Constraints on the Formation of Comets from D/H Ratios Measured in H₂O and HCN

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This report is the follow-up of the paper of A. Drouart *et al.* (1999, *Icarus* 140, 129) in which it was demonstrated that appropriate models of the solar nebula permit us to interpret the deuterium enrichment in water with respect to the protosolar D/H ratio measured in LL3 meteorites and comets. In the present report, we show that the models selected by Drouart *et al.* are also able to explain D/H in HCN measured in Comet C/1995 O1 (Hale–Bopp). We find that the D/H ratio in HCN entering the nebula is $\sim 4 \times 10^{-3}$, which is significantly less than values measured in cold dark clouds, but consistent with values found in hot molecular cores. Both H₂O and HCN ices infalling from the presolar cloud onto the nebula discoid evaporated in the turbulent part of the nebula, isotopically exchanged with hydrogen, and mixed with water vapor coming from the inner part of the nebula. Subsequently, H₂O and HCN ices with D/H ratios measured in Comet Hale–Bopp condensed, agglomerated and were incorporated in cometesimals. In the light of these results, we discuss the story of molecules detected in comets coming from Oort cloud. Most molecules detected in Comet Hale–Bopp originated from ices embedded in the presolar cloud. Ices vaporized prior to entering into the nebula or in the early nebula, and subsequently recondensed, except highly volatile molecules. According to A. Kouchi *et al.* (1994, *Astron. Astrophys.* 290, 1009), water ice condensed in crystalline form. We discuss the possibility that the most volatile species were then trapped in the form of clathrate hydrates. The oversolar C/N ratio and the strong depletion of Ne/O with respect to the solar abundance observed in comets are in agreement with the theory of clathrate hydrates of J. I. Lunine and D. J. Stevenson (1985, *Astrophys. suppl. Ser.* 58, 493). Comets formed in the Kuiper belt may contain amorphous water ice and have kept the isotopic signature of the presolar cloud. New published models of interiors of Uranus and Neptune permit us to calculate that the D/H ratios in proto-uranian and proto-neptunian water ices are in agreement with those measured in comets. This confirms the current assumption that cometesimals and planetesimals that formed the cores of Uranus and Neptune had similar compositions. © 2000 Academic Press

Key Words: solar nebula; deuterium; comets; turbulent diffusion.

1. INTRODUCTION

The D/H ratio in water has been measured in LL3 meteorites (Deloule *et al.* 1998), and in comets P/Halley, C/1996

TABLE I
D/H Ratios in the Solar System Relevant to This Work (in Units of 10^{-5})

Object	Species	D/H	References
Solar Nebula	H_2	2.6 ± 0.7^a	Mahaffy *et al.* 1998
		2.1 ± 0.5^b	Geiss and Gloecker 1998
		$1.8^{+1.1}_{-0.5}{}^c$	Lellouch *et al.* 1997
LL3 meteorites	OH	8.8 ± 1.1 (low-D)	Deloule *et al.* 1998
		73 ± 12 (high-D)	
P/Halley	H_2O	$30.8^{+3.8}_{-5.3}$	Balsiger *et al.* 1995
		31.6 ± 3.4	Eberhardt *et al.* 1995
C/1996 B2 (Hyakutake)	H_2O	29 ± 10	Bockelée-Morvan *et al.* 1998
C/1995 Ol (Hale–Bopp)	H_2O	33 ± 8	Meier *et al.* 1998a
	HCN	230 ± 40	Meier *et al.* 1998b
Uranus today	H_2	$5.5^{+3.5}_{-1.5}$	Feuchtgruber *et al.* 1999
Proto-uranian ices	H_2O	≤ 37	This work^d
Neptune today	H_2	$6.5^{+2.5}_{-1.5}$	Feuchtgruber *et al.* 1999
Proto-neptunian ices	H_2O	≤ 25	This work^d

[a] From *in situ* measurements in Jupiter with the Galileo probe.

[b] From ^{3}He/^{4}He in solar wind.

[c] From ISO observations of Jupiter.

[d] The D/H ratios in proto-uranian and proto-neptunian ices are inferred as in Lécluse *et al.* (1996). Masses of gas, ices, and rocks in Uranus and Neptune are from Podolak *et al.* (2000). Gas is supposed to be composed of H_2 and He in proto-solar proportions. The ices/rocks mass ratio is solar and taken equal to 2.1 from Anders and Grevesse (1989).

B2 (Hyakutake), and C/1995 O1 (Hale–Bopp) (Balsiger *et al.* 1995, Eberhardt *et al.* 1995, Bockelée-Morvan *et al.* 1998, Meier *et al.* 1998a) (Table I). A physical interpretation of these measurements has been made by Drouart *et al.* (1999) (hereafter Paper I), by calculating the deuterium enrichment factor f in water with respect to the protosolar value (in H_2) in the solar nebula as a function of heliocentric distance and time. This computation uses time-dependent temperature, density, and pressure profiles generated by the analytical model of the solar nebula of Dubrulle (1993), which describes the evolution of the nebula subsequent to the formation of the Sun. This model and the associate profiles depend only on three physical parameters: the initial mass of the nebula M_{D0}, its initial radius R_{D0}, and the coefficient of turbulent viscosity α, parameterizing the action of small-scale turbulence (Shakura and Sunyaev 1973). In Paper I, a range of possible values for M_{D0}, R_{D0}, and α was obtained by integrating the equation of diffusion, which rules the temporal and radial evolution of the enrichment factor f for D/H in water in the nebula, and comparing the obtained f to observations (Table I). The comparison with D/H measured in LL3 meteorites, supposed to be formed around 3 AU, proved that water vapor at 3 AU did not come only from the hot inner nebula but mainly originates from ices infalling from the presolar cloud onto the whole nebula discoid. The D/H ratio at 3 AU is due to the reprocessing of the outer component and to its mixing with the inner component. This is also the case for the value in comets coming from the Oort cloud, if ices which formed cometesimals condensed in the turbulent nebula.

When Paper I was written, there was a difficulty coming from the fact that the D/H ratios measured in Uranus and Neptune are much lower than the ratios measured in comets coming from the Oort cloud, while all these objects are currently supposed to have had their cores formed from planetesimals produced at the same time and in the same regions of the nebula. Therefore, several scenarios for the formation of comets were envisaged, and the models of the nebula were constrained only by the value of D/H in LL3 meteorites at 3 AU. As a result, the α coefficient could be between 0.003 and 1.0, and R_{D0} between 8 and 28 AU.

Recent models of the interiors of Uranus and Neptune have changed the situation, however (Podolak *et al.* 2000). The key point is that, according to models of formation of Uranus and Neptune, the D/H ratio in H_2 presently measured in the outer atmosphere of these planets results from the mixing of the D/H ratio in hydrogen originating from the nebula with that in ices substantially enriched in deuterium and contained in the planetesimals which formed the cores of the planets. Under the assumption that a complete isotopic exchange between hydrogen and ices did occur at least once in the history of the planet, the D/H ratio in proto-uranian or proto-neptunian ices can be inferred from the relative proportions of the two deuterated components (Lécluse *et al.* 1996). While previous models announced a modest proportion of gas (Podolak *et al.* 1995), implying that the D/H ratio in proto-neptunian or proto-uranian ices was substantially lower than in comets (Paper I), the recent models of Podolak *et al.* (2000) indicate that the amount of gas (H + He in solar proportions) could be as high as 4.2 Earth mass ($M_\oplus$) for Uranus and 3.2 $M_\oplus$ for Neptune if the mixture of rocks and ices

TABLE II
Solar Nebula Models: Initial Radius R_{D0} and Mass M_{D0}

R_{D0} (AU)	15	17	19	21	23	25	27
M_{D0} min(M$_\odot$)	0.06	0.08	0.11	0.14	0.18	0.22	0.27
M_{D0} max(M$_\odot$)	0.09	0.12	0.16	0.20	0.26	0.30	0.30

was in solar proportions, still higher if the ratio ices/rocks was subsolar. With these numbers, the D/H ratio in proto-uranian or proto-neptunian ices becomes compatible with the cometary values (see Table I). In this case, cometesimals and planetesimals must have been produced simultaneously in the early nebula. This rules out high-viscosity disks which result in too fast a decrease of the deuterium enrichment factor in the Uranus–Neptune region to be compatible with observations (Fig. 9 of Paper I). Quantitatively, this implies that α must be of the order of 0.003, R_{D0} between 14 and 28 AU, and M_{D0} between 0.06 and 0.3 M$_\odot$ (Table II, extracted from Table 2 of Paper I).

