet ices were always cold. Their small mass results in low internal pressures. The two effects together mean that comets have undergone little change since their formation and are therefore the best existing samples of primordial material. Detailed calculations of vaporization rates and temperatures of ices in the solar system have subsequently been published by Watson et al. (1963), Huebner (1965), Delsemme (1966) and Delsemme and Miller (1971).

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Table 1. Molecules and ions observed in comets

Atoms	Molecules	Ions
H	CH	C^+
C	NH	Ca^{+}*
O		OH^+
S	OH	CN^+
Na	C_2	CH^+
K*	CH	CO^+
Ca*	CO	N_2^+
V*	CS	CO_2^+
Mn*	NH_2	H_2O^+
Fe*	C_3	
Co*	H_2O**	
Ni*	HCN**	
Cu*	CH_3CN**	
Cr*	Silicates***	

*Near sun only
**Unconfirmed
***Infrared dust spectra

The second result was to stimulate in me a continuing interest in comets. Their structure and composition and role in providing clues to the primordial conditions existing when they formed are fascinating and significant astonomical problems. An offshoot has been the development of interest in cometary chemistry by chemist colleagues at Goddard, William Jackson and Regina Cody. This collaboration led to an analysis of chemical reactions in the innner coma (Jackson and Donn 1966, 1968) and to a continuing interest by Jackson when he went to Howard University (Jackson et al. 1976, 1980). Regina Cody is continuing the program of laser spectroscopy and photochemistry at Goddard (Donn and Cody 1978; Cody and Donn 1980; Cody et al. 1981). In a different direction, collaboration with the rocket spectroscopy group at Johns Hopkins has resulted in a highly productive, independent program of ultraviolet cometary spectroscopy and analysis (see Feldman 1982).

II. Organic Molecules in Comets

One of Urey's active interests was chemical evolution. Comets have been mentioned in a number of different ways as potentially important contributors to chemical evolution. In the remainder of this paper this subject is examined.

The ultraviolet and visible spectra of comets shows a variety of inorganic and organic compounds and ions. These are listed in Table 1. The occurrence of three molecules in the radio spectrum, H_2O, HCN, and CH_3CN has been reported (Huebner et al. 1974; Jackson et al. 1976; Ulrich and Conklin 1974) but remains uncertain as these species have not been seen in other comets (see Snyder 1982, to be published). Although observational uncertainty exists for water there is convincing evidence (see Delsemme 1982) that it is a major constituent of the nucleus. The emission spectra of all comets for which ultraviolet spectra exist are similar (Feldman 1982) and suggests as a good working hypothesis, that they have the same composition. Delsemme (1982) has considered the composition in considerable detail and his elemental composition is given in Table 2.

Table 2. Composition of cometary ices

Element	Relative abundances
H	1.5
C	0.2
N	0.1
O	1.0
S	0.003

Complex organic compounds may be intrinsic to comets from their formation as suggested by Donn (1972) and examined in more detail by Greenberg (1981, 1982). The strong possibility that comets accumulated in interstellar clouds (Cameron 1973; Donn 1976a; Biermann and Michel 1978) would make cometary ices a repository for the large array of interstellar organic molecules (Delsemme 1975, 1981, 1982). Greenberg has proposed that irradiated ice mantles on interstellar grains, simultated in the Leyden Astrophysics Laboratory experiments, yield a still more complex array of uncharacterized organic compounds. These interstellar grains may form comets according to the theories referred to previously. Therefore, Greenberg suggests, comets possess a biochemically significant composition.

Recent experiments at the Goddard Space Flight Center by Moore and Donn examined the effect of cosmic ray irradiation of simple ice mixtures (H_2O, CH_4, NH_3, CO_2) during a comet's 4.5 billion year residence in the Oort Cloud (Donn 1981; Moore 1981; Moore and Donn 1982). This study was Marla Moore's thesis research to experimentally study Donn's (1976b) hypothesis that the outer several meters of a comet would tend to be polymerized be the accumulative effect of the low energy cosmic rays. A variety of ice mixtures at 12 K were exposed to a 1 MV proton beam from a van de Graaff accelerator. In addition to a number of small molecules produced by the proton beam, a non-volatile residue remained when the sample was warmed to room temperature. This residue comprised about one percent of the original sample. Chromatographic analysis showed the order of a hundred peaks which have not been identified. A combined GC-MS analysis for one residue sample selected between 208 and 272°C yielded a maximum molecular weight of 304 for singly ionized material. A second sample showed a maximum of 383 for a column temperature of 140°C.

