COMPUTATIONAL STUDY OF RADIATION CHEMICAL PROCESSING IN COMET NUCLEI

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Abstract. Cometary nuclei have been exposed to high levels of ionizing radiation since their formation. We present here some results of a computer model calculation of the effect of ionizing radiation on cometary material. The external (cosmic rays) and internal (embedded radionuclides) contributions in the processing of cometary nuclei are considered. As a first approximation we have used the available kinetic data of the liquid water system to model the radiation effects in a frozen cometary environment. Out data suggest that massive radiation chemical processing due to cosmic rays may have taken place only in the outer layers of comets. The internal contribution of radionuclides to the radiation processing of comet cores seems to be modest. Therefore, comets could be carriers of intact homochiral biomolecules.

1. Introduction

Comets are believed to have formed by accretion of interstellar grains in the outer regions of the presolar nebula around 4.6 Ga (Greenberg, 1989; Donn, 1991). This process of grain accumulation led to the formation of cometesimals, which efficiently combined upon colliding to form cometary nuclei (Donn, 1991). It is generally accepted that comets have not undergone significant physical and chemical alteration since their formation (Greenberg, 1989); therefore, they are regarded as the most pristine objects in the solar system (Oró and Berry, 1987; Oró and Mills, 1989). However, theoretical calculations and laboratory experiments suggest that ionizing radiation potentially might have induced significant physical (Prialnik *et al.*, 1987; Prialnik, 1989, Rickman, 1991) and chemical changes (Moore *et al.*, 1983; Draganić *et al.*, 1985; Khare *et al.*, 1989; Johnson, 1991; Moore *et al.*, 1991; Navarro-González *et al.*, 1991; Strazzulla *et al.*, 1991; Castillo-Rojas, *et al.*, 1992; Negrón-Mendoza *et al.*, 1992) to comet nuclei. Two sources of ionizing radiation are relevant to comets: (1) cosmic rays (external); and (2) decay of radionuclides (internal).

Cosmic rays are primarily composed of protons (93%), helium nuclei (6%) and other more heavier weight nuclei (1%) (Meyer *et al.*, 1974). The energy deposited by these particles at the surface of comets has been estimated: (1) from the early balloon measurements of cosmic rays (Whipple, 1977); (2) using the stopping power

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TABLE I

Absorbed doses derived from the decay of internal radionuclides in
cometary nuclei accumulated over 4.5 Ga*

Radionuclides	Adsorbed dose (MGy)
$^{40}K + {}^{235}U + {}^{238}U + {}^{232}Th$	0.290
$^{244}Pu + {}^{129}I + {}^{247}Cm + {}^{10}Be + {}^{237}Np$	2.516
^{26}Al	10.879

* Draganić *et al.*, 1984.

of protons and the energy spectrum for cosmic rays (Donn, 1976) or the interstellar cosmic ray proton differential energy spectrum for energies between 0.001 and 1 GeV (Moore *et al.*, 1983); and (3) introducing a cascade model to calculate the absorbed dose due to protons with energies up to 10^{10} GeV (Ryan and Draganić, 1986). The total dose of ionizing radiation deposited in a comet over its lifetime due to cosmic ray bombardment of protons with energies ranging from 0.001 to 10^{10} GeV can be calculated as a function of depth with the following empirical formula assuming that the density (*p*) of a comet is 1.0 g cm^{-3} (Draganić and Ryan, 1992):

$$\frac{\Delta E(d_0)}{\Delta E(1)} = e^{-0.435 \tanh (0.103d_0)d_0^{1/2}}$$

where, $\Delta E(1) = 401$ MGy; and d_0 is the depth of a layer in decimeters.

Another potential source of alteration of a comet comes from decay of radionuclides distributed throughout the nucleus. Numerous radionuclides have been considered, such as ^{40}K, ^{235}U, ^{238}U, ^{232}Th, ^{26}Al, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, and ^{237}Np (Whipple and Stefanik, 1966; Wallis, 1980; Draganić *et al.*, 1984; Prialnik *et al.*, 1987). Table I summarizes the contributions of these radionuclides to the absorbed dose of comets.

In an earlier report, we presented the results of our studies of the radiolysis of aqueous formaldehyde solutions at 298 K and at 77 K (Navarro-González *et al.*, 1991). Our results enabled us to develop a computer model that predicts the radiation-induced depletion of formaldehyde as a function of depth in comet nuclei. The purpose of the present work is to extend our computer model in order to obtain an estimate of the effects of radiation chemical processing of the volatile fraction of comet nuclei. At the present time, there is no kinetic data available to apply our model to a water ice-dominated system such as that of a comet. As a first approximation, therefore, we have used the kinetic data of the liquid water system to model the radiation effects in comets.

2. Computer Modeling

2.1. SELECTION OF THE CHEMICAL COMPOSITION OF COMETS

Comets are composed of refractory and volatile material in about one-to-one ratio (Delsemme, 1991). Based on the spectroscopic detection of chemical species in the coma and tail of comets and the relative elemental abundances for the atoms H, C, N, O and S in comet Halley, Delsemme (1991) has suggested a model of the composition of the volatile fraction of comet Halley. A simplified version of this model was employed (Table II).

2.2. INTERACTION OF IONIZING RADIATION WITH COMET NUCLEI

Water is the most abundant species in the volatile fraction of comets, and we assume for simplicity that the energy of ionizing radiation has been deposited entirely in the water molecules.

The absorption of ionizing radiation by the silicates is not considered because it leads to radiation heterogeneous catalysis (Negrón-Mendoza and Navarro-González, 1990; Navarro-González et al., 1990).