Since DCN has also been detected in Comet Hale–Bopp, the next logical step is to verify if D/H in HCN measured in this comet is consistent with the models of nebula which permit us to interpret D/H in H₂O. The present report is devoted to this analysis. Meier *et al.* (1998b) inferred a D/H ratio in HCN and H₂O of $(230 \pm 40) \times 10^{-5}$ and $(33 \pm 8) \times 10^{-5}$, respectively, from single dish observations of DCN and HDO radio lines. From radio interferometric maps, Blake *et al.* (1999) suggest D/H values in HCN and H₂O respectively 10 times and 5–10 times higher in jets than in the average coma. Since no variations of the D/H ratio in H₂O have been seen along the Giotto trajectory in the coma of Comet P/Halley (Eberhardt *et al.* 1995), and because we believe that the Blake *et al.* data require further analysis, we will not consider their results in this paper.

The model and the equation of diffusion, which describe the temporal and radial evolution of the deuterium enrichment in HCN throughout the nebula, are presented in section 2. Results of calculations are compared to cometary measurements in section 3. In section 4, we infer the D/H ratio in HCN ices which infall from the presolar cloud onto the nebula and, comparing with constraints from D/H in H₂O, we constrain the region and time of formation of microscopic cometary grains. In the light of our analysis, the story of the molecules and of silicates observed in comets is discussed in section 5. Our conclusion is given in section 6.

2. MODELS OF THE SOLAR NEBULA AND EQUATION OF DIFFUSION

Our solar nebula models are described in Paper I and in Dubrulle (1993). For reasons mentioned above, only models corresponding to $\alpha = 0.003$ and to mass limits given in Table II were considered. Temperature, pressure, and surface density profiles are expressed as a function of heliocentric distance R and of time t (Eq. (8) of Paper I). The origin of time is the moment where the formation of the Sun is almost complete, namely

when the accretion rate begins to diminish. Limiting the initial radius of the turbulent nebula to a given value R_{D0} does not imply that the region outside R_{D0} is empty. In fact, it has been observed that some circumstellar disks extend at very large distances from the central star, up to 1000 AU. As discussed in Paper I, this turbulent nebula may be surrounded by a quiescent Keplerian disk, relics of the collapse of the presolar cloud. This is what we assume in this report.

Under the action of turbulence, the nebula spreads out viscously with time. As a consequence, the radius of the *turbulent* nebula increases with time, at a rate governed by the value of the turbulent viscosity:

$$\frac{dR_D}{dt} = \frac{3}{2}\frac{v}{R_D}, \tag{1}$$

with $R_D = R_{D0}$ at $t = 0$. v is the turbulent viscosity defined in the framework of the α disk theory by

$$v = \alpha \frac{C_s^2}{\Omega}, \tag{2}$$

where C_s is the local velocity of sound and Ω is the Kepler rotation frequency. Equation (1) is derived from dimensional arguments. The prefactor 3/2 has been chosen so that the expansion velocity is the opposite of the accretion velocity. This takes into account the momentum transfer principle according to which part of the material migrates inward, producing the accretion, while the other part migrates outward, taking away the angular momentum. Equation (1) is valid as long as the nebula is turbulent and under the assumption that α does not vary with R and t. The question of the persistence of the turbulence at large heliocentric distances is an open question. An example of the result of integrating Eq. (1) for a selected nebula is shown on Fig. 1.

The temporal evolution of the temperature, pressure, and surface density depends upon the evolution of the accretion rate for which we have followed the prescription of Makalkin and
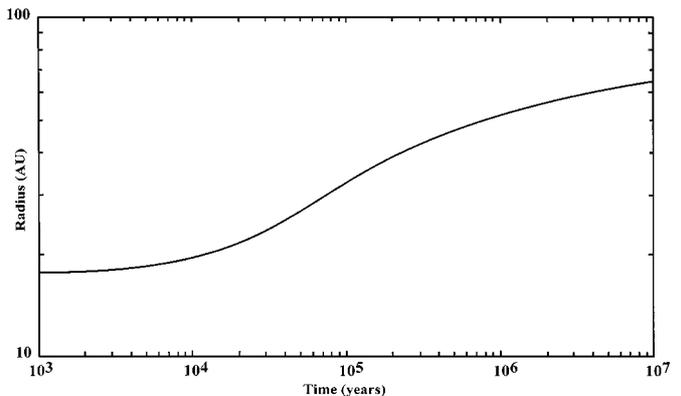
FIG. 1. Radius of the turbulent nebula as a function of time t, for a model characterized by the parameters $M_D = 0.1$ M$_\odot$ and $R_D = 17$ AU at $t = 0$, and $\alpha = 0.003$.

Dorofeyeva (1991). This is a simple power law which depends upon the accretion rate at $t = 0$, $\dot{M}_0$, and the accretion timescale t_0. Both parameters are fixed only by α, R_{D0}, and M_{D0} (Paper I). Interestingly enough, the $\dot{M}_0$ values that we get for the nebulae selected in Paper I are of the order of a few 10^{-6} M$_\odot$ per year, in agreement with the values inferred from the observed evolution of circumstellar disks by Stepinski (1998).

Examples of temperature, pressure, and surface density evolutionary profiles for a nebula defined by $\alpha = 0.003$, $R_{D0} = 17$ UA and $M_{D0} = 0.1$ M$_\odot$ are shown on Figs. 2a, 2b, and 2c. It must be noted that, at 1 million years, the temperature at the edge of the nebula (53 AU) is of a few K only, a value of the order of that in the interstellar medium (ISM). It is likely that, at this location, the hydrodynamics approximation breaks down, and that, beyond this point, the nebula is quiescent and Keplerian, in agreement with our initial assumption.

