

CHEMICAL THEORIES ON THE ORIGIN OF COMETS

TETSUO YAMAMOTO

*Institute of Space and Astronautical Science
Yoshinodai 3-1-1, Sagami-hara
Kanagawa 229
Japan*

ABSTRACT. Firstly, observational data available at present to infer physical conditions of the formation environment of cometary matter are briefly surveyed. These include the chemical and isotopic composition of cometary matter, and the nuclear spin temperature derived from the ortho/para abundance ratio of H₂O molecules. Secondly, theories on the origin of comets—theories based upon the chemical composition of the volatile component of cometary matter—are reviewed. The theories are classified into two types, distinguished by whether cometary volatiles originate as solar nebula condensates or as the sublimation residue of interstellar ices. Observational items helpful to test the theories are pointed out. Thirdly, discussion is given on the physical properties of ices relevant to the chemical theory of the origin of comets.

1. Introduction

A comet is believed to be one of the most pristine objects in the solar system, preserving the matter of the early solar system and even presolar matter that had been in the parent interstellar cloud. Among the relatively pristine materials of the solar system, cometary matter is particularly remarkable in that it is composed of abundant volatiles, i.e., ices consisting mainly of hydrogen, carbon, nitrogen, oxygen, and sulfur. The goal of a chemical theory on the origin of comets is to reveal the formation history and environment of comets on the basis of study of the cometary matter. The first step in the chemical theory was made by Urey (1952) in his book *The Planets*. Now a wealth of the data on cometary matter provided by the investigation of Comet Halley has led this theory to a new stage in its development. It may be hoped that the study of cometary matter will provide clues that reveal not only the origin of comets, but also the physical conditions of the low-temperature region in the solar nebula and the evolution of matter at the stages from interstellar clouds to planetary systems.

There may seem to be some ambiguity in the meaning of the phrase “the origin of comets”; some people think of it as the origin of cometary *bodies*, whose size is on the order of 10 km or larger, and others think of it as the origin (or formation) of cometary *matter*, which is made up of volatile-rich grains that are micrometer-sized or smaller. For

clarity, in this paper, let us use the latter meaning. For the formation of cometary bodies, see the review by Donn (1990) in this volume. Of course, we must keep in mind that the two meanings are not independent, and thus a final theory must include both (see Donn's review, in which modification of the composition in the accumulation process is discussed).

2. The Physical Clues

We can list the following physical clues to the origin of comets available at present or in the near future: (1) Chemical composition, (2) isotopic composition, (3) the ortho/para ratio of H₂O and possibly other molecules, and (4) the crystalline structure of H₂O ice. This paper concentrates on the theories based on (1). We shall discuss (4) and related thermal properties of ice mixtures in Section 4. Brief comments are given for (2) and (3) in this section.

The isotopic composition provides clues to the formation and subsequent chemical history of cometary matter. One of the notable results of the measurements of the isotopic ratios is that for carbon. The isotopic ratio ¹²C/¹³C has been measured for several comets (Ikeya 1963I, Tago-Sato-Kosaka 1969IX, Kohoutek 1973XII) from the observations of C₂ molecules. The ¹²C/¹³C ratios are roughly equal to the terrestrial value (Vanýsek and Rahe, 1978). In Comet Halley, on the other hand, Wyckoff et al. (1989) obtained ¹²C/¹³C = 67 ± 9 from the observation of CN, which is smaller than the solar value. The implications of these results are discussed by Vanýsek (1990) in this volume. The isotopic abundances of various elements composing dust particles in Comet Halley measured by the Giotto and VEGA spacecraft are reviewed by Jessburger (1990) in this volume.

The measurement of the ortho/para abundance ratio of H₂O molecules is a new and potentially powerful source of information on the origin and evolution of comets. In principle, this method can be applied to other molecular species composed of more than two identical atoms, such as CH₄ and H₂S. The ortho/para ratio of H₂O was firstly measured for Comet Halley (Mumma et al., 1986, 1987, 1990; Weaver et al., 1990, in this volume), and subsequently for Comet Wilson (Larson et al., 1988). The ortho/para ratio is a good indicator to infer the "formation temperature" T_{spin} —that is, the temperature of the quenching of the ortho/para ratio of cometary H₂O ice—since the probabilities of the transitions between the ortho and para states both by radiative and collision-induced processes are extremely small (Mumma et al., 1987), and thus the ratio should preserve information on the formation conditions. In thermal equilibrium, the ortho/para ratio is a function of temperature only. At high temperatures (say, $T \geq 60$ K), the ratio approaches 3, the ratio of the statistical weights of the ortho and para states, and it becomes less than 3 at low temperatures.

From an analysis of the observations of comets Halley and Wilson, Mumma et al. (1989) obtained the ortho/para ratio of 2.3 ± 0.1 pre-perihelion and 2.2 ± 0.1 post-perihelion for Comet Halley, and 3.2 ± 0.2 (consistent with the statistical value of 3) for Comet Wilson, which is a new comet. The ortho/para ratio for Comet Halley corresponds to $T_{\text{spin}} \approx 25$ K. According to Mumma et al. (1989), this result implies that the ice near the surface of the nucleus of a new comet has the ortho/para ratio of 3 because of energetic processing such as the irradiation of cosmic rays when the comets had been in the Oort

cloud for a long time, whereas the inner ice retains the “memory” of the formation conditions. The inner ice sublimates to the coma after a comet becomes a short-period one. The surface ice was lost during many revolutions around the Sun. In consequence, $T_{\text{spin}} \approx 25$ K observed for Comet Halley may be regarded as the “formation temperature” of the H₂O ice, although this temperature is higher than that expected for the temperature of the nucleus in the Oort cloud, if the nucleus is assumed to be a gray body (< 10 K). It is worth comparing here the spin temperatures for cometary H₂O with those for molecules in interstellar dark clouds (Irvine, 1990). The ortho/para ratio has been measured for H₂CO, H₂CS, and C₃H₂, and the values are 1 to 2 for H₂CO, 1.8 ± 0.3 for H₂CS, and 2.4 ± 0.2 for C₃H₂. The corresponding spin temperatures are ~ 10 K for all of the three species.