The radiolysis of liquid water at 298 K has been studied extensively (Draganić and Draganić, 1971). The interaction of ionizing radiation with water produces ionization and dissociation of the molecules which form highly reactive intermediates,

TABLE II

Chemical composition of the volatile fraction of comets

Compound	% Abundance	
	Delsemme Model[a]	Values used in this work[b]
H_2O	78.50	81.60
HCO_2H	4.50	4.50
HCHO	4.00	4.00
CO_2	3.50	3.50
N_2	2.60	2.60
CO	1.50	1.50
HCN	1.00	1.00
NH_3	0.80	0.80
CH_4	0.50	0.50
C_2H_2	1.50	0.00
N_2H_4	0.80	0.00
$C_4H_4N_2$	0.40	0.00
C_3H_2	0.20	0.00
H_2S	0.10	0.00
CS_2	0.05	0.00
S_2	0.05	0.00

[a] Delsemme, 1991.
[b] The less abundant components were neglected.

such as hydrogen atoms (H·), hydroxyl radicals (·OH) and hydrated electrons (e_{aq}^-), and stable molecules, such as molecular hydrogen and hydrogen peroxide (reaction 1):

$$H_2O \longrightarrow\!\!\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\!\!\longrightarrow H\cdot + e_{eq}^- + \cdot OH + H^+ + H_2O_2 + H_2 \qquad (1)$$

The radiation chemical yields of these intermediates depend on the type of radiation and its energy, more specifically on the radiation linear energy transfer (LET) (Draganić and Draganć, 1971).

Cometary nuclei have been exposed mainly to cosmic rays (Ryan and Draganić, 1986). The cosmic ray protons are the dominating ionizing particles in the interstellar medium, about 95% of the cosmic ray flux. Most abundant are the protons which have energies of about 2 GeV (Draganić and Draganić, 1988) and a LET similar to gamma rays (Draganić et al., 1984). Therefore, gamma ray irradiation could be a suitable energy source for the simulation of 2 GeV proton irradiation of cometary nuclei (Draganić et al., 1984). Table III summarizes the radiation chemical yields of the primary species of water radiolysis by gamma rays.

The radiolysis of liquid water can be modeled with reactions 1 to 48 (see Table IV). The rate constants of these reactions are well documented and were taken from the comprehensive compilations of Anbar et al. (1971, 1975), Dorfman and Adams (1973), Ross (1975), Ross and Ross (1977), Bielski et al. (1985), and Buxton et al. (1988).

The radiolysis of water ice at 77 K has not been studied as extensively (Kevan, 1968). The irradiation of water ice at low temperatures leads to the formation of the same products as in liquid water (reaction 1) except that hydrated electrons would be replaced by trapped electrons, e_t^-. The radiation chemical yields of the

TABLE III

Chemicals yields (G) of primary species produced by gamma-ray
radiolysis of water at pH 3–13[a]

Species	G	
	298 K[b]	77 K[c]
H_2O	4.1[d]	0.5[d]
H_2	0.45	0.1
H_2O_2	0.7	0.1
H·	0.6	0.3
·OH	2.7	0.3
H^+	2.6	0.0002
e_{aq}^-	2.6	—
e_t^-	—	0.0002

[a] G values are given in number of molecules formed or destroyed
per 100 eV of energy absorbed.
[b] Draganić and Draganić, 1971.
[c] Navarro-González et al., 1991.
[d] Yield of destruction.

TABLE IV

Reactions involved in the radiolysis of water

No.	Reaction		Rate constant[a]
2	$H \cdot + H \cdot$	$\longrightarrow H_2$	$k = 7.8 \times 10^9$
3	$H \cdot + e_{aq}^-$	$\overset{H_2O}{\longrightarrow} H_2 + OH^-$	$k = 2.5 \times 10^{10}$
4	$H \cdot + \cdot O^-$	$\longrightarrow OH^-$	$k = 2.0 \times 10^{10}$
5	$H \cdot + \cdot OH$	$\longrightarrow H_2O$	$k = 7.0 \times 10^9$
6	$H \cdot + OH^-$	$\longrightarrow e_{aq}^- + H_2O$	$k = 2.2 \times 10^7$
7	$H \cdot + H_2O$	$\longrightarrow H_2 + \cdot OH$	$k = 1.0 \times 10^1$
8	$H \cdot + H_2O_2$	$\longrightarrow H_2O + \cdot OH$	$k = 9.0 \times 10^7$
9	$H \cdot + O_2$	$\longrightarrow HO_2 \cdot$	$k = 2.1 \times 10^{10}$
10	$H \cdot + HO_2 \cdot$	$\longrightarrow H_2O_2$	$k = 1.0 \times 10^{10}$
11	$e_{aq}^- + e_{aq}^-$	$\overset{2H_2O}{\longrightarrow} H_2 + 2OH^-$	$k = 5.5 \times 10^9$
12	$e_{aq}^- + H^+$	$\longrightarrow H \cdot$	$k = 2.3 \times 10^{10}$
13	$e_{aq}^- + \cdot O^-$	$\overset{H_2O}{\longrightarrow} 2OH^-$	$k = 2.2 \times 10^{10}$
14	$e_{aq}^- + \cdot OH$	$\longrightarrow OH^-$	$k = 3.0 \times 10^{10}$
15	$e_{aq}^- + H_2O$	$\longrightarrow H \cdot + OH^-$	$k = 1.9 \times 10^1$
16	$e_{aq}^- + O_2$	$\longrightarrow \cdot O_2^-$	$k = 1.9 \times 10^{10}$
17	$e_{aq}^- + \cdot O_2^-$	$\overset{H_2O}{\longrightarrow} 2OH^-$	$k = 1.3 \times 10^{10}$
18	$e_{aq}^- + HO_2^-$	$\overset{H_2O}{\longrightarrow} \cdot OH + 2OH^-$	$k = 3.5 \times 10^9$
19	$e_{aq}^- + H_2O_2$	$\longrightarrow \cdot OH + OH^-$	$k = 1.1 \times 10^{10}$
20	$\cdot OH + \cdot OH$	$\longrightarrow H_2O_2$	$k = 5.5 \times 10^9$
21	$\cdot OH + \cdot O^-$	$\longrightarrow HO_2^-$	$k \leq 2.0 \times 10^{10}$
22	$\cdot OH + OH^-$	$\longrightarrow H_2O + \cdot O^-$	$k = 1.3 \times 10^{10}$
23	$\cdot OH + H_2$	$\longrightarrow H_2O + H \cdot$	$k = 4.2 \times 10^7$
24	$\cdot OH + HO_2 \cdot$	$\longrightarrow H_2O + O_2$	$k = 6.0 \times 10^9$
25	$\cdot OH + HO_2^-$	$\longrightarrow OH^- + \cdot O_2^- + H^+$	$k = 7.5 \times 10^9$
26	$\cdot OH + H_2O_2$	$\longrightarrow H_2O + \cdot O_2^- + H^+$	$k = 2.7 \times 10^7$
27	$\cdot OH + H_2O_2 \cdot^+$	$\longrightarrow H_2O + O_2 + H^+$	$k = 1.2 \times 10^{10}$
28	$\cdot OH + \cdot O_2^-$	$\longrightarrow OH^- + O_2$	$k = 8.0 \times 10^9$
29	$\cdot OH + \cdot O_3^-$	$\longrightarrow \cdot O_2^- + HO_2 \cdot$	$k = 8.5 \times 10^9$
30	$\cdot O^- + \cdot O^-$	$\overset{H_2O}{\longrightarrow} HO_2^- + OH^-$	$k = 8.3 \times 10^9$
31	$\cdot O^- + H^+$	$\longrightarrow \cdot OH$	$k = 1.0 \times 10^{11}$
32	$\cdot O^- + H_2$	$\longrightarrow H \cdot + OH^-$	$k = 8.0 \times 10^7$
33	$\cdot O^- + H_2O$	$\longrightarrow \cdot OH + OH^-$	$k = 1.8 \times 10^6$
34	$\cdot O^- + HO_2^-$	$\longrightarrow OH^- + \cdot O_2^-$	$k = 4.0 \times 10^8$