The enrichment factor f is defined as the ratio of D/H in the considered deuterated species to D/H in hydrogen. For instance, for water we have

$$f = \frac{1/2}{1/2} \frac{\mathrm{HDO/H_2O}}{\mathrm{HD/H_2}}, \qquad (3)$$

while for HCN we have

$$f = \frac{\mathrm{DCN/HCN}}{1/2\,\mathrm{HD/H_2}}. \qquad (4)$$

The evolution of f in the nebula is described by the differential equation (Paper I):

$$\partial_t f = k(T)P(A(T) - f) + \frac{1}{\Sigma R}\partial_R(\kappa R \Sigma \partial_R f). \qquad (5)$$

The first member on the right side of Eq. (5) describes the isotopic exchange between HD and the concerned deuterated molecule, namely in this report either HDO or DCN. Function $k(T)$ is the rate of isotopic exchange, P is the total pressure, and $A(T)$ is the fractionation at equilibrium. Rate $k(T)$ is difficult to measure at the laboratory at room temperatures T because the rate of isotopic exchange drastically decreases with temperature. For instance, $k(T)$ for the exchange HDO–H$_2$ decreases by 5 orders of magnitude when the temperature varies from 1000 to 300 K. However, it has been measured for H$_2$O and CH$_4$ by Lécluse and Robert (1994). Since no experimental determination of $k(T)$ is available for the isotopic exchange of DCN with H$_2$, we use that of CH$_4$, and we have taken the expression given in Lécluse *et al.* (1996). We thus assume that the activation energy for CH is the same in the CH$_4$ and in the HCN molecules. $k(T)$ for CH$_4$ is about 2 orders of magnitude lower than $k(T)$ for H$_2$O. The isotopic exchange between DCN and H$_2$ is then expected to be substantially slower than the isotopic exchange between HDO and H$_2$. $A(T)$ is taken from the tabulations of Richet *et al.* (1977) for both HDO/H$_2$O and DCN/HCN, and is extrapolated to temperatures lower than 0°C.
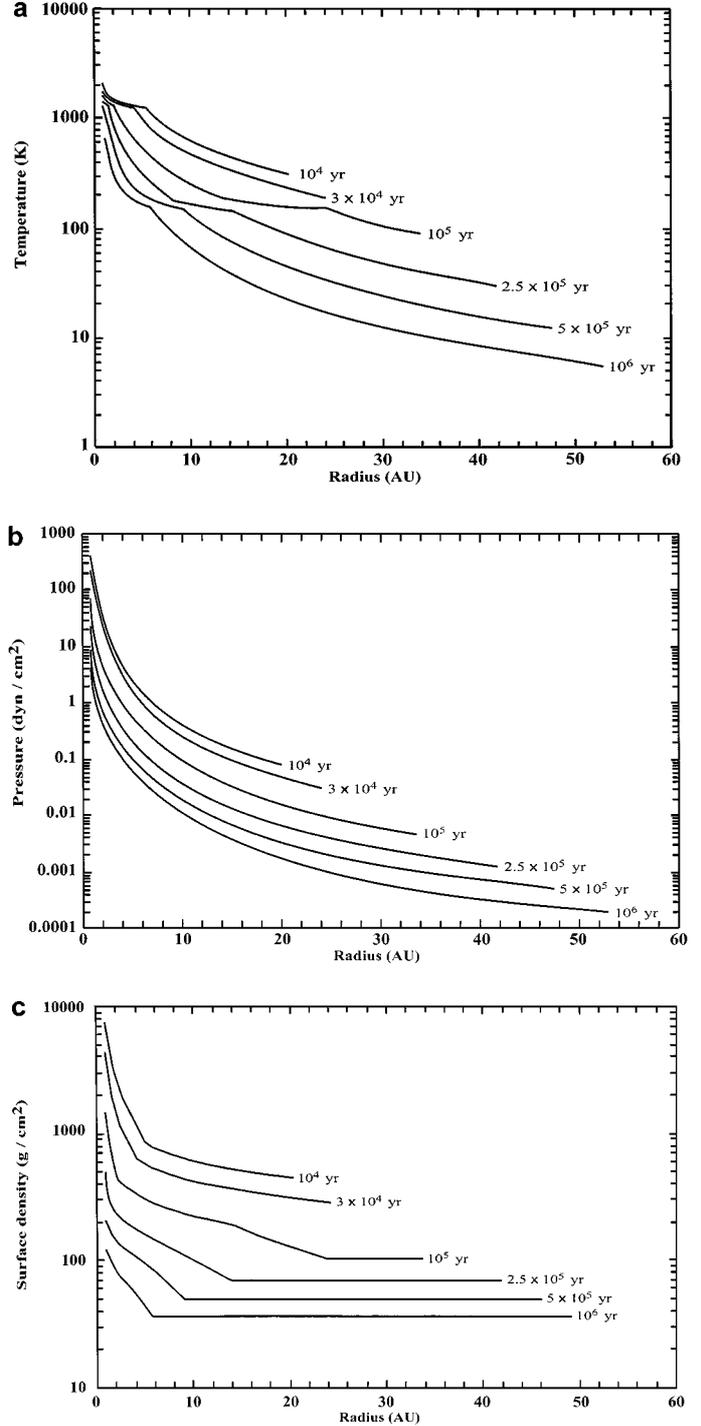
FIG. 2. Radial profiles in the turbulent nebula characterized by the parameters $M_D = 0.1$ M$_\odot$ and $R_D = 17$ AU at $t = 0$, and $\alpha = 0.003$, for various values of t in years: (a) temperature profiles, (b) pressure profiles, (c) surface density profiles. The radius of the nebula evolves with time as shown on Fig. 1.

The isotopic exchange term becomes negligible either at high temperatures, where $A(T)$ and f are both close to 1, or at low temperatures, where $k(T)$ becomes close to zero. A substantial isotopic exchange may thus occur only at intermediate

temperatures in the nebula. However, even in the absence of isotopic exchange, the turbulent mixing tends to reduce any radial gradient of D/H ratios.

The second member on the right side of Eq. (5) describes the diffusion throughout the nebula. It depends upon the surface density profile $\Sigma(R, t)$ and upon the turbulent diffusivity κ, which in turn depends on the nature of the turbulence. We assume that κ is the ratio of the turbulent viscosity to the Prandtl number P_r, which is taken equal or close to 1 for reasons developed in Paper I. Since P_r cannot be higher than unity (Dubrulle and Frisch 1991), this choice represents a lower estimate of the efficiency of the transport.

Equation (5) is valid as long as the considered species (H₂O or HCN) do not condense. The key point is that no isotopic exchange occurs between the vapor phase and the solid phase; this implies that *the value of the enrichment in microscopic ices is that obtained at the time and at the location where the vapor condenses*. Microscopic ices are well mixed with the nebula gas (H₂) and are transported with it throughout the whole turbulent nebula (Dubrulle *et al.* 1995). As soon as grains reach millimeter sizes, they are uncoupled from the gas, continue to grow up, and form planetesimals and cometesimals. Whatever the subsequent evolution of these bodies, their D/H ratio is that of microscopic grains. In other words, the D/H ratio in H₂O and in HCN in comets is that of these species when they condensed.

The enrichment factor $f(R, t)$ is obtained by integrating Eq. (5), which requires spatial and temporal boundary conditions. Spatial boundary conditions are determined by specifying $\partial f/\partial R = 0$ at both $R = 1$ AU and $R = R_D(t)$; that is we neglect the matter flux at disk limits for reasons discussed in Paper I. When condensation occurs within R_D, we take $\partial f/\partial R = 0$ at the radius of condensation. The initial conditions depend upon the scenario assumed for the origin of water (and hydrogen cyanide) in the nebula. If the species is formed uniquely in the hot inner part of the nebula from the recombination of elements, there is no initial enrichment in water ($f = 1$). Assuming $f(R) = 1$ at $t = 0$ when integrating Eq. (5) reveals that $f(R, t)$ would never exceed 1.4 in the story of the nebula, in conflict with enrichments in water observed in meteorites, Uranus, Neptune, and comets (Paper I). To the contrary, it has been demonstrated, as summarized above in section 1, that appropriate models of nebula fit the observed enrichments when it is assumed that water in the nebula mainly originated from icy grains infalling from the presolar cloud onto the whole nebula discoid, which were strongly enriched in deuterium in the ISM through ion–molecule reactions.