Finally, it must be pointed out that there remain uncertainties in the interpretation of the spin temperature. It is possible that the ortho/para abundance-ratio changes in various processes that H₂O molecules have experienced up to the time when they are observed in a cometary coma. Mumma et al. (1987) confirmed that the ortho/para ratio was kept invariant in sublimation from the nucleus and in the subsequent collisional and radiative processes in the coma. However, the rate of the change in the ortho/para ratio in a time scale much longer than that in the processes stated above is uncertain in both gas and solid phases; in the latter phase, the rotation of H₂O molecules is hindered. The equilibration time scale between the ortho and para states is an important quantity to be clarified in interpreting the observed spin temperatures in connection with the formation conditions of cometary ice. Furthermore, the effect of irradiation and other processes that may change the ortho/para ratio need to be examined in detail in future study.

3. Characteristics of the Chemical Composition

The chemical composition of the nucleus is the basic datum for chemical theories on the origin of comets. The matter composing the nucleus is classified into volatiles (i.e., ice composed mainly of simple compounds of H, C, N, O, and S) and refractories (i.e., dust including silicates and organic refractories, so-called ‘CHON particles’). Since volatiles are a sensitive indicator of the temperature and radiation in the environment where they condensed and have been placed, they act as a good probe for studying the formation environment of cometary matter. The volatile component of the nucleus is observed as gaseous molecules in the coma. Most of the molecular species observed in the coma are secondary products such as radicals and ions produced via photolysis and other chemical reactions from parent molecules composing the volatiles of the nucleus. To obtain a clue to the origin of comets, we have to know the composition of the parent molecules.

Table 1 lists candidate parent molecules and their abundances observed in the coma of Comet Halley. Although the abundance values have uncertainties, they indicate the remarkable characteristic of coexistence of both oxidized (CO, CO₂) and reduced (CH₄, NH₃) species, indicating that the nuclear volatiles are a mixture of oxidized and reduced compounds. It should be noted that the chemical equilibrium condensation theory of a gas of cosmic abundance (e.g., Lewis, 1974) predicts reduced compounds. The observed abundance of the cometary molecules indicates that cometary ice formed in nonequilibrium conditions.

Table 1. Abundance of Molecules in the Coma of Comet Halley

Species	X/H_2O	References
H ₂ O	1	
CO	0.15 - 0.2 ^a	Eberhardt et al., 1987; Festou et al., 1986; Woods et al., 1986
CO ₂	≤ 0.07 ^b , ~ 0.05 0.02 - 0.04	Combes et al., 1988; Moroz et al., 1987 Allen et al., 1987; Moroz et al., 1987; Krankowski et al., 1986; Combes et al., 1988
CH ₄	0.005 - 0.02	Allen et al., 1987; Kawara et al., 1988
NH ₃	0.01 - 0.02	Allen et al., 1987
N ₂	< 0.02	Allen et al., 1987; Balsiger et al., 1986
HCN	0.001	Schloerb et al., 1987
H ₂ CO	(0.04)	Combes et al., 1988
POM	(0.1)	Huebner et al., 1987

^a At distances larger than 15,000 km from the nucleus.

^b At distances less than 10,000 km from the nucleus.

4. Chemical Theories for the Formation Environment

What are the implications of the volatile abundance? Two types of theories have been proposed for the formation of cometary volatiles within the framework of the formation of cometary bodies in the primordial solar nebula:

- (1) Cometary volatiles are formed in the solar nebula from a gas whose composition was quenched at a high temperature (Lewis and Prinn, 1980; Prinn and Fegley, 1989; Fegley and Prinn, 1989). Another theory of this type is that cometary volatiles are clathrate hydrates formed in the solar nebula (Lunine, 1989).
- (2) Cometary volatiles had originally condensed in the parent interstellar cloud and lost very volatile species by sublimation in the solar nebula (Yamamoto et al., 1983; Yamamoto, 1985a).

In short, the difference between the two theories is summarized as: Are cometary volatiles (1) *condensates in the solar nebula*, or (2) *a sublimation residue of interstellar ices*?

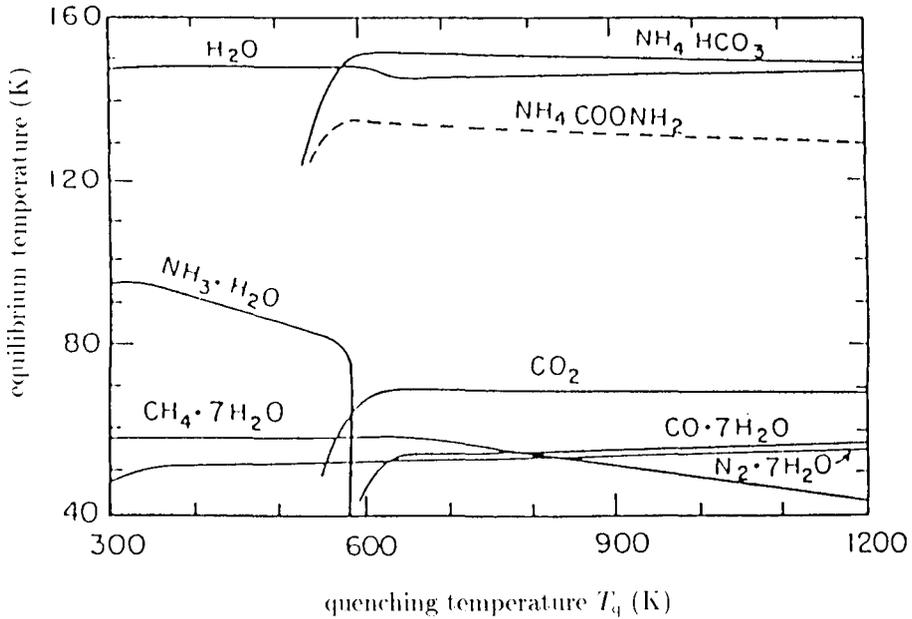


Figure 1. Equilibrium temperature of low-temperature condensates formed from a gas of solar composition, as a function of the quenching temperature. (Based on Lewis and Prinn, 1980.)

