Thermal evolution of cometary nuclei by radioactive heating and possible formation of organic chemicals

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ABSTRACT

Thermal evolution of large cometary nuclei (radii \geq 40 km) due to heating by decay of 238 U, 235 U, 40 K and 232 Th is investigated by adopting chemical models based on observations of P/Halley and mineral compositions of C1 chondrites. If the thermal diffusivity of crystallized ice is sufficiently small ($\kappa_c \leq 0.0015$ cm s⁻¹), the central temperature may reach the melting point of H₂O in large nuclei (radii \approx 200 km), while if the diffusivity is 0.003 or greater, the central temperature will not reach the melting point.

The high temperature attained within cometary nuclei allows molecules such as HCN and NH₃ to form various organic compounds such as amino acids through oligomerization, and such compounds might be delivered to the Earth through disintegrations of the large nuclei, which subsequently impact the Earth. The extraterrestrial amino acids found in the K/T boundary layer and in the dust of P/Halley might have been processed in cometary interiors.

Key words: molecular processes – comets: general.

1 INTRODUCTION

Comets are commonly regarded as consisting of pristine material, whether they formed within the primitive solar nebula or in dense interstellar clouds. As long as they remain orbits with large perihelion distances (q > 1000 au, say), they are unaffected by the solar radiation.

On the other hand, it is almost certain that they contain radioactive elements such as uranium, thorium and 40 K. These elements, if exist in sufficient quantity, release heat as they decay and may thus modify the original composition of cometary nuclei. Thus Whipple & Stefanik (1966) and Yabushita & Wada (1988) have argued that moderate heating in the cometary nuclei may expel volatile molecules such as CO or N_2 toward the surface, which could account for the activities at large heliocentric distances (see also Whipple 1992). On the assumption that cometary nuclei contain radioactive elements according to the cosmic abundance, temperatures could attain between 25 and 55 K, depending on the values of the thermal diffusivity. These results are based on the presumption that the cometary radius $\approx 10 \text{ km}$.

However, much larger comets have been observed. Chiron, for example, is likely to have a radius ≥ 150 km. It is a comet (and not an asteroid) in that it has a coma. Since the effect of thermal conduction in such a large nucleus is expected to be smaller than in smaller nuclei, it seems

reasonable to expect that much higher temperatures can be attained. It is the object of the present paper to calculate the temperatures that can be expected in large cometary nuclei $(R \ge 40 \text{ km})$ and to discuss the implications regarding the processes that are expected to result from the high temperatures.

The problem may be of importance in relation to the formation of complex chemical molecules such as amino acids. The primary requirement for the formation of amino acids is now regarded as the existence of molecules such as HCN, NH₂ and melted H₂O. If the temperature deep inside a large cometary nucleus should reach 273 K, organic molecules such as amino acids might well be expected to form. The interiors of large nuclei could therefore provide a site for the formation of such organic compounds as amino acids that have been inferred to exist in the dust of P/Halley.

The question of whether a cometary nucleus can attain a temperature which corresponds to the melting point of H_2O was first discussed by Wallis (1980). He investigated the possibility of heating due to the decay of ^{26}Al and showed that, if the abundance of ^{26}Al were a fraction (0.1–0.5) of that of chondritic material, part of the water ice in the nucleus would melt and there would be droplets in the central region. Whether ^{26}Al could melt the ice would depend on when cometary nuclei formed. Because of the short half-life of ^{26}Al (7.4 × 10⁵ yr), the formation would have to take place within

a few million years after the explosion of a supernova for the scenario to work. In the present work, we are concerned with the elements that have much longer half-lives and hence must have liberated energy on decay, unless one supposes that cometary nuclei have a mineral composition totally different from that of chondrites.