In Paper I, we have assumed $f(R) = 25$ at $t = 0$ for D/H in water. This value corresponds to that measured in the highly enriched component (D/H = $(73 \pm 12) \times 10^{-5}$) in LL3 meteorites (Deloule *et al.* 1998) compared to a protosolar value assumed to be equal to 3×10^{-5}. We considered that this high D value originates from grains that were not reprocessed in the nebula. In fact, recent results suggest that they may have even

escaped to a substantial reprocessing during the collapse of the presolar cloud or at the shock when entering the nebula disk (see discussion in section 4). Indeed, solid HDO has been detected from ISO in grain mantles by Teixeira *et al.* (1999). These authors have found D/H in W33A to be between 40×10^{-5} and 150×10^{-5}, consistent with the value found in LL3 meteorites.

On the other hand, the protosolar value has been revised down, both from a reanalysis of HD/H₂ measured *in situ* in Jupiter by the mass spectrometer aboard the Galileo probe (Mahaffy *et al.* 1998), and from a reanalysis of Ulysses measurements of helium isotopic ratios in the solar wind (Geiss and Gloecker 1998). Therefore, we conservatively adopt in the present work a protosolar deuterium abundance equal to $(2.5 \pm 0.5) \times 10^{-5}$ and all f values are calculated with respect to this protosolar D/H ratio. Accordingly, $f(R)$ in water at $t = 0$ becomes equal to 30.

The D/H ratio in HCN in Comet Hale–Bopp has been measured as equal to $(230 \pm 40) \times 10^{-5}$ (Meier *et al.* 1998b). This corresponds to an enrichment factor of 92^{+43}_{-29}, with respect to the protosolar value. It is assumed that ices of HCN, as water ices, infell onto the nebula from presolar grains, but we cannot safely assume a value for the D/H ratio in these grains, considering the complexity of the phenomena occurring during the collapse of the cloud (Chick and Cassen 1997). Therefore, we have integrated the equation of diffusion (Eq. (5)), assuming different values of $f(R)$ at $t = 0$, and compared the resulting $f(R, t)$ to observations.

$f(R, t)$ has been calculated for models of the nebula defined by initial radii and masses located in the range indicated in Table II.

3. RESULTS

The evolution of the enrichment factor $f(R, t)$ in H₂O is shown on Fig. 3 for a nebula defined by $\alpha = 0.003$, $R_{D0} = 17$ AU, and $M_{D0} = 0.1$ M$_\odot$. The values measured in comets Halley, Hyakutake, and Hale–Bopp are shown for comparison. Taking into account the uncertainties on measurements as well as on the protosolar value, the enrichment factors for P/Halley are between 8.5 and 17.3 (Balsiger *et al.* 1995) or between 9.4 and 17.5 (Eberhardt *et al.* 1995). For comets Hyakutake and Hale–Bopp, they are between 6.3 and 19.5 (Bockelée-Morvan *et al.* 1998) and between 8.3 and 20.5 (Meier *et al.* 1998a), respectively.

As discussed in detail in Paper I, and recalled in section 2, the values of f in ices are those acquired at the time and the location where H₂O condensed. Cometary values are fitted by ices formed between $t = 10^5$ years and $t = 4 \times 10^5$ years, and between 10.5 and 23 AU, if we consider the extreme values of D/H measured in the three comets. Similar calculations were done for the 14 models defined by the values of R_{D0} and M_{D0} indicated in Table II. We found that the times needed to form ices with observed cometary deuterium enrichments do not vary
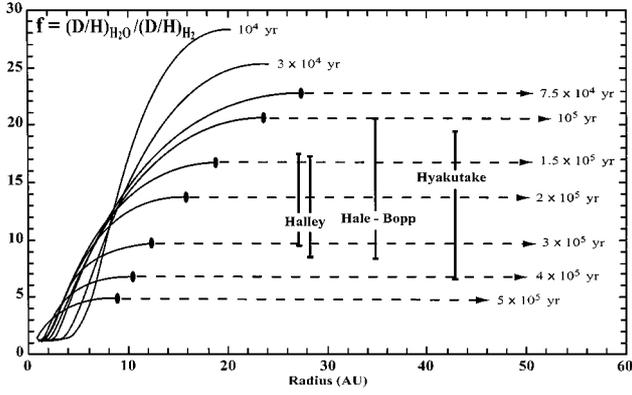
FIG. 3. Calculated deuterium enrichment factor f in H_2O as a function of the heliocentric distance R, at various epochs in years of the evolution of the nebula. The model of nebula is the same as that used in Figs. 1 and 2. The initial enrichment factor $f(R)$ at $t = 0$ is equal to 30. Dots indicate the heliocentric distance where H_2O condenses. Dashed lines correspond to the value of f in ices. D/H enrichments obtained in comets Halley, Hyakutake, and Hale–Bopp are shown for comparison (measured values of D/H are given in Table I). The location of comets is arbitrary.

much with the considered nebula model: the resulting time range is between $t = 0.75 \times 10^5$ and $t = 5 \times 10^5$ years. On the other hand, the region of formation of ices increases with increasing R_{D0} and with M_{D0} since the radial temperature profile of the nebula warms up when these two parameters increase (for a given α).

$f(R, t)$ for HCN shown on Figs. 4, 5, and 6 was calculated with the same nebula model as that used for Fig. 3. On Fig. 4, the initial enrichment $f(R)$ at $t = 0$ is taken as equal to $f_0 = 92$, which corresponds to the central value of D/H measured in Comet Hale–Bopp by Meier *et al.* (1998b). Radial profiles at different times clearly show that DCN is reprocessed in the vapor
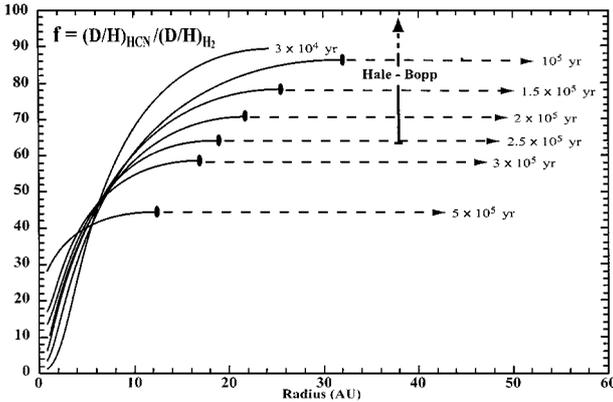

FIG. 4. Calculated enrichment factor f in HCN as a function of the heliocentric distance R at various epochs, in years, of the evolution of the nebula. The model of the nebula is the same as that used in Figs. 1–3. The initial enrichment factor $f(R) = f_0$ at $t = 0$ is equal to 92, which is the central value measured in Comet Hale–Bopp. Dots indicate the heliocentric distance where HCN condenses. The enrichment measured in Comet Hale–Bopp is shown for comparison. The location of the comet is arbitrary.
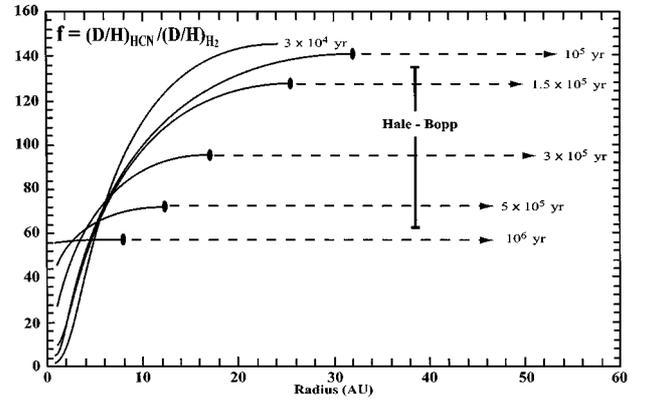

FIG. 5. Same as Fig. 4, except the initial enrichment factor $f(R) = f_0$ is equal to 150.

phase and isotopically exchanges with hydrogen. At $t = 0$, HCN is entirely vaporized in the turbulent nebula. However, the nebula expands (Fig. 1) so that, at $t = 10^5$ years, condensation occurs at 32 AU with an enrichment factor of 82, compatible, within error bars, with the Hale–Bopp D/H value.