4.1. THE QUENCHING MODEL

This model has been discussed in the context of the origin of the atmospheres of the Jovian planets and satellites. In this model, the solar nebula is assumed to be initially hot ($> 1,000$ K). The gaseous composition at this temperature is mainly H_2O , CO , and N_2 , plus H_2 and He , of which the latter two are irrelevant to condensation. Note that the nebular gas is of oxidized composition at high temperatures. As the solar nebula cools down, the gaseous composition is fixed at a certain temperature (called the quenching temperature T_q), since the time scale for achieving chemical equilibrium increases very rapidly as the temperature gets lower, and becomes longer than the nebular dynamical time scale. As a result, the gaseous composition at T_q is maintained at temperatures lower than T_q , which is the point of this model. It should be pointed out that the condensation process itself is treated in an equilibrium manner in which the kinetics of condensation such as nucleation and grain growth, and the resultant supercooling (Yamamoto and Hasegawa, 1977; Draine and Salpeter, 1977; Kozasa and Hasegawa, 1987) are not taken into account.

Figure 1 shows the species of condensates and their equilibrium temperature (i.e., the temperature at which a bulk solid and a gas coexist) as a function of the quenching

temperature (Lewis and Prinn, 1980) for a hypothetical nebular condition, which assumes the pressure to be $\sim 10^{-3}$ to 10^{-5} bar with an adiabatic temperature distribution (Lewis, 1974), though this is not clearly stated by Lewis and Prinn (1980) in the context of Figure 1. The composition of the condensates changes drastically at a critical quenching temperature $T_{qc} \approx 580$ K for the solar nebula model adopted in this figure. For $T_q < T_{qc}$, which implies that the chemical equilibrium is maintained down to low temperatures, H_2O and other reduced compounds such as NH_3 and CH_4 condense as expected from the equilibrium theory. For T_q higher than the critical temperature, on the other hand, the condensation occurs in a gas of oxidized composition. In this case, H_2O condenses at ~ 150 K, and CO_2 at ~ 70 K. Part of the H_2O ice transforms to NH_4HCO_3 and NH_4COONH_2 via reactions with gaseous NH_3 and CO_2 . These ices can be sources of NH_3 and CO_2 observed in the comet. At 60 to 50 K, CO and N_2 condense as clathrate hydrates. Direct condensation of CO and N_2 requires a temperature lower than 25 K.

Let us compare this result with the observed abundances shown in Table 1. The abundances of NH_4HCO_3 and NH_4COONH_2 relative to H_2O are on the order of 0.01, which is roughly in agreement with the observed NH_3 and CO_2 abundances. According to this model, the source of cometary CO and N_2 is expected to be the clathrate hydrates formed around 50 to 60 K, though it is known from experiments that clathrate hydrates do not form below ~ 100 K for species such as H_2S , ethane, acetylene, and some other species (Bertie and Devlin, 1983; Richardson et al., 1985; Consani and Pimentel, 1987). But there have been no experimental studies for the formation conditions of CO and N_2 clathrates.

In their recent work, Prinn and Fegley (1989), and Fegley and Prinn (1989) propose a two-component model to explain the characteristics of the molecular abundance of Comet Halley as described in Section 3. In this model, the volatiles in Comet Halley are a mixture of materials originating from the outer planet subnebulae and those originating either from the solar nebula or the interstellar medium. The reduced components, such as CH_4 - and NH_3 -rich materials, may be formed in the subnebulae, since the total pressure of their hypothetical Jovian subnebula is much higher than that of the solar nebula, and thus $CH_4/CO \ll 1$ and $NH_3/N_2 \sim 1$ are realized at the quenching temperature. On the other hand, the oxidized CO- and N_2 -rich materials originate from the solar nebula. From the CO/CH_4 and N_2/NH_3 abundance ratios of Comet Halley, Fegley and Prinn (1989) deduced the mixing ratio to be 90% solar nebula or interstellar material and 10% subnebula material, though these materials are not specified. The mixing mechanisms that Prinn and Fegley (1989) suggest are:

- (1) Sweep-up of the gas of the reduced composition in the Jovian subnebulae by the objects of the oxidized composition in the solar nebula, or vice versa.
- (2) Partial mixing of the subnebula gas with the solar nebula gas.

A study is needed to examine whether or not these mechanisms are efficient enough to be able to produce the estimated total mass of comets.

One of the clues to test the quenching model is the crystalline structure of cometary H_2O ice. It is experimentally known (see Section 5) that the crystalline structure of H_2O ice depends upon the temperature at which the ice condensed. At the low pressures relevant to cometary ice, the structure of ice is amorphous when condensed at low temperatures, and it is crystalline when condensed at high temperatures. For H_2O ice, the

transition temperature is 130 to 140 K; the ice condensed at temperatures higher than the transition temperature is cubic (I_c) or hexagonal (I_h) ice, again depending upon the condensation temperature. According to the quenching model, the equilibrium temperature of H_2O ice is about 150 K, and thus this theory predicts that the cometary ice should be crystalline. Although some cometary phenomena suggest that fresh cometary ice has an amorphous structure, whether the fresh ice of the inner nucleus is amorphous or not is still an open question. Clarification of the crystalline structure of cometary ice will provide another constraint on the condensation temperature of the ice, as do the measurements of the ortho/para ratio of H_2O described in Section 2.