Table IV (continued).

No.	Reaction		Rate constant[a]
35	$\cdot O^- + H_2O_2$	$\longrightarrow H_2O + \cdot O_2^-$	$k \leq 5.0 \times 10^8$
36	$\cdot O^- + O_2$	$\longrightarrow \cdot O_3^-$	$k = 3.6 \times 10^9$
37	$\cdot O^- + \cdot O_2^-$	$\xrightarrow{H_2O} O_2 + 2OH^-$	$k = 6.0 \times 10^8$
38	$\cdot O^- + \cdot O_3^-$	$\longrightarrow O_2 + O_2^{2-}$	$k = 8.0 \times 10^8$
39	$\cdot O_2^- + H^+$	$\longrightarrow HO_2 \cdot$	$k = 1.0 \times 10^{11}$
40	$\cdot O_2^- + H_2O$	$\longrightarrow HO_2 \cdot + OH^-$	$k = 1.0 \times 10^9$
41	$\cdot O_2^- + HO_2^-$	$\xrightarrow{H_2O} H_2O_2 + O_2 + 2OH^-$	$k = 2.0$
42	$\cdot O_2^- + H_2O_2$	$\longrightarrow OH^- + \cdot OH + O_2$	$k = 1.3 \times 10^{-1}$
43	$HO_2 \cdot + HO_2 \cdot$	$\longrightarrow H_2O_2 + O_2$	$k = 3.4 \times 10^6$
44	$HO_2 \cdot + H_2O_2$	$\longrightarrow \cdot OH + O_2 + H_2O$	$k = 3.7$
45	$HO_2^- + H_2O$	$\longrightarrow H_2O_2 + OH^-$	$k = 5.0 \times 10^7$
46	$H_2O_2 + OH^-$	$\longrightarrow HO_2^- + H_2O$	$k = 1.0 \times 10^{10}$
47	H_2O	$\longrightarrow H^+ + OH^-$	$k = 2.5 \times 10^{-5}$
48	$H^+ + OH^-$	$\longrightarrow H_2O$	$k = 1.4 \times 10^{11}$

[a] The first and second order rate constants have units of s^{-1}, and dm^3 $mol^{-1} s^{-1}$, respectively, and were determined at 298 K.

primary species of the radiolysis of water ice have been derived from experiments carried out at 77 K but the measurements were done after the samples had been warmed to room temperature (Navarro-González *et al.*, 1991). The yield of decomposition of water decreases from G = 4.1 at 298 K to G = 0.5 at 77 K.

Rates of reactions 2 to 48 (Table IV) have not been measured at 77 K because of the complexity of deriving absolute rate constants of complex chemical systems particularly at the frozen stage. We have assumed that the *relative* ratios for the rate constants are unchanged from room temperature to 77 K. This assumption is supported by the observation that the *relative* reaction rates of solvated electrons with a variety of solutes in ice at 77 K is quantitatively similar to those in liquid water at 300 K (Kevan, 1967); also, the product distribution is unchanged from 300 K to 77 K (Draganić *et al.*, 1985).