2 HEAT RELEASED IN COMETARY NUCLEI

There is no direct way of measuring the amount of radioactive elements in cometary nuclei and one must make a few assumptions regarding heat generation rate in order to study the thermal evolution in cometary nuclei. One method is to assume that radioactive material in a cometary nucleus is a fraction f of that in chondrites and extrapolate it back to 4.5×10^9 yr when comets are supposed to have formed (Whipple & Stefanik 1966). Assuming that the composition of a cometary nucleus is given by the solar abundance of Goldberg, Müller & Aller (1960) and that elements heavier than C, N, O give the non-volatile component, Whipple & Stefanik (1966) obtained f=0.11 per gram of the nucleus. Table 1 gives the values adopted by them for heat generation due to decay of the radioactive elements in comets.

A second method, which is a modification of the first, is to take Si in the nucleus as a reference element, and to assume that radioactive elements are present at levels corresponding to their abundances in chondrites. By taking into account the *Vega I* observation of P/Halley, Delsemme (1988) gives the Si content (mass fraction) as 5.0 per cent of the nucleus. For the radioactive elements, we make the assumption that the

abundances of the elements relative to Si are the same as in C1 chondrites. Wasson & Kallemeyn (1988) give the relative abundances as shown in Table 2. A straightforward calculation then yields the rate of heat generation in cometary nuclei as given in Table 2.

In arriving at the above result, some explanation is needed regarding the adopted numerical values. The heat generation rates per gram of the element concerned are taken from Allen (1976). The mass abundance of the potassium group is taken as 5.52×10^{-3} relative to Si. The heat generation rate estimate based on this consideration will be designated model 1.

A third method is to take the element composition of dust particles of P/Halley as measured by Vega-I spacecraft at face value and to estimate the amount of radioactive elements. According to table 1 of Jessberger, Christoforids & Kissel (1988), potassium, K, occupies a mass fraction 1.92×10^{-4} of P/Halley dust particles. This is 69 per cent of the fraction of K given in Table 2 (model I). This model will be called model II in the following. Uranium and thorium will be supposed to exist in the same proportion to K as in C1 chondrites.

Finally, we consider the total amount of heat generated over the possible age of a cometary nucleus. From the knowledge of the half-life $T_{1/2}$ of a radioactive element and the rate of heat generation when the comet formed, it is straightforward to calculate the total heat generated. The result of the calculation is summarized in Table 3.

It is immediately seen that ⁴⁰K gives the largest contribution and that ²³⁸U gives the second-largest contribution, but is not overwhelmingly important. It may be noted that if

Table 1. Radioactive elements and the rate of heat generation adopted by previous authors.

Elements	Half-life ($T_{1/2}$, yr)	Rate of heat generation (cal g ⁻¹ yr ⁻¹) Whipple & Stefanik (1966)	Yabushita & Wada (1988)
^{238}U	4.47×10^9	0.168×10^{-8}	3.15×10^{-8}
^{235}U	7.04×10^{8}	0.302×10^{-8}	6.3×10^{-9}
²³² Th	1.41×10^{10}	0.119×10^{-8}	2.76×10^{-8}
40 K	1.24×10^9	2.81×10^{-8}	4.6×10^{-8}

Table 2. Adopted values for heat generation rate (model I).

Element	Heat generation per gram of element (cal g^{-1} yr ⁻¹)	Mass fraction relative to Si	Heat generation rate per gram of comet (cal g^{-1} yr ⁻¹)	$4.5 \times 10^9 \text{ yr BP}$
238 U	0.73	0.775×10^{-7}	0.282×10^{-8}	0.57×10^{-8}
^{235}U	4.63	0.006×10^{-7}	0.014×10^{-8}	1.2×10^{-8}
²³² Th	0.20	0.28×10^{-6}	0.28×10^{-8}	0.35×10^{-8}
40 K	$26 \times 10^{-6} (\text{of K})$	5.52×10^{-3}	0.72×10^{-8}	8.9×10^{-8}

Table 3. Heat generated over the lifetime of a comet.