The Leyden ultraviolet irradiation experiments also yielded a non-volatile residue (Greenberg 1981, 1982) stable to 400–500 K. The infrared spectra of their residue is appreciably different from ours. The reported molecular weight of the Leyden residue with a single value of 514 is extremely puzzling. A sample prepared by an essentially uncontrolled process of irradiation of a light gaseous mixture, followed by warmup would be expected to show many components.

It is apparent that several ways of examining the composition of comets lead to the conclusion that a few percent of cometary ices consist of an arry of complex organic molecules.

The role of comets in the next step of molecular evolution, from organic compounds to biogenic material, is controversial. Organic material in the outer layers has been ejected into space as the cometary coma developed and dissipated. In this book "The Planets" Urey (1952) apparently made the earliest suggestion the the disintegration of comets should have provided volatile elements to the earth and terrestrial planets from which biochemical compounds could be formed (Oro 1961) . The accumulation of cometary volatiles by the earth is reviewed by Lazcano-Araujo and Oro (1981). In addition to accumulation of cometary material by the earth through capture of interplanetary cometary debris, accretion by cometary impact on the earth was also possible. Such a process would lead to capture of essentially all the comet with mass between 10^{15}–10^{20} g. A collision would have heated the material, initially destroying the complex molecules. In the subsequent expansion and cooling of the cloud, reformation of similar compounds are expected to form and be "frozen in". In this view of a cometary contribution to molecular evolution at least part of the terrestrial biochemistry processes start with a pre-existing array of organic compounds rather than a water-ammonia-methane type atmosphere, although some of these simple compounds could also have been incorporated to the Earth by comets.

Hoyle and Wickramasinghe (1978, 1981) argued that cometary interiors rich in radioactive ^{26}Al could have been liquid for long periods of time. During this interval, they propose that the mixture of organic compounds and liquid water was favorable for the production of actual micro-organisms. A general similar view was advanced by Irvine et al. (1980) and Wallis (1980). This mechanism for molecular evolution requires the comet to have accumulated from a cloud rich in the short lived ^{26}Al isotope, half-life = 7.4×10^5 yrs. The comet must be sufficiently heated in the interior to melt water-ice. According to Wallis' calculation this requires about a 5 km radius nucleus. For the typical composition deduced by Delsemme (1982) the C/O ratio is 0.2. If the primary carbon molecule is CO_2, the CO_2/H_2O ratio is 1/3. At the melting point of water, $P(CO_2) \sim 30$ atmospheres. If the mass fraction of CO_2 is 0.1, vaporization of all CO_2 will produce a pressure of 50 atmospheres in the melted volume. Hence there is sufficient CO_2 to sustain the 30 atmosphere pressure. A mixture of $CO + CO_2$ will make the pressure greater. The central pressure for a 10 km nucleus is only 0.1 atm and reaches 1 atm at a 30 km radius. An icy nucleus is an extremely fragile object with little cohesion between the grains comprising the structure (Donn and Rahe 1982). There appears to be little possibility of a few km radius nucleus being able to sustain an excess pressure three hundred times that due to self-gravity.

Temperatures above 0°C would be much more favorable, if not necessary, for the formation of complex, biochemically significant molecules. More effective heating would be required and result in still higher pressures. Although there is evidence for comets with radii of tens of kilometers (Donn and Rahe 1982) they are rare and the probability of a collision with the earth to release material from the central core becomes very low.

In the present state of our knowledge about comets, they are indeed sources of a variety of organic compounds. However, as a place where life in the galaxy may have originated, present evidence for comets is unfavorable.

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