4.2. THE CLATHRATE HYDRATE MODEL

Lunine (1989) discusses the formation environment of comets in the solar nebula by comparing the observed abundances of molecules with the composition of volatiles incorporated into H_2O ice. The basic idea of this model is that fractionation occurs in the incorporation process of volatile molecules (CO , CH_4 , CO_2) into the pre-existing H_2O ice grains in the solar nebula. For example, the ratio q of the amount of CO to that of CH_4 incorporated into H_2O ice is expressed by

$$q = \frac{p_{CO}}{p_{CH_4}} \cdot \frac{C_{CO}}{C_{CH_4}},$$

where p_X is partial pressure of the species X in the solar nebula, and C_X is the probability of occupancy of the clathrate cage by X , which is called the Langmuir constant. C_X is the fractionation factor, which expresses the degree of fractionation in the incorporation process (in thermal equilibrium). Since C_X is different for different species, the composition of volatiles incorporated into the clathrate hydrate differs from that in the nebular gas.

The results obtained from this model may be summarized as:

- (1) The ratio of CO/CH_4 of the nebular gas in the formation region of cometary volatiles was very high; $CO/CH_4 \sim 10^2$. This is due to C_{CO} being much smaller than C_{CH_4} ($C_{CO}/C_{CH_4} \sim 10^{-2}$), so that a high p_{CO}/p_{CH_4} is required to reproduce the observed q of about 4, the CO/CH_4 ratio for Comet Halley adopted by Lunine.
- (2) The same holds for N_2 . N_2 was a dominant nitrogen compound in the nebular gas in the formation region, but was not efficiently incorporated into the ice grains. The results for the nebular gas composition are in accordance with the result of the quenching model for high quenching temperature.
- (3) The NH_3 abundance was $NH_3/H_2O \sim 10^{-3}$ to 10^{-2} in the formation region.
- (4) CO_2 should be present in Comet Halley as both dry ice and gas trapped in H_2O ice. See Engel et al. (1990) for more recent and extensive work based on the clathrate model. They obtain the results that the observed CH_4/CO and CO_2/CO ratios of Comet Halley can be reproduced, but the observed NH_3/N_2 ratio is too high to be reproduced by clathration of the solar nebula gas.

One of the assumptions in this model is that cometary ice is a clathrate hydrate. The maximum abundance of guest molecules is limited by the number of vacancies in the H₂O ice, about 18% of the H₂O molecular abundance. On the other hand, the observed abundances of the molecules other than H₂O are near the upper limit, or may, in view of the uncertainties of the observed abundances, exceed the limit (Combes et al., 1988). Furthermore, it is claimed (Fegley and Prinn, 1989) that clathrate formation in the solar nebula is improbable because of the high activation energy for clathrate formation compared with the thermal energy of the solar nebula. In any case, we need clear observational evidence to determine whether fresh ice of the nucleus is clathrate hydrate or not. See also Fegley and Prinn (1989) for comments from chemical viewpoint, and Lunine (1989) for the reply to their comments.

As a second requirement, the model assumes crystalline H₂O ice in the calculation of the Langmuir constant C_X . For crystalline ice formation, the condensation temperature should be higher than 130 to 140 K, as stated in Section 4.1, or the ice should have experienced a temperature higher than this transition temperature at some time. The crystalline structure of cometary ice is again a key to test this model, as it was in the quenching model.

4.3. THE INTERSTELLAR-ICE RESIDUE MODEL

Yamamoto et al. (1983) and Yamamoto (1985a) proposed, from comparison of the abundances of cometary and interstellar molecules, that cometary ice is a sublimation residue of interstellar ice. In this model, the formation process is divided into two stages (Yamamoto, 1985b).

First is the interstellar cloud stage, with the cloud being the parent cloud of the solar nebula. At this stage, gaseous molecules in the cloud condense onto grain surfaces to form icy mantles on them. The grain temperature in dense regions of the cloud is as low as ~ 10 K, so even very volatile gaseous species can condense onto the grain surface. The mantle composition will reflect the interstellar gas phase composition, apart from positive ions. These grains in dense molecular clouds have been characterized by Greenberg (1982); the volatile mantle is composed of a mixture of oxidized and reduced species. Note that the chemical composition of the gas and mantles is far from that expected under chemical equilibrium. The chemistry prevailing in interstellar clouds is not thermal chemistry, but rather is based on ion-molecule reactions in the gas phase, because of the low density and temperature of the cloud, as well as irradiation by ultraviolet and cosmic rays penetrating into the cloud. There is also the possibility of molecule formation on the grain surfaces, although the relative importance of such heterogeneous processes in producing molecules observed in the gas phase is not certain.

The second stage occurs when the solar nebula has formed from the interstellar cloud. The important quantities are the temperature distribution of the solar nebula and its time variation, which are, however, not well known at present. In the inner region, most of the grains would have sublimed, and as the gas cooled down, grains would have subsequently recondensed. In the outer solar nebula, on the other hand, there must have been a region where the grains coated with ice mantles survived. Since the solar nebula was warmer than the interstellar cloud, however, very volatile species in the ice mantles would be lost by sublimation. The degree of sublimation depends upon the distance from

the Sun. The formation region of comets is the region where the observed volatile abundances are realized. Comets are planetesimals accreted from the grains in this region.

On the basis of this scenario, Yamamoto et al. (1983) and Yamamoto (1985) deduced the following results from a comparison of the observed cometary molecular abundances with the interstellar values:

- (1) The observed molecular abundances in comets are roughly reproduced from the interstellar abundances, except for CO and N₂.
- (2) CO and N₂ in comets are depleted by more than one order of magnitude compared with the interstellar abundances of CO and N₂. Note that both CO and N₂ are very volatile species, which are expected to be the species lost from the grains by sublimation.
- (3) From (1) and (2), the formation temperature is estimated to be $T_{\text{subl}}(\text{N}_2) \approx 20 \text{ K} < T < T_{\text{subl}}(\text{CO}_2) \approx 70 \text{ K}$ (Figure 2).