2.3. RADIOLYSIS OF A COMETARY SYSTEM

In addition to the 48 chemical reactions used to model the radiolysis of water, we have included 30 more reactions to model the radiation-induced decomposition of some of the other the volatile components in comets (Table V), for which the rate constants are known at room temperature. Some molecules are reactive with all species produced by the radiolysis of water, such as formaldehyde, carbon monoxide, hydrogen cyanide, formic acid and their ions. Others, such as carbon

TABLE V

Reactions considered in the radiation-induced damage in comets[a]

No.	Reaction		Constant[b]
49 HCO_2H	$\rightleftharpoons$	$HCO_2^- + H^+$	$K = 1.8 \times 10^{-4}$
50 $HCO_2H + e_{aq}^-$	$\longrightarrow$	$HCO_2^- + H \cdot$	$k = 1.4 \times 10^8$
51 $HCO_2H + H \cdot$	$\longrightarrow$	$\cdot CO_2H + H_2$	$k = 4.4 \times 10^5$
52 $HCO_2H + \cdot OH$	$\longrightarrow$	$\cdot CO_2H + H_2O$	$k = 1.3 \times 10^8$
53 $HCO_2^- + H \cdot$	$\longrightarrow$	$\cdot CO_2^- + H_2$	$k = 2.1 \times 10^8$
54 $HCO_2^- + \cdot OH$	$\longrightarrow$	$\cdot CO_2^- + H_2O$	$k = 3.2 \times 10^9$
55 $HCHO + e_{aq}^-$	$\xrightarrow{H_2O}$	$\cdot CH_2OH + OH^-$	$k = 1.0 \times 10^7$
56 $HCHO + H \cdot$	$\longrightarrow$	$\cdot CHO + H_2$	$k = 3.3 \times 10^6$
57 $HCHO + H \cdot$	$\longrightarrow$	$\cdot CH_2OH$	$k = 6.7 \times 10^5$
58 $HCHO + \cdot OH$	$\longrightarrow$	$\cdot CHO + H_2O$	$k = 1.0 \times 10^9$
59 $CO_2 + H_2O$	$\rightleftharpoons$	$H^+ + HCO_3^-$	$K = 3.5 \times 10^{-7}$
60 $OH^- + HCO_3^-$	$\rightleftharpoons$	$CO_3^{2-} + H_2O$	$K = 5.0 \times 10^{-11}$
61 $CO_2 + e_{aq}^-$	$\longrightarrow$	$\cdot CO_2^-$	$k = 7.7 \times 10^9$
62 $HCO_3^- + \cdot OH$	$\longrightarrow$	$\cdot CO_3^- + H_2O$	$k = 8.5 \times 10^6$
63 $CO_3^{2-} + \cdot OH$	$\longrightarrow$	$\cdot CO_3^- + OH^-$	$k = 3.9 \times 10^8$
64 $CO + e_{aq}^-$	$\xrightarrow{H_2O}$	$\cdot CHO + OH^-$	$k = 1.7 \times 10^9$
65 $CO + \cdot H$	$\longrightarrow$	$\cdot CHO$	$k = 3.3 \times 10^7$
66 $CO + \cdot OH$	$\longrightarrow$	$\cdot CO_2H$	$k = 2.9 \times 10^9$
67 $^-CN + H_2O$	$\longrightarrow$	$HCN + OH^-$	$k = 5.2 \times 10^4$
68 $HCN + OH^-$	$\longrightarrow$	$^-CN + H_2O$	$k = 3.7 \times 10^9$
69 $HCN + e_{aq}^-$	$\xrightarrow{H_2O}$	$\cdot CH = NH + OH^-$	$k = 6.6 \times 10^8$
70 $^-CN + e_{aq}^-$	$\xrightarrow{H_2O}$	$^- \cdot C = NH + OH^-$	$k = 5.0 \times 10^5$
71 $HCN + H \cdot$	$\longrightarrow$	$\cdot CH = NH$	$k = 3.3 \times 10^7$
72 $^-CN + H \cdot$	$\longrightarrow$	$^- \cdot C = NH$	$k = 2.6 \times 10^9$
73 $HCN + \cdot OH$	$\longrightarrow$	$\cdot CH = N - OH$	$k = 6.0 \times 10^7$
74 $^-CN + \cdot OH$	$\longrightarrow$	$^- \cdot C = N - OH$	$k = 6.5 \times 10^9$
75 $NH_3 + H_2O$	$\rightleftharpoons$	$NH_4^+ + OH^-$	$K = 5.8 \times 10^{-10}$
76 $NH_4^+ + e_{aq}^-$	$\longrightarrow$	$NH_3 + \cdot H$	$k = 2.0 \times 10^6$
77 $NH_3 + \cdot OH$	$\longrightarrow$	$\cdot NH_2 + H_2O$	$k = 1.0 \times 10^8$
78 $CH_4 + \cdot OH$	$\longrightarrow$	$\cdot CH_3 + H_2O$	$k = 1.1 \times 10^8$

[a] The rate constants were taken from Anbar *et al.* (1971, 1975), Dorfman and Adams (1973), Ross (1975), Ross and Ross (1977), Bielski *et al.* (1985), Buxton *et al.* (1988).

[b] Rate constants (k) have units of dm^3 mol^{-1} s^{-1}; equilibrium constants are distinguished by the symbol K.

dioxide, bicarbonate, and carbonate ions as well as ammonia and the ammonium ion, are reactive mainly with hydroxyl radicals or hydrated electrons. Molecular nitrogen is totally unreactive with any of the species produced by the radiolysis of water.