On Fig. 5, $f(R, t)$ is calculated for an initial enrichment f_0 equal to 150 (D/H = 7.5×10^{-3}). In this case, enrichments in ices consistent with the Hale–Bopp value are reached at times between 1.2×10^5 and 5.2×10^5 years, and at heliocentric distances varying from 10 to 30 AU.

On Fig. 6, $f(R, t)$ is calculated for an initial enrichment factor f_0 of 350 (D/H = 8.5×10^{-3}). We have chosen this high value to examine to which extent high initial enrichments, as those found in dense interstellar clouds ($\sim$900, see discussion in section 4), could provide enrichments in the solar nebula compatible with the cometary value. The calculated enrichments are clearly above the Hale–Bopp value for times less than 1 million years. Cometary cores may or may not have been completed at this time. This question is discussed in section 5.1.2.

Similar calculations have been made for the 14 other models of the nebula with initial radii and masses given in Table II. All models permit us to simultaneously fit the D/H in water in the
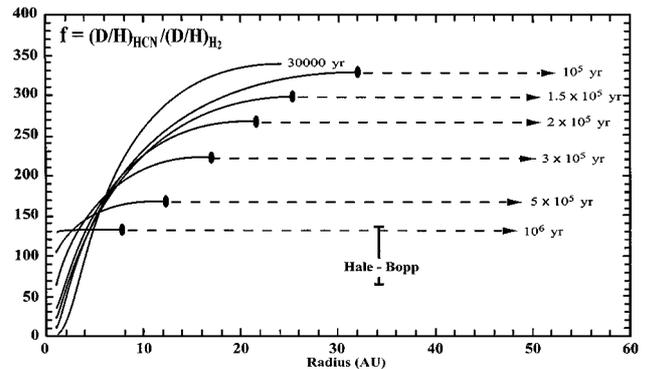

FIG. 6. Same as Fig. 5, except the initial enrichment factor $f(R) = f_0$ is equal to 350.

three comets and D/H in HCN in Comet Hale–Bopp, provided an appropriate value for the initial enrichment factor in HCN is taken. Models calculated for disk masses intermediate between the maximum and minimum values indicated on Table II also permit us to fit D/H in Hale–Bopp.

4. DCN/HCN IN INTERSTELLAR ICES INFALLING ONTO THE NEBULA

Our scenario implies that HCN ices infalling from the presolar cloud onto the nebula discoid were enriched in deuterium with respect to the protosolar abundance in H_2. Figures 4, 5, and 6 show that DCN/HCN in Comet Hale–Bopp constrains the amount of this enrichment. However, the fact that comets were formed from grains containing both H_2O and HCN ices provides a more precise constraint, as shown on Fig. 7.

On this diagram, $f(HCN)$ values reached at the radius of HCN condensation are plotted as a function of $f(H_2O)$ at H_2O condensation radius at the same time. Several initial HCN enrichments f_0 are considered. To each f_0 corresponds a line on which the times are indicated. Horizontal lines indicate the range of enrichments in HCN on Hale–Bopp. Vertical lines indicate the range of observed enrichments in water. We have chosen to take the value measured in water on Hale–Bopp, rather than consider the values in the three comets, since DCN has been detected in this comet only. This procedure defines a rectangle in which acceptable f_0 values are contained. It also indicates at what time in the history of the nebula icy grains of H_2O and HCN with D/H ratios consistent with the values observed in

Hale–Bopp condensed. For this specific nebula, it is between 10^5 and 3.5×10^5 years after the origin of the time that we have defined for our models of the nebula, namely the moment when the Sun reached its present mass.

Figure 7 indicates that the most plausible value is around $f_0 = 150$, with an uncertainty of ±40%. This exercise has been redone for the 14 models indicated in Table II. Interestingly enough, *all diagrams give similar results on the most plausible initial enrichment which is found to be of the order of* 150 (D/H = 3.75×10^{-3}). In order to evaluate the sensibility of the result to the assumed value of the coefficient of isotopic exchange $k(T)$ between DCN and H_2, we have redone the diagram shown on Fig. 7 by multiplying our adopted value by 10 and 0.1, respectively. In the first case, the inferred f_0 increases by about 10%. In the second case, it decreases by 10%. Considering the error bars on the determination of DCN/HCN in Hale–Bopp, we believe that the uncertainty on the rate $k(T)$ has a negligible effect on the determination of f_0.

The value of D/H in HCN we inferred is substantially less than the DCN/HCN values found in dense molecular clouds: 2.3×10^{-2} in TMC1 (Wootten 1987), 4×10^{-2} in the Orion Ridge Cloud (Schilke *et al.* 1992), 2×10^{-2} in cores in ρ Ophiuchi (Wootten 1987, Mangum *et al.* 1991, Helmich *et al.* 1996). It could be argued that it is close to values found in hot cores, around 3×10^{-3} in the Orion Hot Core (Schilke *et al.* 1992), and of the same order in other hot cores (Hatchell *et al.* 1998), but a hot core is a shell surrounding a massive star, and this is not the image that we have of the presolar cloud. However, it has been advocated that most HCN in cold clouds must be in icy grains (Bergin *et al.* 1995). These ices evaporate in hot cores. Under the assumption that no substantial reequilibration with H atoms occurs in hot cores, as suggested by chemical modeling taking into account recent quantum calculations of HCN–H isotopic exchange rates (Hatchell *et al.* 1998, 1999), the D/H ratio in HCN measured hot cores could be that present in grains in cold dark clouds, as it is advocated for D/H in H_2S (Hatchell *et al.* 1999). In other words, in cold dark clouds the D/H ratio in HCN ices would be lower than that in gaseous phase. If this statement is correct, grains present in the presolar cloud, which contain more HCN than the gas phase (Bergin *et al.* 1995), would have evaporated during the collapse of the cloud or in the early nebula and have produced the major part of the HCN gas initially present in the region of formation of comets. This would explain that we infer an initial deuterium enrichment substantially lower than that measured in the gaseous phase of cold clouds. The difficulty is explaining why HCN in solid phase would have a D/H ratio lower than the value in the gaseous phase.

Let us explore other scenarios. Prior to being thermally reprocessed in the nebula, interstellar ices can be reprocessed by two physical mechanisms: cloud collapse and shock when entering into the dense nebula (Cassen and Chick 1997, Chick and Cassen 1997). The efficiency of these mechanisms may be very important near the center of the nebula, but should decrease at large heliocentric distances.
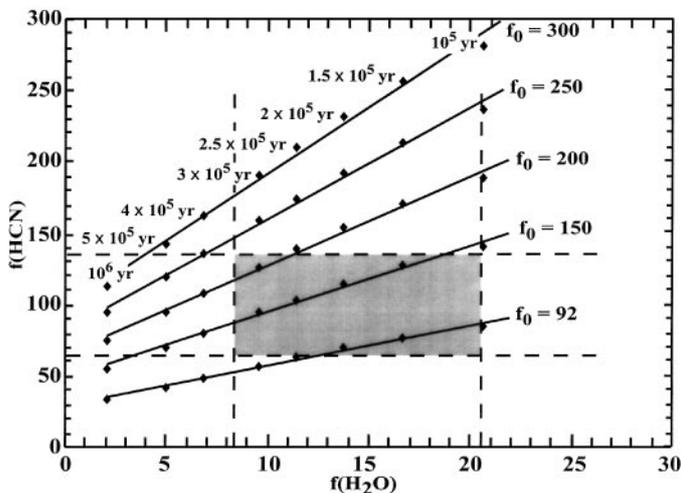

FIG. 7. Calculated enrichment factor in HCN ices as a function of the enrichment factor in H_2O ices, at a given time. The model of nebula is the same as in previous figures. Results at a given time are indicated by diamonds, and the time is in years. Points corresponding to a given initial enrichment f_0 in HCN are aligned. Vertical dashed lines correspond to the minimum and maximum values of f in H_2O measured in Comet Hale–Bopp. Horizontal dashed lines correspond to minimum and maximum values of f in HCN measured in Comet Hale–Bopp. The gray box indicates acceptable solutions for f_0.