Note that the “formation temperature” derived from the ortho/para ratio (see Section 2) is within this temperature range and is close to the lower limit. The formation distance of comets corresponding to this temperature range is estimated to be $14 < r < 80$ to 110 AU, depending upon the temperature distribution of the solar nebula (these values assume a radiative equilibrium or adiabatic distribution). The probable distance would be the region of CO sublimation, which is 65 to 82 AU from the Sun. This may be compared with the distance of 150 to 290 AU that is estimated from the spatial distribution of the aggregates of planetesimals, derived from the kinetics of planetesimals formed by the gravitational fragmentation of the dust layer in the solar nebula (Yamamoto and Kozasa, 1988). It should be kept in mind, however, that the actual distance of comet formation will depend upon the solar nebula model, in particular, upon the actual temperature distribution together with its time variation, and upon the radial transport of the nebular materials.

One of the assumptions made in this model is the simplification of the sublimation process for ice mixtures. Namely, it is assumed that each molecular species composing the ice sublimates independently. However, recent laboratory experiments (see Section 5) reveal that the sublimation of ice mixtures is a complex process, and show that the assumption of independent sublimation is invalid in the temperature range higher than the sublimation temperatures of pure ices.

The second assumption concerns the composition of interstellar ice. This model adopts an interstellar molecule (i.e., *gaseous*) abundance. The composition of the ice mantle (e.g., *solid* composition) is not necessarily the same as the gaseous composition (e.g., d’Hendecourt et al., 1985). The study of the ice in interstellar molecular clouds is an important subject for revealing the initial composition of cometary volatiles; much progress has now been made in infrared observations of interstellar ice, as well as in related laboratory experiments.

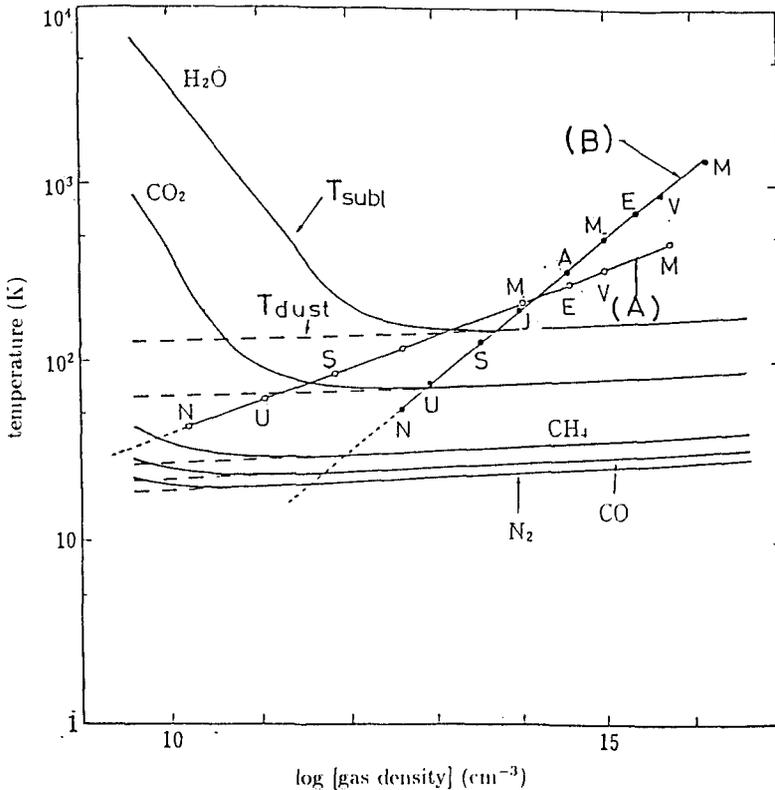


Figure 2. Sublimation temperatures T_{subl} of the candidate parent molecules of the cometary ice as a function of the gas density of the solar nebula. T_{subl} is the temperature of the nebular gas at which each of the molecular species sublimates, and T_{dust} is the corresponding grain temperature. Two temperature distributions of the solar nebula are shown with the formation regions of the planets indicated by M, V, E, ...: (A) the radiative equilibrium distribution (Hayashi, 1981), and (B) the adiabatic distribution (Cameron, 1978).

5. Concluding Remarks

5.1. THERMAL PROPERTIES OF ICES

The thermal properties of ices are of fundamental importance for the study of the origin of comets from the chemical viewpoint, as well as for the study of the thermal evolution of a cometary nucleus (see also Klinger, 1990, in this volume).

Recent experimental studies have revealed the complex behavior of ice sublimation. Even for pure H₂O ice, it has been demonstrated (Kouchi, 1987) that the vapor pressure depends not only on the temperature, but also on the temperature of the substrate on which

Table 2. Sublimation Behavior of H₂O Ice ($H_2O/CO = 0.5$) (based on Kouchi, 1989)

Starting at 14 K	Sublimation of CO _{as}
Starting at 23 K	Sublimation of α -CO
Starting at 34 K	Sublimation of CO adsorbed on H ₂ O _{as}
Starting at 80 K	Sublimation of H ₂ O _{as} (I)
143 < T < 146 K	Transformation of H ₂ O _{as} (III) to I _c
~ 157 K	Transformation from I _c to I _h
≥ 160 K	Sublimation of I _h

Note: The suffixes indicate crystalline structure of H₂O ices; 'as' stands for amorphous, 'c' for cubic, and 'h' for hexagonal.

the vapor condenses and the rate of condensation, although further experiments will be required to confirm this result. For mixtures such as H₂O-CO ice, the sublimation rates of H₂O and CO show rather complicated behavior as a function of temperature (Bar-Nun et al., 1985, 1987; Schmitt and Klinger, 1987; Grim and Greenberg, 1987; Laufer et al., 1987; Moore et al., 1988; Sanford and Allamandola, 1988, Sanford et al., 1988; Schmitt et al. 1989; Kouchi, 1989). For a H₂O-CO ice mixture ($CO/H_2O = 0.5$) condensed at 10 K, for example, distinct sublimation of H₂O and CO is observed in seven temperature ranges, which are summarized in Table 2, with identifications of the processes (Kouchi, 1988).