	Whipple & Stefanik $(4.5 \times 10^9 \text{ yr}) (\text{cal g}^{-1})$	Present work (model I) $(4.5 \times 10^9 \text{ yr})$	Model II
²³⁸ U	5.4	17	12
^{235}U	3.0	12	8
²³² Th	48	13	9
40 K	46	142	98
Total	102	183	127

comets contained 26 Al as in chondrites (Wallis 1980), the heat generated would be 2000η cal g⁻¹, where η is the fraction (0.1-0.5) of the chondritic material in a nucleus. Since 26 Al has a half-life much less than those of the elements considered here, the heat generation rate we use in the present work is more than one order of magnitude less than that for 26 Al. Finally, one may refer to a result of Geiss (1988), who derives 3.6 per cent as the Si abundance in the cometary nuclei. This is some 70 per cent of the Si content derived by Delsemme mentioned above. If radioactive elements are assumed to exist with the same proportions in C1 chondrites, it follows that the amount of radioactive elements will be similar to that for model II.

3 THERMAL PROPERTIES

3.1 Specific heat and conductivity

In order to investigate the thermal evolution of a cometary nucleus, we must know the specific heat of the nuclear material as well as the thermal conductivity. Here, we first consider the specific heat. In doing so, one needs to know the chemical composition of the nucleus. According to Yamamoto (1991), the abundances of CO, CO₂, CH₄, NH₃, N_2 and HCN relative to H₂O are 0.15–0.20, 0.02–0.04, 0.005–0.02, 0.01–0.02, <0.02 and 0.001, respectively. The abundances of N_2 and CO as given by Delsemme (1988) based on observations of P/Halley relative to H₂O are 0.5 and 1.5 per cent, respectively, much smaller than those quoted by Yamamoto. As a canonical model, we consider H₂O as the dominant volatile and CO, N_2 , etc. as subsidiaries.

A cometary nucleus is an aggregate of icy particles, which consists of the volatile molecules just mentioned and non-volatile dust grains. H₂O is the most dominant molecule and so we consider the specific heat of water ice.

According to the classical experiment of Giaque & Stout (1936), the specific heat at constant pressure of water ice can be represented by two straight lines in 16 < T < 273 K. To be more specific,

$$C_p = 0.0406 T - 0.340 \text{ cal deg}^{-1} \text{ mole}^{-1} \quad 10 < T < 110 \text{ K},$$

 $0.0302 T + 0.809 \quad 110 < T < 270 \text{ K}.$

Thus, if a comet nucleus were wholly made of water ice,

$$C_p = 0.00225 T - 0.0189 \text{ cal g}^{-1} \text{ deg}^{-1}$$
 $10 < T < 110 \text{ K}$,
 $0.00168 T + 0.0449$ $110 < T < 270 \text{ K}$.

It is of some interest to calculate the heat required to raise the temperature of a gram of water ice from 10 K, say, to 273 K. One then finds that

$$\int_{10}^{273} C_{\rm p} dT = 71 \, \text{cal g}^{-1}.$$

A cometary nucleus is such that nearly one half by mass consists of dust grains (45 per cent by mass, see Delsemme 1988). There are no data on specific heats for these, but the values are probably less than that for water ice. The specific heat for water ice will therefore be taken as that of a nucleus. Next, we consider thermal diffusivity. Wallis (1980) adopted the following values for thermal properties of cometary nuclei:

k(thermal conductivity) =
$$7 \times 10^{-3}$$
 cal cm⁻¹ s⁻¹ K⁻¹:
 $C_{\rm p} = 0.35$ cal g⁻¹ K⁻¹ solid ice plus dust;
 $\rho = 1.0$ g cm⁻³.
 $k = 4 \times 10^{-4}$:
 $C_{\rm p} = 0.35$ cal g⁻¹ K⁻¹ loose snow;
 $\rho = 0.25$ g cm⁻³.