2.4. COMPUTER PROGRAM

The chemical reactions in Tables IV and V were translated into differential equations and solved numerically by *Acuchem* (version 1.4) (Braun *et al.*, 1988). *Acuchem* solves a system of differential equations describing the temporal behavior of spatially homogeneous, isothermal, multicomponent chemical reactions. Mass and charge balances are maintained in the computations. Zeroth, first and second order reactions are allowed. Termolecular reactions are not handled explicitly; a two-step mechanism must be employed. There is no allowance for the input of equilibrium constants; reactions have to be entered separately in the forward and reverse reactions.
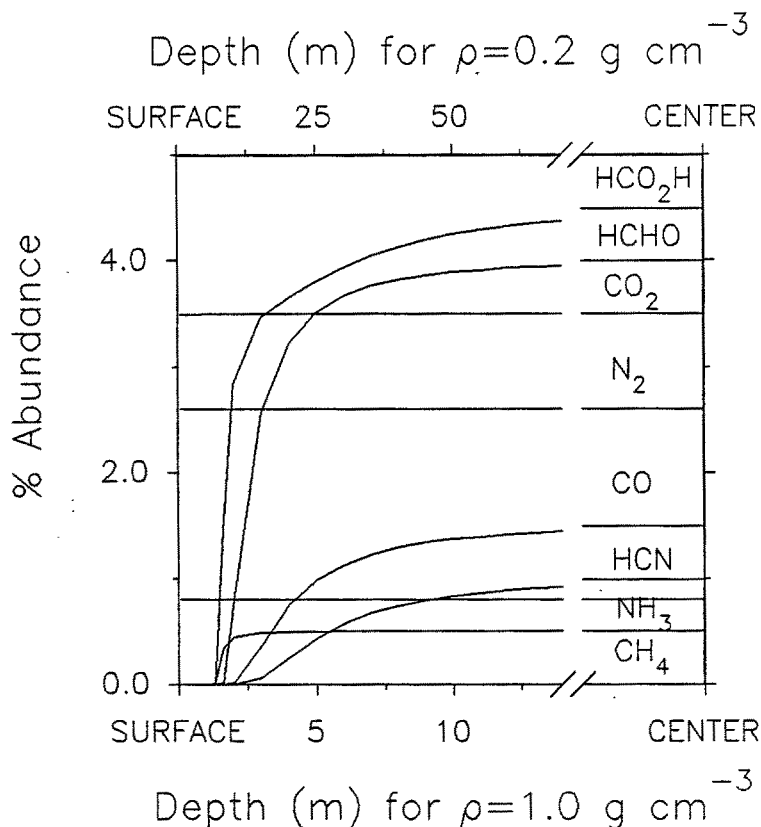

Fig. 1. Radiation damage-depth curve for the volatile fraction of comet nuclei induced by cosmic ray-protons (energies from 10^3 to 10^{19} eV) and the decay of ^{40}K, ^{235}U, ^{238}U and ^{232}Th at 77 K.

3. Results and Discussion

3.1. RADIATION DAMAGE OF THE VOLATILE FRACTION IN COMETS

Figure 1 shows the radiation damage of the volatile fraction as a function of depth in comet nuclei at 77 K induced by cosmic rays and decay of embedded radionuclides such as ^{40}K, ^{235}U, ^{238}U, ^{232}Th. The only species that seem to be stable to radiation damage are carbon dioxide, nitrogen, and ammonia. Within the first few meters of the comet surface (2.5 m for $\rho = 1.0$ g cm^{-3} or 12.5 m for $\rho = 0.2$ g cm^{-3}), there is a heavy radiation-processing due to cosmic rays for the rest of the constituents. In the next few meters from the surface (2.5 m or 12.5 m depending on the density), the compounds most readily depleted are hydrogen cyanide, and carbon monoxide followed by formaldehyde, methane and finally, formic acid. At greater depths, radiation chemical processing seems to be modest.

If we now include the additional contributions of ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, ^{237}Np (Figure 2) as well as ^{26}Al (Figure 3) to the absorbed dose, the results are similar
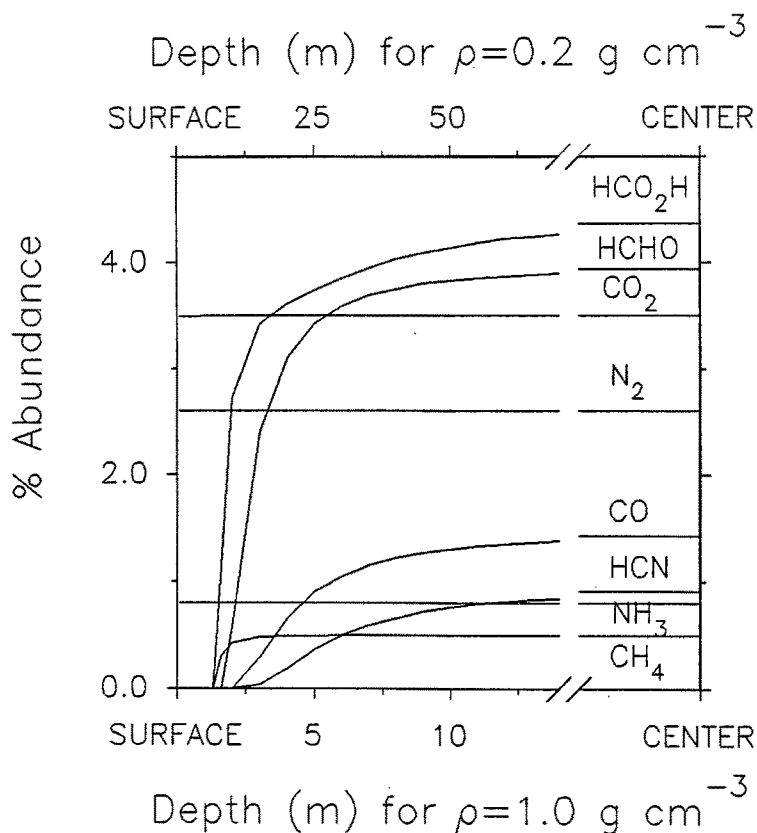

Fig. 2. Radiation damage-depth curve for the volatile fraction of comet nuclei induced by cosmic ray-protons (energies from 10^3 to 10^{19} eV) and the decay of ^{40}K, ^{235}U, ^{238}U, ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be and ^{237}Np at 77 K.

to figure 1 for the outer layers of comet nuclei and the differences are only in the center of the comets. Finally, if we consider that a liquid core was developed by radiogenic heating produced by decay of ^{26}Al, then it is predicted that the original composition of comets was completely altered (Figure 4). Table VI summarizes the destruction of the volatile fraction under different conditions in the center of comet nuclei. The chemical components of our model system can be divided into two groups: (1) a group more susceptible to radiation damage that includes hydrogen cyanide, carbon monoxide, formic acid and formaldehyde; and (2) an another group less vulnerable to radiation damage that includes methane, carbon dioxide, ammonia and nitrogen.