Although we should be careful in applying the results for laboratory ices to cosmic ices because of differences in the physical conditions, these results have the following implications for the chemical theories of the origin of comets. One of the notable results of these experiments is that CO and other species are retained in H₂O ice up to higher temperatures than the sublimation temperature of pure CO or other components of the ice. This implies that the presence of CO in a cometary nucleus does not necessarily indicate a formation temperature as low as $T_{\text{subl}}(\text{CO}) \approx 20$ to 25 K. More basically, we have to note that the molecular abundance observed in the coma may not simply be equal to the composition of the ice in the nucleus. Namely, there will be fractionation in the sublimation process, when the sublimation temperature is lower than that of H₂O ice. In contrast with the increase in experimental data, theoretical work on this question has hardly been done at all. Theoretical modelling of the sublimation process of ice mixtures, as well as further experimentation, is very much needed to understand the elementary processes and to correctly apply the experimental results to cometary ice and cosmic ices in general.

5.2. CRYSTALLINE STRUCTURE OF COMETARY ICE

The crystalline structure of the ice of a cometary nucleus is one of the keys to testing the theories described in Section 4. The theory of the solar-nebula condensates

predicts the condensation temperature of H₂O ice to be about 150 K for the assumed nebular pressure of $\sim 10^{-3}$ to 10^{-5} bar. This temperature is higher than the transition temperature of amorphous ice to crystalline ice. On the other hand, the theory of interstellar-ice residue predicts that the condensation occurs at the temperature of grains (~ 10 K) in the interstellar cloud and that the ice has not experienced temperatures higher than the transition temperature. Thus, crystalline ice is predicted by the former theory and amorphous ice by the latter theory. Observations to clarify the crystalline structure of fresh nuclear ice are very important for determining which theory is plausible.

5.3. POSSIBLE ALTERATION PROCESSES OF THE ORIGINAL ICE

One has to note various alteration processes that fresh ice of a cometary nucleus would have suffered from the time of condensation up to the present time. These processes are of two distinct types. One includes the processing before or during accretion to form cometary bodies (i.e., at the stage of grains and their aggregates), and the other the processing of the ice of the nucleus after the accretion.

For the first group, Donn (1990, in this volume) discusses heating at collisions of grain aggregates during the accretion of grains to planetesimals (cometesimals) in the solar nebula or in the interstellar cloud. Another is heating during the high-temperature phase at the formation of the solar nebula. Yamamoto (1985) briefly discusses the effect of this heating. Engel et al. (1990) discusses heating of grains falling into the solar nebula.

The second group of processes involves alteration of the ice in a cometary nucleus. One of the alteration processes is the thermal evolution of cometary nuclei during revolution around the Sun. This effect may lead to changes in both the crystalline structure and the chemical composition of the ice near the surface of the nucleus. The possibility that we can observe "fresh" ice depends on the depth to which the ice suffers thermal alteration, and on what fraction of the molecules that we observe originates from "fresh" ice. These are the quantities to be clarified from the study of the thermal evolution. See Rickman (1990, in this volume) for a review of the thermal evolution.

Irradiation by charged particles also leads to alteration of the ice (Moore et al., 1983; Strazzulla and Johnson, 1990, in this volume). This processing is effective not only for the ice on the surface of the nucleus during residence in the Oort cloud, but also for the ice on grain surfaces before accretion to form cometary bodies.

Radioactive heating is another possible alteration process of the ice in the interior of the nucleus. Whipple and Stefanik (1966) first discussed this effect in their theory of the splitting of a cometary nucleus resulting from redistribution of volatiles in the nucleus. Various kinds of possible alteration of the ice in the nucleus are discussed, such as the presence of a liquid phase in the central region of a cometary nucleus just after accretion due to heating by the short-lived nucleid ²⁶Al (Wallis, 1980), transition of amorphous ice to crystalline ice (Priainik et al., 1987), and formation of a layered structure in the chemical composition of the nucleus (Yabushita and Wada, 1988).

Acknowledgements

The author thanks Dr. B. Donn and Prof. W.M. Irvine for invaluable comments, which much improved the original manuscript. Thanks are also due to R. Newburn, Jr.,

as an editor for his patient help in completing the manuscript. This work was partly supported by the Special Research Project on Evolution of Matter, University of Tsukuba, and by Grant-in-Aid (62611004) from the Ministry of Education, Science, and Culture of Japan.

References

- Allen, M., Delitsky, M., Huntress, W., Yung, Y., Ip, W.-H., Schwenn, R., Rosenbauer, H., Shelley, E., Balsiger, H., and Geiss, J. (1987). 'Evidence for methane and ammonia in the coma of comet P/Halley,' *Astron. Astrophys.* 187, 502–512.
- Balsiger, H., Altweg, K., Bühler, F., Geiss, J., Ghielmetti, A.G., Goldstein, B.E., Goldstein, R., Huntress, W.T., Ip, W.-H., Lazarus, A.J., Meier, A., Neugebauer, M., Rettenmund, U., Rosenbauer, H., Schwenn, R., Sharp, R.D., Shelley, E.G., Ungstrup, E., and Young, D.T. (1986). 'Ion composition and dynamics at comet Halley,' *Nature* 321, 330–334.
- Bar-Nun, A., Herman, G., Laufer, D., and Rappaport, M.L. (1985). 'Trapping and release of gases by water and implications for icy bodies,' *Icarus* 63, 317–332.
- Bar-Nun, A., Dror, J., Kochavi, E., and Laufer, D. (1987). 'Amorphous ice and its ability to trap gases,' *Phys. Rev.* B35, 2427–2435.
- Bertie, J.E., and Devlin, J.P. (1983). 'Infrared spectroscopic proof of the formation of the structure I hydrate of oxirane from annealed low-temperature condensate,' *J. Chem. Phys.* 78, 6340–6341.
- Cameron, A.G.W. (1978). 'Physics of the primitive solar accretion disk,' *Moon and Planets* 18, 5–40.
- Combes, M., Moroz, V.I., Crovisier, J., Encrenaz, T., Bibring, J.-P., Grigoriev, A.V., Sanko, N.F., Coron, N., Crifo, J.F., Gispert, R., Bockelée-Morvan, D., Nikolsky, Yu.V., Krasnopolsky, V.A., Owen, T., Emerich, C., Lamarre, J.M., and Rocard, F. (1988). 'The 2.5 - 12 μ m spectrum of comet Halley from the IKS-VEGA experiment,' *Icarus* 76, 404–436.
- Consani, K., and Pimentel, G.C. (1987). 'Infrared spectra of the clathrate hydrates of acetylene and of acetylene/acetone,' *J. Phys. Chem.* 91, 289–293.
- d'Hendecourt, L.B., Allamandola, L.J., and Greenberg, J.M. (1985). 'Time dependent chemistry in dense molecular clouds I. Grain surface reactions, gas/grain interactions and infrared spectroscopy,' *Astron. Astrophys.* 152, 130–150.
- Donn, B. (1990). 'The accumulation and structure of comets,' in this volume.
- Draine, B.T., and Salpeter, E.E. (1977). 'Time-dependent nucleation theory,' *J. Chem. Phys.* 67, 2230–2235.
- Eberhardt, P., Krankowski, D., Schulte, W., Dolder, U., Lammerzähl, P., Berthelier, J.J., Woweries, J., Stubbemann, U., Hodges, R.R., Hoffman, J.H., and Illiano, J.M. (1987). 'The CO and N₂ abundance in comet P/Halley,' *Astron. Astrophys.* 187, 481–484.
- Engel, S., Lunine, J.I., and Lewis, J.S. (1990). 'Solar nebula origin for volatiles in Halley's comet,' preprint, *Icarus*, in press.
- Fegley, B., Jr., and Prinn, R.G. (1989). 'Solar nebula chemistry: Implications for volatiles in the solar nebula,' *The Formation and Evolution of Planetary Systems*, H.A. Weaver, and L. Danley (eds.), Cambridge University Press, Cambridge, pp. 171–211.