These values are supposed appropriate at $T \approx 200$ K. The thermal diffusivity, κ , then turns out to be 2×10^{-2} cm² s⁻¹ for solid ice plus dust and 4.6×10^{-3} cm² s⁻¹ for loose snow.

It is likely that cometary nuclei formed in an environment where the temperature was below 100 K, and water ice which forms in such an environment is amorphous. For amorphous ice, $\kappa \approx 10^{-3}$ cm² s⁻¹. However, as Rickman (1991) suggested, what he calls macroporosity (a nucleus being an aggregate of units of different sizes) might drastically lower the value of diffusivity. We therefore investigate, in the following, the cases where κ is one order of magnitude less than for amorphous ice. Once the ice becomes crystalized, the situation is different. We note that, according to the experiment of Ratcliffe (1962), the thermal conductivity, k, of compact water-ice is given by

$$k = \frac{7.8}{T} - 0.00615 \,(\text{J cm}^{-1} \,\text{s}^{-1} \,\text{K}^{-1})$$

provided that the temperature, T, is above 120 K.

Specific heats per gram of hydrocarbons at low temperatures are comparable to that of H_2O ice but those of mineral grains are significantly less. Since H is almost contained as H_2O in the nucleus, the adopted value for the specific heat will be the lower bound, which means that the following calculation will not overestimate the temperature attained.

4 OBJECT CHIRON

In the present paper, we are concerned with large comets, because the effect of heating is more important for them than for small nuclei. Among the observed comets that are known to have large radii, comet Schwassman−Wachmann 1(SW1) and comet Chiron may be mentioned. The former probably has a radius ≃ 38 km (Nakamura, Watanabe & Kawakami 1991), but the latter is probably greater. Because nuclear radius plays a dominant role in characterizing the thermal evolution, as will be seen, we here consider object Chiron in some detail.

Chiron was discovered in 1978, and has been the object of observations since. It is a comet, not an asteroid, because it has a coma. If *R* is the radius expressed in km, then (Zellner 1979)

$$\log R = 2.821 - 0.2V - 0.5 \log p$$

where V and p are the absolute magnitude in blue, and the albedo, respectively. For Chiron, V=6.62 (Institute for Theoretical Astronomy 1991). Then, one finds that R=99 and 140 km for p=0.10 and 0.05, respectively. It appears that the comet has a radius ranging from 100 to 140 km. A radius as large as 200 km is not regarded unlikely.

Thus the likely radii for large comets are probably 40-200 km. In the following calculation, we therefore consider the two cases R=40 and R=160 km as typical ones, and consider the R=200 km nucleus as an exceptional case.

THERMAL EVOLUTION

The thermal history of cometary nuclei can now be followed by integrating an equation of thermal diffusion, provided the value of thermal diffusivity is known. However, the diffusivity is not well-known and so one is forced to consider various combinations of parameters. The equation which governs the evolution reads

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\rho r} \right) + \frac{1}{C_p} \sum_{i=1}^4 Q_i e^{-\lambda_i t}$$
 (5.1)

where T denotes the temperature, C_p the specific heat, and Q_i the rate of heat generation at epoch t=0; $\lambda = 0.6931/T_{1/2}$ and i denotes the ith nuclear species. For C_p , we use the value for H₂O ice.

In addition to the heat from radioactive decay, one needs to take into account the heat liberated on crystallization of H₂O ice. The heat liberated is some 20 cal g⁻¹ of amorphous ice. We have taken H₂O to occupy half of the nuclear mass. From the specific heat of H₂O ice at 150 K, the heat generated is such as to raise the temperature by 30 K or

so. This effect should be added to Equation (5.1). Once the ice is crystallized, a greater value of thermal diffusivity must be adopted. The diffusivity for the part of the nucleus with crystallized ice is denoted by κ_c .

We have evolved the model from an initial state where the temperature is everywhere equal to 10 K. The boundary condition imposed is that of heat loss due to radiation into space where the background temperature is assumed to be 10 K. Fig. 1 gives the variation of central temperature and the temperature profile in a nucleus with radius R = 40 km.