We are not aware of calculations relative to a reprocessing of DCN during the cloud collapse. The cloud collapse is quite fast but the isotopic chemistry in such conditions has never been modeled so far.

On the other hand, the shock chemistry may have drastic effects. Prinn and Fegley (1989) have considered the effect of the shock chemistry for producing HCN, but only in the nebula as a result of lightning. They indicate that the shock heating of a CO, N_2 bearing gas parcel produces HCN via the net reaction:

$$2CO + N_2 + 3H_2 \rightarrow 2HCN + 2H_2O.$$
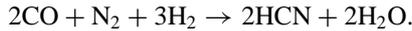
This reaction produces HCN at high temperatures so that DCN/HCN is equal to D/H in H_2 ($f = 1$). According to Prinn and Fegley (1989), the maximum conversion of N_2 to HCN resulting from lightning in the nebula is of the order of 0.3% of the total nitrogen abundance. This is too small to significantly affect our results.

We conclude that the question of the interpretation of D/H in HCN in the early nebula is still open.

5. CHEMICAL COMPOSITION OF COMETESIMALS

5.1. Comets of the Oort Cloud

5.1.1. Mixing of precometary ices. H_2O and HCN ices must have been incorporated into cometesimals which formed the comets of the Oort cloud. In other words, we must determine the region of the nebula in which microscopic icy grains of both species were simultaneously present, and of course with D/H ratios consistent with the Hale–Bopp values. This information may be derived from Fig. 7. We have previously mentioned that icy grains incorporated in cometesimals which formed Comet Hale–Bopp were produced, for the considered model of nebula, between $t = 1 \times 10^5$ years and $t = 3.5 \times 10^5$ years.

The variation of the radius of condensation of HCN and H_2O with time for this model is shown on Fig. 8. For the times mentioned above, H_2O condenses between 11.5 and 23.6 AU, and HCN condenses between 15.7 and 32 AU. Diagrams similar to that shown on Fig. 7 were done for the 14 models of Table II and lead to the conclusion that icy grains incorporated in Comet Hale–Bopp were formed between $t = 8 \times 10^4$ years and $t = 4.8 \times 10^5$ years. H_2O ices condensed at heliocentric distances between 11.5 and 37 AU, while HCN ices condensed between 13 and 44 AU.

For the considered model of the nebula, H_2O and HCN ices condensed at distances separated by 8 AU at $t = 1 \times 10^5$ years and by 4 AU at $t = 3 \times 10^5$ years (Fig. 8). However, they are rapidly mixed in the turbulent nebula. In order to evaluate the mixing time of H_2O and HCN ices, we have solved, as a function of time, the differential equation which describes the diffusive transport of small grains in the nebula (Morfill and Völk 1984). We assume that the microscopic icy grains and the gas are well mixed and have the same radial velocity (Dubrulle *et al.*
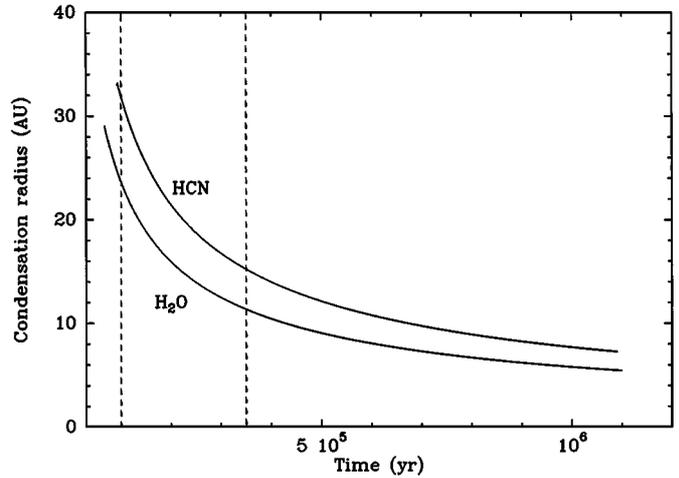

FIG. 8. Radii of condensation of H_2O and of HCN in the nebula as a function of time. The model used is the same as in previous figures. Vertical dashed lines indicate the range of times when ices of the two species exhibit D/H ratios consistent with observations in Comet Hale–Bopp. These limits are derived from Fig. 7.

1995). Sublimation is taken into account. The matter flux at the disk limit is taken as equal to zero, as we want to investigate the mixing of ices formed in the turbulent nebula. Figure 9 shows a numerical simulation of the time evolution of the number density of icy grains formed at $R = 20$ AU from the Sun and $t = 2 \times 10^5$ years. For simplicity, the initial distribution of grains is represented by a Gaussian function. Radial turbulent mixing is very rapid and fully occurs within 10^5 years. In fact, grains separated by a few astronomical units are mixed in much less than 10^5 years. This implies that cometesimals, when they
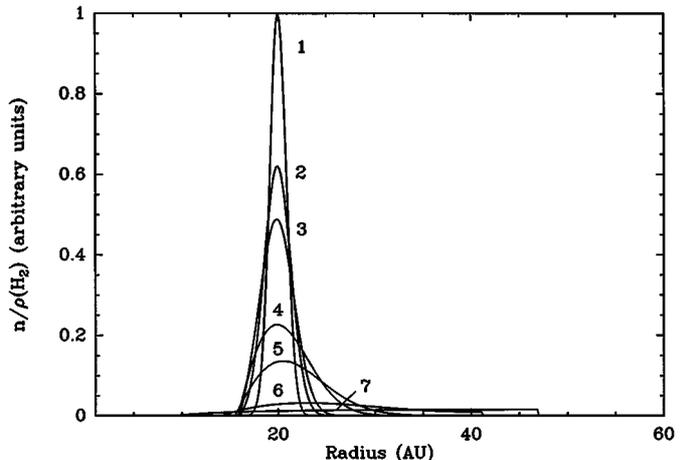

FIG. 9. Numerical simulation of the diffusion of ices in the turbulent nebula. At $t = 2 \times 10^5$ years, the number density of icy grains with respect to the density of H_2 is represented by a Gaussian distribution whose maximum is taken equal to 1 at 20 AU (curve 1). The different curves show the evolution of the distribution posterior to $t = 2 \times 10^5$ years: curves 2, 3, 4, 5, 6, and 7 correspond to 500, 1000, 5000, 10,000, 50,000, and 100,000 years, respectively, after 2×10^5 years.

formed, incorporated both H_2O and HCN ices, as well as other microscopic grains initially present or which early condensed in the outer part of the turbulent nebula.