- Festou, M.C., Feldman, P.D., A'Hearn, M.F., Arpigny, C., Cosmovici, C.B., Danks, A.C., McFadden, L.A., Gilmozzi, R., Patriarchi, P., Tozzi, G.P., Wallis, M.K., and Weaver, H.A. (1986). 'IUE observations of comet Halley during the Vega and Giotto encounters,' *Nature* 321, 361–363.
- Greenberg, J.M. (1982). 'What are comets made of? A model based on interstellar dust,' *Comets*, L.L. Wilkening (ed.), University of Arizona Press, Tucson, pp. 131–163.
- Grim, R.J.A., and Greenberg, J.M. (1987). 'Photoprocessing of H₂S in interstellar grain mantles as an explanation for S₂ in comets,' *Astron. Astrophys.* 181, 155–168.
- Hayashi, C. (1981). 'Structure of the solar nebula, growth and decay of magnetic fields and effect of magnetic and turbulent viscosities on the nebula,' *Suppl. Prog. Theor. Phys.* No. 70, 35–53.
- Huebner, W.F., Boyce, D.C., and Sharp, C.M. (1987). 'Polyoxymethylene in Comet Halley,' *Astrophys. J.* 320, L149–L152.
- Irvine, W.M. (1990). 'Cold, dark interstellar clouds: Can gas-phase reactions explain the observations?', *Chemistry and Spectroscopy of Interstellar Molecules*, N. Kaifu (ed.), University of Tokyo Press, in press.
- Jessburger, E. (1990). 'Chemical properties of cometary dust,' in this volume.
- Kawara, K., Gregory, B., Yamamoto, T., and Shibai, H. (1988). 'Infrared spectroscopic observation of methane in comet P/Halley,' *Astron. Astrophys.* 207, 174–181.
- Krankowski, D., Lämmerzahl, P., Herrwerth, I., Wowerth, J., Eberhardt, P., Dolder, U., Herrmann, U., Schulte, W., Berthelier, J.J., Illiano, J.M., Hodges, R.R., and Hoffman, J.H. (1986). '*In situ* gas and ion measurements at comet Halley,' *Nature* 321, 326–329.
- Klinger, J. (1990). 'Physical properties of frozen volatiles—Their relevance to the study of comet nuclei,' in this volume.
- Kouchi, A. (1987). 'Vapour pressure of amorphous H₂O ice and its astrophysical implications,' *Nature* 330, 550–552.
- Kouchi, A. (1989). 'Evaporation of H₂O ice and its astrophysical implications,' to be published in *J. Crystal Growth (Proc. Int. Conf. Crystal Growth, held in Sendai, August, 1988)*.
- Kozasa, T., and Hasegawa, H. (1987). 'Grain formation through nucleation process in astrophysical environments. II,' *Prog. Theor. Phys.* 77, 1402–1410.
- Larson, H.P., Weaver, H.A., Mumma, M.J., and Drapatz, S. (1988). 'Airborne infrared spectroscopy of Comet Wilson (1986) and comparison with Comet Halley,' *Astrophys. J.*, 338, 1106–1114.
- Laufer, D.E., Kochavi, E., and Bar-Nun, A. (1987). 'Structure and dynamics of amorphous water ice,' *Phys. Rev.* B36, 9219–9227.
- Lewis, J.S. (1974). 'The temperature gradient in the solar nebula,' *Science* 186, 440–443.
- Lewis, J.S., and Prinn, R.G. (1980). 'Kinetic inhibition of CO and N₂ reduction in the solar nebula,' *Astrophys. J.* 238, 357–364.
- Lunine, J.I. (1989). 'Primitive bodies: Molecular abundances in Comet Halley as probes of cometary formation environment,' *The Formation and Evolution of Planetary Systems*, H.A. Weaver, L. Danley, and F. Paresce (eds.), Cambridge University Press, Cambridge, pp. 213–242.
- Moore, M.H., Donn, B., and Hudson, R.L. (1988). 'Vaporization of ices containing S₂ — Implications for comets,' *Icarus* 74, 399–412.