One notes in Fig. (1a) a sharp rise in temperature. This is due to the effect of release of energy by the transformation of H₂O ice. At first glance, it might appear strange that curve I (for which the heat generation rate is given by model I in Table 1) is lower than curve II for model IIa (for which the heat generation is less than model I). For model I, the temperature near the centre exceeds that for crystallization at epoch $t \approx 2.5 \times 10^8$ yr so that part of the nucleus consists of crystallized ice and hence has a higher diffusivity, while for model II, the temperature is always lower than that of the crystallization, and the diffusivity remains less than in model I. This is the reason why curve I is below curve IIa for $t \ge 5 \times 10^8 \text{ yr.}$

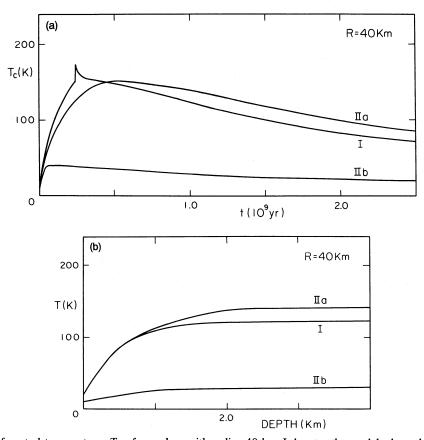


Figure 1. (a) Variation of central temperature, T_c , of a nucleus with radius 40 km. I denotes the model where the radioactive elements are assumed to have the abundances shown in Table 2. The thermal diffusivity of amorphous ice is taken as $\kappa_a = 0.0001$ cm² s⁻¹, while that of the portion of the nucleus that has crystallized is taken as $\kappa_c = 0.0015$ cm² s⁻¹. This case is denoted as model I. The case where $\kappa_c = 0.003$ is almost indistinguishable from the case $\kappa_c = 0.0015$. The reason is that only a small portion of the nucleus near the centre undergoes crystallization. There is a spike due to the release of heat associated with the crystallization. Models II a and b denote the cases where the abundances of radioactive elements are supposed to be the same as those of P/Halley dust particles. IIa denotes the case where $\kappa_a = 0.0001$ cm² s⁻¹ and $\kappa_c = 0.03$ cm² s⁻¹. Ilb denotes the case where $\kappa = 0.0046$ throughout the nucleus. The adopted value is the same as that of Wallis (1980). (b) Temperature profile within an R = 40 km nucleus.

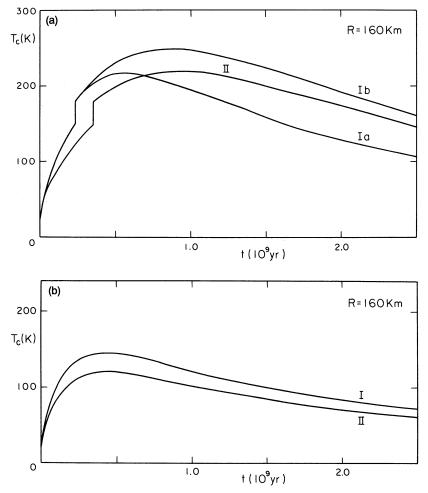


Figure 2. (a) Variation of the central temperature of an R = 160 km nucleus. Models I denote the cases where the abundances of radioactive elements are as shown in Table 2. For Ia, $\kappa_a = 0.0001$, $\kappa_c = 0.0015$ cm² s⁻¹. For model II, the abundances are taken as those of P/Halley dust particles and $\kappa_a = 0.0001$, $\kappa_c = 0.0015$ cm² s⁻¹. (b) The variation of central temperature with time is plotted. For models I and II, the thermal diffusivity is taken as 0.0046 cm² s⁻¹.