5.1.2. Formation of cometary cores. Forming cometary cores from microscopic grains introduces additional uncertainties on the time and the region when and where cometary cores were formed. Weidenschilling (1997) has calculated that the timescale for forming kilometer-sized comets from a uniform mixture of microscopic grains embedded in the nebula around 30 AU is less than 2.5×10^5 years. This could imply that comets were completed no later than 7.5×10^5 years after the formation of the Sun. However, the calculations of this author assumed no turbulence in the disk and all condensed material present initially. According to Weidenschilling (2000, pers. commun.), introducing turbulence and continuous addition of icy grains would result in substantially longer formation times. In turn, ices with smaller D/H ratios than the lower limit of present observations could have been incorporated in cometary grains, and the region of formation of comets of the Oort could be somewhat larger than mentioned above. The isotopic composition of cometary cores would then be inhomogeneous. This is a prediction which cannot be verified from presently available measurements. It requires *in situ* measurements of D/H at the surface of the core of a comet. Planned or envisaged cometary space missions might provide such data.

5.1.3. Origin and composition of cometary ices. Keeping in mind the warning mentioned above, our results support for the moment the current assumption that Oort cloud comets were formed in the Uranus–Neptune region. The question of the origin of the other volatiles present in cometary ices then arises: a list of the abundances of molecules detected in Comet Hale–Bopp can be found in Bockelée-Morvan *et al.* (2000). The comparison with the composition of the ISM strongly suggests that all these molecules were present, in the form of gas or in the form of ices, in the presolar cloud. However, these molecules exhibit low condensation temperatures (see, e.g., Bockelée-Morvan 1997), in fact lower than that of H_2O, and thus likely vaporized either during the cloud collapse, or during the shock when entering into the nebula. Cassen and Chick (1997) estimate that water ices infalling from the presolar cloud may have vaporized outward to 30 AU, prior to entering the nebula. Their conclusion is presumably also valid for all ices of volatiles detected in Comet Hale–Bopp. Of course, silicates escape to sublimation at distances higher than 1 AU.

Even if interstellar ices did not vaporize when infalling, they did it in the early turbulent nebula. Figure 2a indicates that, for the considered nebula, all molecules present in Hale–Bopp vaporized at heliocentric distances smaller than $\sim$30 AU and at times less than $\sim$100,000 years. Subsequently, they recondensed and their ices mixed together in the nebula, as discussed above for H_2O and HCN grains.

Are the molecular abundances observed in comets consistent with this scenario? The abundances of the major constituents of cometary ices (H_2O, CO, CO_2, CH_3OH, CH_4) present strong similarities with those measured in interstellar ices (e.g., Ehrenfreund *et al.* 1997). Bockelée-Morvan *et al.* (2000) have extended this comparison to a large number of organic molecules observed both in Comet Hale–Bopp and in molecular hot cores and bipolar flows, as the gaseous composition of these interstellar sources is believed to reflect that of interstellar grains. They show that there is good agreement between cometary abundances and those measured in other objects. Although a thermodynamical study of the stability of these molecules in the protosolar nebula has not been performed so far, such observations suggest that interstellar molecules are quite resistant to pyrolysis and are probably chemically inert over a wide range of temperatures and pressures. Since the activation energies for isotopic exchanges are much lower than those for chemical reactions or molecular pyrolysis, the D/H ratios of interstellar molecules are not preserved while their relative (pristine) abundances could remain essentially unchanged. In other words, the isotopic exchange with protosolar H_2 is a much faster process than the destruction rates of molecules. These qualitative statements could be quantitatively verified through a theoretical study of the destruction/formation rates of interstellar molecules in the turbulent solar nebula. Until this work is not done, it is premature to conclude that the similarity of the cometary abundances with those observed in interstellar ices, hot cores, and bipolar flows implies that ices did not vaporize in the nebula.

In addition to our analysis of the deuterium enrichment in H_2O and HCN, the nature of the silicates detected in comets also favors the scenario of a progressively mixed nebula, in agreement with modern views on the structure and the evolution of this object (Cassen 1994). Indeed, in addition to amorphous silicates, crystalline silicates have been detected in several comets (Hanner *et al.* 1994) and clearly confirmed by ISO observations of forsterite in Comet Hale–Bopp (Crovisier *et al.* 1997), while silicates have been observed so far only in amorphous form in molecular clouds of the ISM (the detection of crystalline silicates in dust shells around evolved stars (Waters *et al.* 1996) does not imply their presence in the ISM). Forming crystalline silicates requires temperatures above $\approx$800 K (Gail 1998), consistent with those estimated to have occurred in the inner part of the early nebula, and with the fact that silicates are entirely crystalline in meteorites. In other words, the detection of crystalline silicates in Comet Hale–Bopp is consistent with our turbulent model of the nebula and the mixing of matter present in the outer region with matter coming from the inner region.

5.1.4. Trapping of volatiles in clathrate hydrates. The case of CH_4, CO, and N_2 presents a problem because of their low temperatures of condensation: 31, 24, and 22 K, respectively. With our nebula model, the condensation would occur quite far in the nebula and later than the time required for forming cometesimals of the size of cometary cores (see Fig. 2a). We suggest that these gases have been trapped by water ices in the

form of clathrate hydrates during the cooling of the nebula. The presence of clathrate hydrates in comets was proposed long ago by Delsemme and Swings (1952), and their formation in the outer nebula has been studied in depth by Lunine and Stevenson (1985). Since this scenario is not currently considered, it deserves some explanation.

When water vapor condenses at around 150 K in the nebula, it is necessarily in the *crystalline* form (Kouchi *et al.* 1994). When the temperature continues to decrease, $NH_3 \cdot H_2O$ hydrates form around 85 K for pressures of the order of 10^{-8} bar, which, in our model shown on Fig. 2, are reached at 30 AU and $t = 1.5 \times 10^5$ years. Sometime later, clathrate hydrates of CH_4 and of CO are formed around 60 and 50 K, respectively (Lunine and Stevenson 1985). These clathrates were incorporated in cometesimals. Some amorphous ices might have formed in the nebula at very low temperatures, but the pressure of the remaining vapor was then so low that only a tiny amount of amorphous ices was produced. Interestingly enough, crystalline ices have been detected from ISO in the cold part of the dusty circumstellar disk surrounding the young star HD 142527 (Malfait *et al.* (1999): 90% of the ice is found crystalline in the region where the temperature is between 30 and 60 K. The main difficulty concerning the formation of clathrate hydrates under solar nebula conditions is that most laboratory experiments relative to clathrate hydrates have been made at temperatures and pressures higher than those occurring in the nebula. However, recently, Ehrenfreund *et al.* (1999) have analyzed by spectroscopy clathrate hydrates of CH_3OH in a high-vacuum chamber and at 10 K. Similar experiments on other clathrate hydrates seem technically possible.

The process described here is consistent with the analysis of Kouchi *et al.* (1994), who conclude that ices condensed from the vapor phase in the nebula are predominantly crystalline; they claim that amorphous ices can be present only if they formed in the presolar cloud and subsequently did not evaporate during the collapse of the cloud and the evolution of the nebula. Therefore, we believe that the experiments made by Bar Nun *et al.* (1985, 1988) on the trapping of gases by *amorphous* water ice are not applicable to any region of the nebula where water ices sublimate. To the contrary, they are applicable to the ISM where ice is amorphous (Kouchi *et al.* 1994) or to nonturbulent regions of the nebula, located farther than about 50 AU, as discussed below. Considering the region of formation of the Oort cloud comets that we have inferred above, the interpretation of the abundances of the very volatile species in these comets must be made in the light of a scenario invoking their trapping in clathrates and not their trapping in amorphous water ice.