The radiolysis of the volatile fraction of comets by cosmic rays and the decay of internal radionuclides leads to a variety of radicals and radical-ions, such as $\cdot CO_2H$, $\cdot CH_2OH$, $\cdot CHO$, $\cdot CO_2^-$, $\cdot CO_3^-$, $\cdot CH = NH$, $^-\cdot C = NH$, $\cdot CH = N\text{-}OH$, $^-\cdot C = N\text{-}OH$, $\cdot NH_2$ and $\cdot CH_3$ (Table V). Their reactions were not included in our computer model because there is no data available regarding their specific mode
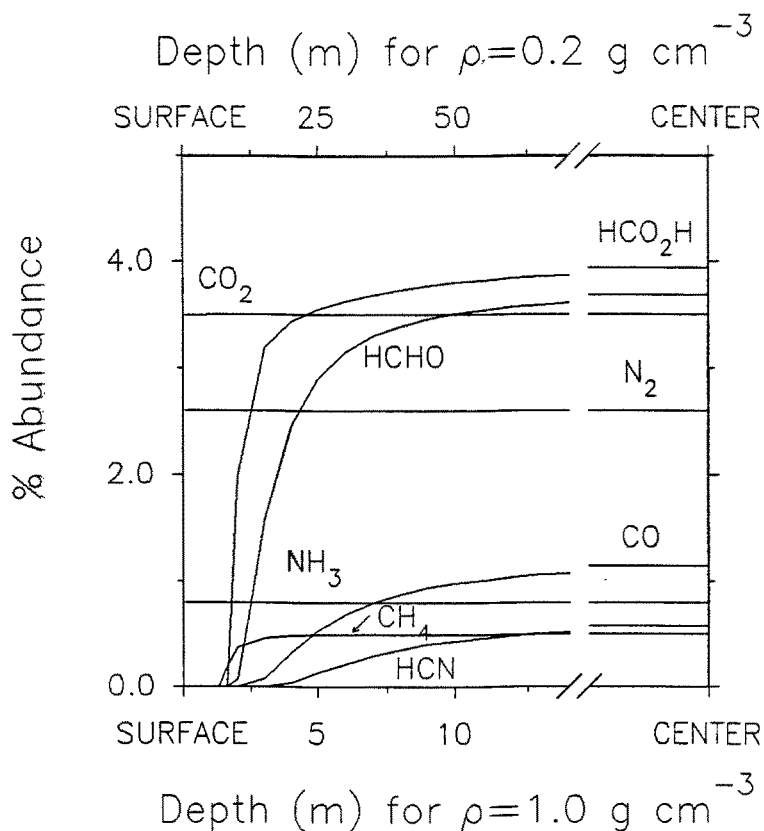

Fig. 3. Radiation damage-depth curve for the volatile fraction of comet nuclei induced by cosmic ray-protons (energies from 10^3 to 10^{19} eV) and the decay of ^{40}K, ^{235}U, ^{238}U, ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, ^{237}Np and ^{26}Al at 77 K.
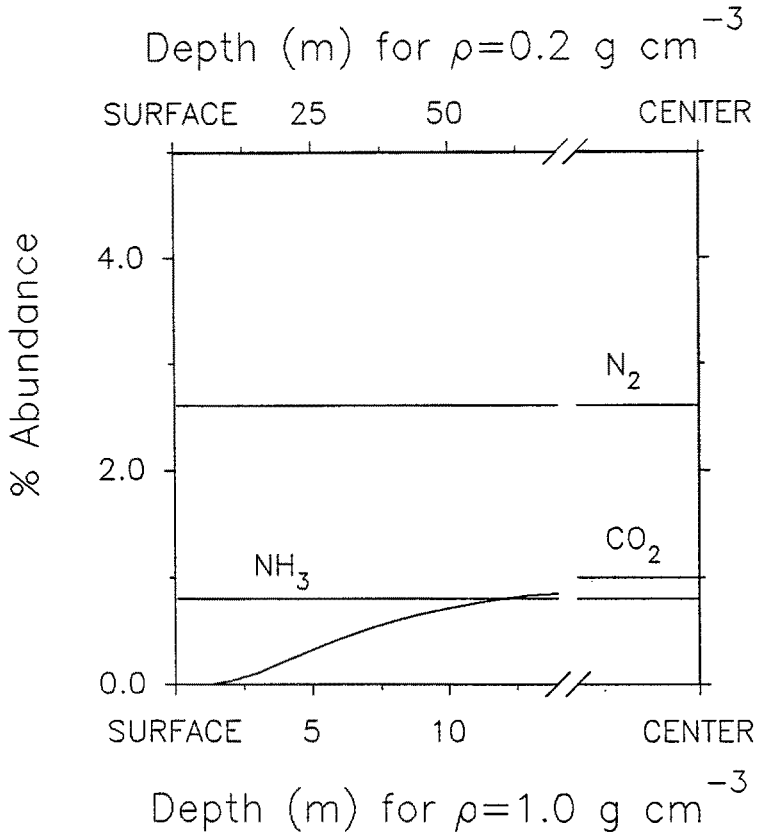
Depth (m) for $\rho=0.2$ g cm^{-3}

Fig. 4. Radiation damage-depth curve for the volatile fraction of comet nuclei induced by cosmic ray-protons (energies from 10^3 to 10^{19} eV) and the decay of ^{40}K, ^{235}U, ^{238}U, ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, ^{237}Np and ^{26}Al at 298 K.