In Fig. 2 are plotted the variations of central temperatures with time in nuclei with R = 160 km. Here, the crystallization occurs for both models I and II, provided that the diffusivity is taken as $\kappa_c \le 0.0015$ cm² s⁻¹. The temperature profile is not much different from the case with R = 200 km. The evolution of the central temperature as well as the temperature profile in nuclei with R = 200 km is shown in Fig. 3. In order to see how sensitive the central temperature is to adopted values of diffusivity, we have calculated the case where the diffusivity is taken as $0.02 \text{ cm}^2 \text{ s}^{-1}$ irrespective of the temperature. This case is shown by curve Ib. This curve falls below curve IIb, for which the diffusivity of amorphous ice is 0.0001 cm² s⁻¹ and that of crystallized ice, 0.02 cm² s⁻¹. Since model II contains fewer radioactive elements than model I, one would expect curve IIb to lie below curve Ib, if the diffusivities were equal.

The most interesting feature here is curve Ia, which attains a temperature of 273 K for about 5×10^8 yr. This part is shown by the dotted horizontal line in Fig. 3a. Droplets of H₂O would form near the centre. Strictly speaking, one would need a more elaborate model than the one given here, where it is assumed that excess heat is simply consumed by melting H₂O ice.

The value of thermal diffusivity, however, is a major uncertainty. A recent measurement of Kouchi et al. (1992) indicates that the thermal conductivity of amorphous H₂O ice may be several orders of magnitude less than hitherto accepted. In their work, the density of the amorphous H₂O ice is not known so that it is not possible to derive a reliable value for the thermal diffusivity. If a much smaller value is confirmed, it will definitely increase the central temperature calculated here.

DISCUSSION

Modification of structure

We present a number of calculations on the thermal evolution of cometary nuclei. Although the cometary radii are observational data, there is a major uncertainty regarding the value of the thermal diffusivity. Keeping this in mind, several implications will be discussed here.

It has been found that if the nuclear radius is greater than 40 km, say, the central temperature will rise above that of the sublimation temperature of molecules such as CH₄ and NH₃ and, needless to say, CO and N2, provided that the diffusivity

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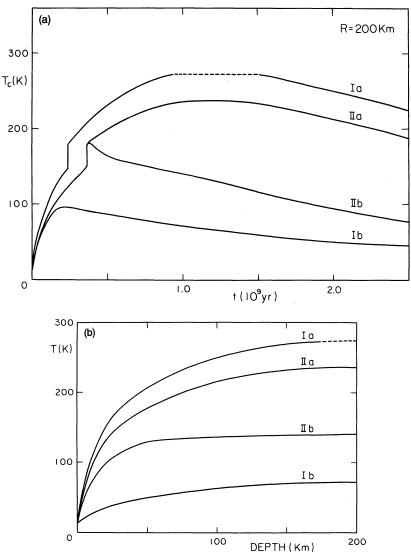


Figure 3. (a) Central temperatures of nuclei with R = 200 km are plotted against time. For model Ia, the thermal diffusivity of amorphous ice $\kappa_a = 0.0001$ cm² s⁻¹ and that of crystallized ice $\kappa_c = 0.0015$. For model Ib, $\kappa = 0.002$ cm² s⁻¹ throughout the nucleus. For model IIa, $\kappa_a = 0.0001$ and $\kappa_c = 0.0015$ cm² s⁻¹, while for model IIb, $\kappa_a = 0.0001$ and $\kappa_c = 0.02$. (b) Temperature profiles of R = 200 km nuclei at $t = 10^9$

is close to 10^{-4} cm² s⁻¹ at T < 150 K. In this case, it seems reasonable to expect that these molecules will diffuse towards the surface, where they recondense owing to the low temperature (Table 4). Thus it is reasonable to suppose that large nuclei have a layered structure, as argued earlier by Whipple & Stefanik (1966), and by Yabushita & Wada (1988). A similar modification will result for nuclei with $R \ge 160$ km, even if the diffusivity is as large as 0.0046 cm² s¹, as adopted by Wallis (1980).