The calculations of Lunine and Stevenson (1985) are indeed consistent with the information we have so far on CO, CH_4, and N_2 relative abundances in comets. These authors have studied the trapping of these volatiles in clathrate hydrates, and showed that, in a solar composition nebula where carbon is in the form of CO or CH_4 and nitrogen in the form of N_2 or NH_3, the ratio of CO to CH_4 incorporated in clathrates is always higher than the ratio of N_2 to CH_4, whatever the CO/CH_4 ratio in the nebula (Fig. 23 of Lunine and Stevenson 1985). As a result, the C/N ratio in the nebula becomes an oversolar ratio in clathrates, in agreement with the oversolar C/N ratio observed in P/Halley (Mumma 1997, Schulze *et al.* 1997).

The trapping of noble gases in clathrates compared to their abundances in comets would be a key test. For the moment, the only information we have concerns neon for which an upper limit, 25 times lower than the solar Ne/H_2O ratio, has been obtained in Comet Hale–Bopp (Krasnopolsky *et al.* 1997). This depletion is also consistent with the calculations of Lunine and Stevenson (1985) who showed that neon is poorly trapped in clathrate hydrates.

5.1.5. Cometary activity and clathrate hydrates. The presence of clathrate hydrates in comets was proposed by Delsemme and Swings (1952) to explain the almost simultaneous onset of activity in all observed gaseous species (including water tracers) at 2–3 AU from the Sun. This concept had received wide attention until the 1980s, but was contradicted by the observation of larger percentages of CO/H_2O than can be trapped within the clathrate hydrate lattice (17%), and the accumulating number of comets showing distant activity. In their study of the evolution of gaseous cometary activity in presence of clathrate hydrates, Delsemme and Swings (1952) and following papers assumed that the latent heat of clathrate hydrates is that of pure crystalline ice, and that the volatile molecules trapped within the H_2O lattice come out upon heating simultaneously with H_2O. Subsequent to their work, experimental studies showed that, to the contrary, the decomposition of clathrates first proceeds by the diffusion of the guest species outside the clathrate cages (Schmitt 1986, Klinger *et al.* 1986). The equilibrium pressure of the guest species with respect to the chlatrate hydrate is much higher than the vapor pressure of ordinary water ice. For comets, this means that the outgassing of volatile species (such as CO) encaged in clathrate hydrates is efficient at large distances from the Sun where H_2O sublimation is inhibited. Taking into account that CO vapor should diffuse from inner layers of the nucleus, its abundance relative to water measured in the coma can well be higher than the theoretical maximum occupation in the clathrate lattice, even near perihelion. We conclude that cometary activity could be explained by the presence of clathrate hydrates in cometary nuclei. Present nucleus models show that the presence of amorphous ice with trapped volatiles in cometary nuclei satisfactorily explains cometary activity at large heliocentric distances (Enzian *et al.* 1998, Capria *et al.* 1999), including outbursts triggered by runaway crystallization (Prialnik and Bar-nun 1992). New models must be developed to investigate whether the presence of clathrate hydrates in cometary nuclei is a satisfying alternative explanation.

It might be also objected that there is some observational indication that amorphous ice is present in cometary nuclei. Indeed, Davies *et al.* (1997) observed the near infrared signatures of water icy grains in the coma of Comet Hale–Bopp when it was at

7 AU from the Sun. From the absence of the 1.65-μm absorption feature of crystalline ice, they suggest that the ice is in an amorphous state. However, the marginal quality of the data and the unsatisfactory fit of the long-wavelength part of the spectrum makes this result not entirely conclusive.

5.2. Kuiper Belt Comets

The so-called comets of the Kuiper Belt, or comets of the Jupiter family, may have been formed quite far from the Sun, even out to a few hundred astronomical units. We mentioned in section 2 that the turbulent nebula might have been surrounded by a quiescent and Keplerian disk which did not mix with the turbulent part. This far-off region was probably rather cold, and interstellar icy grains infalling onto this part of the disk from the presolar cloud were presumably not reprocessed and certainly not if they did not evaporate. Water ice in this region was thus probably amorphous. Therefore the trapping of volatiles could have occurred as predicted by Bar-Nun *et al.* (1985) and in many subsequent papers as the one of Owen and Bar-Nun (1995). In addition, H₂O and HCN kept the D/H ratio acquired in the ISM. Note that the highly enriched deuterium component found in LL3 meteorites could have originated from these outer regions. Provided that an icy grain moving toward the Sun did not reach the 3-AU region in less than 1 million years, it never vaporized and thus may have been incorporated in meteorites without having been reprocessed.

Therefore, the determination of the isotopic composition of a Kuiper Belt comet would be of tremendous interest. The comparison of the nature of the ices in comets of the Kuiper Belt with that of comets of the Oort cloud would be enlightening. Another key test would be the comparison of relative abundances of noble gases.

6. CONCLUSION

The turbulent evolutionary model of the solar nebula that we used in the present report permits us to interpret the deuterium enrichments in H₂O and HCN measured in Comet Hale–Bopp. Due to the fact that the apparent discrepancy between D/H in comets and D/H in Uranus and Neptune has been solved thanks to new models of the interiors of these two planets, the parameters which define our models are much more constrained than in Drouart *et al.* (1999). In particular, the coefficient of turbulent viscosity α must be of the order of 0.003.

More sophisticated models of the solar nebula must be elaborated (2D models, non-α-disks models, etc.). They might exhibit temperature and density radial profiles different from those presented in this work, but in order to be validated they will have to reproduce all deuterium observations in objects which are relics of the nebula.

Our calculations indicate that both HCN and H₂O ices infalling from the presolar cloud have been reprocessed prior to being incorporated in cometary grains. Icy grains vaporized, either prior to entering the nebula, or in the nebula inside about

30 AU. The high D/H ratios acquired in the ISM in both water and hydrogen cyanide decreased as a result of isotopic exchange with hydrogen and of the mixing with gases coming from the inner part of the nebula.

The D/H ratio in HCN molecules entering the nebula is evaluated to be of the order of 4×10^{-3}. This is lower by a factor of at least 6 than the D/H ratios measured in gaseous phase in cold molecular clouds, but quite in agreement with values measured in hot cores. The interpretation of these results requires more studies.

Most volatiles presently detected in Comet Hale–Bopp should have an interstellar origin, but water, at least, should contain a component formed in the hot inner part of the nebula and subsequently transported outward to the region of cometary formation; moreover, crystalline silicates detected in comets must have originated from the hot inner part of the nebula. Interstellar ices vaporized and subsequently recondensed while the nebula cooled down. However, very volatile species such as N₂, CH₄, CO, and some noble gases were probably trapped in clathrate hydrates after H₂O had condensed in a crystalline form, as clearly stated a few years ago by Kouchi *et al.* (1994). Amorphous water ice was in too tiny of an amount outward to 30 AU to be able to trap a substantial amount of volatiles. The case of comets of the Kuiper Belt formed farther than Neptune, and possibly in a nonturbulent nebula, can be completely different and comets of this family may contain mainly amorphous ice formed in the presolar cloud.

Our approach suggests that microscopic icy grains that formed the comets of the Oort cloud were produced no later than 5×10^5 years after the Sun was completed. However, the time and the location of formation of cometesimals from microscopic grains are still uncertain and require further studies. In spite of these limitations, there is some presumption that the three comets in which deuterated species have been detected were formed in the region of Uranus and Neptune, as currently considered for the comets of the Oort cloud from dynamical considerations. Icy planetesimals which formed the cores of Uranus and Neptune were produced at the same time as cometesimals and probably with a similar composition since they had the same D/H ratio in water, their most abundant component. Future *in situ* measurements from space missions to comets are of primordial importance.

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