TABLE VI

% Destruction of the volatile fraction in the center of comet nuclei

Compound	% Destruction			
	Case 1 (Figure 1)	Case 2 (Figure 2)	Case 3 (Figure 3)	Case 3 (Figure 4)
	77 K			298 K
HCN	0.88	8.55	41.80	100.00
CO	0.44	4.37	23.85	100.00
HCO_2H	0.32	2.98	12.44	100.00
HCHO	0.14	1.38	8.06	100.00
H_2O	0.03	0.26	1.16	1.92
CH_4	0.01	0.12	0.74	99.57
CO_2	0.00	0.00	0.01	71.52
NH_3	0.00	0.00	0.00	0.00
N_2	0.00	0.00	0.00	0.00

Case 1: Cosmic rays, ^{40}K, ^{235}U, ^{238}U and ^{232}Th.
Case 2: Cosmic rays, ^{40}K, ^{235}U, ^{238}U and ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, ^{237}Np.
Case 3: Cosmic rays, ^{40}K, ^{235}U, ^{238}U and ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, ^{237}Np and ^{26}Al.

of reactions as well as their kinetic parameters. Experimental simulations of the radiolysis of volatile ices suggest that such radicals could generate some of the parent molecules or form other volatile (such as hydrocarbons, aldehydes, alcoholes, etc.) and non-volatile (amino acids, carboxylic acids, oligomers and polymers) materials (Moore *et al.*, 1983; Draganić *et al.*, 1985; Khare *et al.*, 1989; Moore *et al.*, 1991; Castillo-Rojas, *et al.*, 1992; Negrón-Mendoza *et al.*, 1992).

3.2. IMPLICATION TO COMETARY CHEMISTRY AND THE ORIGINS OF LIFE

Our model predicts that massive radiation chemical processing has taken placed in the outer layers of comets due to cosmic rays. This radiation chemical processing rapidly diminishes at greater depths. The internal contribution of radionuclides (such as ^{40}K, ^{235}U, ^{238}U, ^{232}Th, ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be and ^{237}Np) to the radiation processing of comet cores seems to be modest, unless appreciable ^{26}Al was present during comet formation. If comets accreted at the same time at which the parent bodies of meteorites did, then it could be predicted that the decay of ^{26}Al might have led to the radiogenic melting of primordial cometary interiors of bodies larger than 10 Km in radius (Wallis, 1980). Even if a melting temperature was not reached, heating to only 137 K may lead to significant physical alteration in the cometary structure since there would be an irreversible phase transition from amorphous ice to cubic ice (Prialnik *et al.*, 1987). The eruptive behavior of comet Halley suggests that comets have survived the various phases of radiogenic heating in its amorphous form and crystallization had not taken place. Based on this assumption, Prialnik *et al.* (1987) have estimated that comets formed when the abundance of ^{26}Al had decreased about 100 times that found in the inclusions of the Allende meteorite. This implies that comets formed about five million years later than the parent bodies of meteorites (Prialnik *et al.*, 1987). Therefore, the original composition of cometary nuclei has not been significantly altered, and so the study of the chemical composition of comets should provide information about the composition of the presolar nebula.

Could our model explain some of the differences between new (from the Oort cloud) and evolved (periodic) comets? Astronomical observations indicate that new comets have greater brightness than evolved comets (Whipple, 1978). This behavior is generally interpreted to be due to super-volatile ices in the outer layers of comet nuclei. Whipple (1977) has speculated that these super-volatile ices could have resulted from cosmic ray radiation of the surfaces of cometary nuclei since their formation in the Oort cloud. The radicals thus produces in the outermost layers would react exothermically with moderate solar heating as a new comet approaches the Sun. As these outer layers are removed after its first perihelion passage, the brightness of the comet would decrease by several magnitudes during its next apparition. Laboratory experiments indicate that irradiated ice mixtures exhibit thermoluminescence activity when they are warmed (Moore *et al.*, 1983). An additional consequence of cosmic ray bombardment of the surface of comets would be the development of a polymerized crust (Donn, 1976; Johnson, 1991). Furthermore,
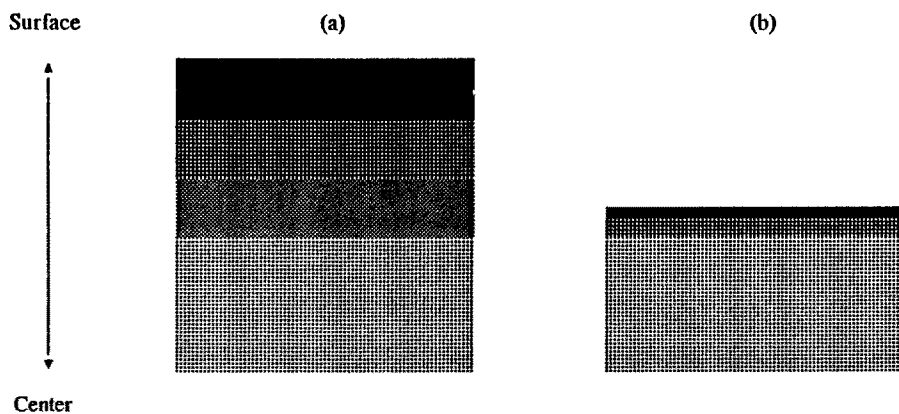
▉ : Severely processed; ▓ : Moderately processed; ▒ : Slightly processed; and ▦ : Essentially pristine

Fig. 5. Hypothetical cross sections of the upper most layers of comet nuclei in the Oort cloud (a) and after several passages through perihelion (b).

it has been suggested that the dark surfaces of cometary nuclei could be attributed to radiation effects (Cruikshank, 1989). The formation of polymers from irradiated ices is well established by laboratory experiments (Moore *et al.*, 1983; Draganić *et al.*, 1985; Khare *et al.*, 1989; Navarro-González *et al.*, 1991; Strazzulla, *et al.*, 1991; Castillo-Rojas, *et al.*, 1992; Negrón-Mendoza *et al.*, 1992). Figure 5 shows schematically the differences between new and evolved comets.