Nakamura et al. (1991) discussed sporadic outbursts of P/Schwassman-Wachmann I and argued that the outbursts could be accounted for by sublimation of highly volatile molecules in the trenches which come to be irradiated from time to time by the rotation of the nucleus.

With regard to the modification of the structure, it is of great interest to see whether supervolatile molecules such as CO or N₂ are transported from the central region towards the surface. A preliminary numerical result has already been

Table 4. Condensation temperature of certain molecules. Data taken from Nakagawa (1982).

Molecule	Gas density (cm ⁻³)			
	10^3	105	10^{7}	
HCN	64.5	68.9	73.9	
NH ₃	52.6	56.1	60.0	
CH ₄	16.9	18.0	19.5	
CO	14.8	16.1	17.5	
N_2	12.1	12.9	13.9	

obtained for the equations of thermal evolution and of gas diffusion, which are coupled by sublimation (or recondensation) and loss (or gain) of latent heat (as formulated by Rickman (1991)). When the solutions are compared with the one presented here, it will be possible to decide whether the gas diffusion will modify the effective thermal diffusivity.

6.2 Formation of organic molecules

Finally, we discuss the rather controversial subject of whether highly complex organic molecules can be formed in cometary nuclei. Observations of P/Halley revealed the existence of various types of complex organic compounds. The organic molecules inferred to exist in the dust particles as analysed by the PUMA mass spectrometer on board Vega 1 (Kissel & Krueger 1987) include purine, adenine and amino acids. It is also known that approximately 3 per cent of the organic carbon in carbonaceous chondrites is in the form of amino acids (see Zhao & Bada 1989). The carbonaceous chondrites are commonly believed to originate from comets. Chyba et al. (1990) argued that organic molecules which are important for the origin of terrestrial life were injected into the primitive Earth by comets; planetary scientists now accept that a primitive atmosphere which is neutral and rich in CO2 molecules does not provide a suitable environment for the formation of organic molecules such as amino acids. Chyba et al. (1990) thus suggest that the amino acids were formed in the low-temperature environment of interstellar space.

However, the fact that a high temperature could be attained in the interior of large comets, provided that the diffusivity remains sufficiently small, suggests the possibility that amino acids and other organic molecules might have been formed there. When molecules such as HCN and NH₃ are mixed with melted H₂O, various compounds such as formic acid may form. In an important experiment, Oró & Kamat (1961) showed that amino acids form directly from hydrogen cyanide dissolved in water and Oró (1961) even suggested that chemicals such as CN, CH, NH, NH, then known to exist in comets provided material for the formation of amino acids on Earth. Clark (1988) later discussed various types of reactions which are expected to take place in a cometary pond which, he argued, would form by the impact of a comet on the primitive Earth. For such reactions to take place, the existence of melted water with solvents such as HCN and NH₃ (Schwarz & Goverde 1982) is required. What we have shown here is that many ponds could be realized in the form of droplets in large cometary nuclei which are moderately heated by radioactivity. If such large cometary nuclei undergo a series of disintegrations, amino acids and other organic molecules as found in P/ Halley could be accounted for. One of the processes that lead to cometary disintegrations is simply collisions with small but numerous asteroids.

It is not to be argued, however, that such complex organic compounds processed in the depths of the nuclei would have provided the material needed for the origin of terrestrial life. As shown in Fig. 3, the heating by radioactive elements of the nucleus to a temperature close to 273 K requires some 109 yr, whilst the origin of life on Earth is commonly accepted to have taken place between 4.5 and 3.8×10^9 yr ago (Chyba et al. 1990). However, various amino acids found in the Cretaceous-Tertiary boundary layer which are believed to be extraterrestrial (Zhao & Bada 1989) could very well be of cometary origin, having formed in the manner discussed here.

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