- Moore, M.H., Donn, B., Khanna, R., and A'Hearn, M.F. (1983). 'Studies of proton-irradiated cometary-type ice mixtures,' *Icarus* 54, 388–405.
- Moroz, V.I., Combes, M., Bibring, J.P., Coron, N., Crovisier, J., Encrenaz, T., Crifo, J.F., Sanko, N., Grigoriev, A.V., Bockelée-Morvan, D., Gispert, R., Nikolsky, Y.V., Emerich, C., Lamarre, J.M., Rocard, F., Krasnopolsky, V.A., and Owen, T. (1987). 'Detection of parent molecules in comet Halley, from the IKS-Vega experiment,' *Astron. Astrophys.* 187, 513–518.
- Mumma, M.J., Blass, W.E., Weaver, H.A., and Larson, H.P. (1990). 'Measurements of the ortho-para ratio and nuclear spin temperature of water vapor in comet P/Halley,' *Icarus*, in press.
- Mumma, M.J., Weaver, H.A., and Larson, H.P. (1986). 'The ortho/para ratio of water vapor in comet Halley,' 20th ESLAB Symposium on the Exploration of Halley's Comet, ESA SP-250, vol. 1, pp. 341–346.
- Mumma, M.J., Weaver, H.A., and Larson, H.P. (1987). 'The ortho-para ratio of water vapor in comet P/Halley,' *Astron. Astrophys.* 187, 419–424.
- Prialnik, D., Bar-Nun, A., and Podolak, M. (1987). 'Radiogenic heating of comets by ^{26}Al and implications for their time of formation,' *Astrophys. J.* 319, 993–1002.
- Prinn, R.G., and Fegley, B., Jr. (1989). 'Solar nebula chemistry: Origin of planetary, satellite, and cometary volatiles,' *Origin and Evolution of Planetary and Satellite Atmospheres*, S. Atrea, J. Pollack, and M. Matthews (eds.), University of Arizona Press, Tucson, pp. 78–136.
- Richardson, H.H., Wooldridge, P.J., and Devlin, J.P. (1985). 'FT-IR spectra of vacuum deposited clathrate hydrates of oxirane H_2S , THF, and ethane,' *J. Chem. Phys.* 83, 4387–4394.
- Rickman, H. (1990). 'The thermal history and structure of cometary nuclei,' in this volume.
- Sanford, S.A., and Allamandola, L.J. (1988). 'The condensation and vaporization behavior of $\text{H}_2\text{O}:\text{CO}$ ices and implications for interstellar grains and cometary activity,' *Icarus* 76, 201–224.
- Sanford, S.A., Allamandola, L.J., Tielens, A.G.G.M., and Valero, G.J. (1988). 'Laboratory studies of the infrared spectral properties of CO in astrophysical ices,' *Astrophys. J.* 329, 498–510.
- Schloerb, F.P., Kinzel, W.M., Swade, D.A., and Irvine, W.M. (1987). 'Observations of HCN in comet P/Halley,' *Astron. Astrophys.* 187, 475–480.
- Schmitt, B., and Klinger, J. (1987). 'Different trapping mechanisms of gases by water ice and their relevance for cometary nuclei,' *Proc. Symposium on the Diversity and Similarity of Comets*, ESA SP-278, pp. 613–619.
- Schmitt, B., Greenberg, J.M., and Grim, R.J.A. (1989). 'The temperature dependence of the CO infrared band strength in $\text{CO}:\text{H}_2\text{O}$ ices,' *Astrophys. J.* 340, L33–L36.
- Strazzulla, G., and Johnson, R.E. (1990). 'Irradiation effects on comets and cometary debris,' in this volume.
- Urey, H. (1952). *The Planets*, Oxford University Press, Oxford.
- Vanýsek, V. (1990). 'Isotopic ratios in comets,' in this volume.
- Vanýsek, V., and Rahe, J. (1978). ' $^{12}\text{C}/^{13}\text{C}$ ratio in comets,' *Moon and Planets* 18, 441–445.
- Wallis, M.K. (1980). 'Radiogenic melting of primordial comet interior,' *Nature* 284, 431–433.

- Weaver, H.A., Mumma, M.J., and Larson, H.P. (1990). 'Infrared spectroscopy of cometary parent molecules,' in this volume.
- Whipple, F.L., and Stefanik, R.P. (1966). 'On the physics and splitting of cometary nuclei,' *Mem. Soc. Roy. Sci. Liège, Sér. 5*, 12, 33–52.
- Woods, T.N., Feldman, P.D., Dymond, K.F., and Sahnou, D.J. (1986). 'Rocket ultraviolet spectroscopy of comet Halley and abundance of carbon monoxide and carbon,' *Nature* 324, 436–438.
- Wyckoff, S., Lindholm, E., Wehinger, P.A., Peterson, B.A., Zucconi, J.-M., and Festou, M.C. (1989). 'The $^{12}\text{C}/^{13}\text{C}$ abundance ratio in comet Halley,' *Astrophys. J.* 339, 488–500.
- Yabushita, S., and Wada, K. (1988). 'Radioactive heating and layered structure of cometary nuclei,' *Earth, Moon, and Planets* 40, 303–313.
- Yamamoto, T. (1985a). 'Formation environment of cometary nuclei in the primordial solar nebula,' *Astron. Astrophys.* 142, 31–36.
- Yamamoto, T. (1985b). 'Formation history and environment of cometary nuclei,' *Ices in the Solar System*, J. Klinger, D. Benest, A. Dollfus, and R. Smoluchowski (eds.), D. Reidel Publishing Co., Dordrecht, pp. 205–219.
- Yamamoto, T., and Hasegawa, H. (1977). 'Grain formation through nucleation process in astrophysical environment,' *Prog. Theor. Phys.* 58, 816–828.
- Yamamoto, T., and Kozasa, T. (1988). 'The cometary nucleus as an aggregate of planetesimals,' *Icarus* 75, 540–551.
- Yamamoto, T., Nakagawa, N., and Fukui, Y. (1983). 'The chemical composition and thermal history of the ice of a cometary nucleus,' *Astron. Astrophys.* 122, 171–176.