Bonner (1991) has recently suggested that the synchrotron circularly polarized ultraviolet light produced off-angle to the orbit of electrons accelerated around the rotating neutron star remanents of supernova explosions interacted with interstellar grains from the presolar nebula producing chiral organic molecules such as amino-acids and hydroxy-acids. Furthermore, he has also suggested that comets were the carriers of extraterrestrial sources of molecular homochirality from interstellar space to the primitive Earth. If this scenario indeed took place, could the internal ionizing radiation resulting from the decay of radionuclides lead to the racemization of the biomolecules possibly present in the interiors of comet nuclei? It is known that amino-acids in solution undergo radioracemization (Bonner, 1991). This racemization is initiated by hydrogen atom abstraction on the chiral center of amino- ($X = NH_2$) or hydroxy ($X = OH$) acids by hydrogen atoms and hydroxyl radicals produced by the radiolysis of water (reaction 79). The radicals thus produced disproportionate, regenerating the parent molecules in racemate form. In addition to racemization, amino- and hydroxy-acids undergo decomposition (reactions 80 and 81).
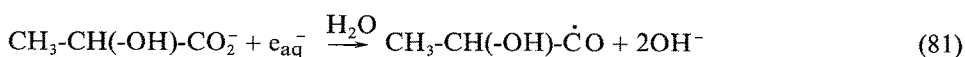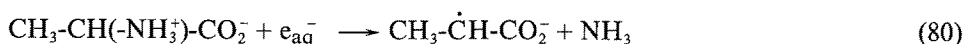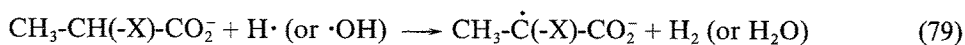
$$CH_3\text{-}CH(\text{-}X)\text{-}CO_2^- + H\cdot \text{ (or } \cdot OH) \longrightarrow CH_3\text{-}\dot{C}(\text{-}X)\text{-}CO_2^- + H_2 \text{ (or } H_2O) \tag{79}$$

$$CH_3\text{-}CH(\text{-}NH_3^+)\text{-}CO_2^- + e_{aq}^- \longrightarrow CH_3\text{-}\dot{C}H\text{-}CO_2^- + NH_3 \tag{80}$$

$$CH_3\text{-}CH(\text{-}OH)\text{-}CO_2^- + e_{aq}^- \xrightarrow{H_2O} CH_3\text{-}CH(\text{-}OH)\text{-}\dot{C}O + 2OH^- \tag{81}$$

TABLE VII

Rates of reactions of hydrogen atom, hydroxyl radical and hydrated electron with alanine and lactic acid in aqueous solution at 298 K[a]

Hydroxy- or amino-acid form	H ·	· OH	e_{aq}^-
CH_3-CH(-OH)-CO_2H	2.0×10^7	4.3×10^8	7.2×10^8
CH_3-CH(-OH)-CO_2^-		3.8×10^8	$<1.0 \times 10^7$
CH_3-CH(-NH_3^+)-CO_2H	2.3×10^5	5.4×10^7	
CH_3-CH(-NH_3^+)-CO_2^-		7.7×10^7	9.0×10^6
CH_3-CH(-NH_2)-CO_2^-		7.5×10^8	
Maximum value (selected):	2.0×10^7	7.5×10^8	7.2×10^8

[a] The rate constants were taken from Buxton et al. (1988) and have units of $dm^3\ mol^{-1}\ s^{-1}$.

These reactions and their rates (Table VII) were incorporated into our computer model to evaluate the possible degree of destruction of the amino- and hydroxy-acids possibly present in comets. If these compounds were present in comets at abundances comparable to those found in carbonaceous chondrites, 60 and 15 ppm, respectively (Cronin et al., 1988), and if alanine and lactic acid were the only representatives of these classes of organic compounds at such abundances, then the degree of radiation-induced racemization and destruction is expected to be about 0.2%, if only ^{40}K, ^{235}U, ^{238}U and ^{232}Th are considered (Table VIII). If we now include the additional contributions of ^{244}Pu, ^{129}I, ^{247}Cm, ^{10}Be, ^{237}Np and ^{26}Al, then the degree of radiation-induced racemization and destruction could increase by as much as 12.6%. These figures do not change if the abundance of amino- and hydroxy-acids is increased by two orders of magnitude. Complete destruction of these compounds would be expected only if a liquid core had developed in comet nuclei. Since there is no evidence for the development of liquid cores in comet nuclei, we may conclude that comets are possible carriers of intact homochiral biomolecules.

3.3. LIMITATIONS OF THE COMPUTER APPROACH AND POSSIBLE IMPROVEMENTS

It must be recognized that there are several serious limitations to our computer

TABLE VIII

% Destruction of alanine and lactic acid in the center of comet nuclei[a]

Compound	Abundance (ppm)	% Destruction			
		Case 1	Case 2	Case 3	Case 3
		77 K			298 K
Alanine	60–6000	0.2	2.2	12.6	100.0
Lactic acid	15–1500	0.2	2.2	12.6	100.0

[a] See Table VI for details of each case.

modeling technique. The most important is that our model uses the kinetic parameters for the radiolysis of water and aqueous solutions of different simple compounds in a liquid phase. Since at the present time there are no kinetic data available to apply our model to an icy water dominated system such as that of a comet, this approach has enabled us to obtain only a rough picture of what the radiation damage to comet nuclei could be. Our computer modeling needs improvements. We should:

(1) Consider the termination reactions among the species produced in Table IV;

(2) Carry out the computer simulations under non-homogeneous kinetics;

(3) Determine experimentally the rates of reactions given in Tables III and IV at low temperature; and,

(4) Consider the direct effect of ionizing radiation on other substances besides water including silicates.

Acknowledgements

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