Reports

Photochemical Production of Formaldehyde in Earth's Primitive Atmosphere

Abstract. *Formaldehyde could have been produced by photochemical reactions in Earth's primitive atmosphere, at a time when it consisted mainly of molecular nitrogen, water vapor, carbon dioxide, and trace amounts of molecular hydrogen and carbon monoxide. Removal of formaldehyde from the atmosphere by precipitation can provide a source of organic carbon to the oceans at the rate of 10^{11} moles per year. Subsequent reactions of formaldehyde in primeval aquatic environments would have implications for the abiotic synthesis of complex organic molecules and the origin of life.*

The photochemical oxidation of methane (CH_4) is known to be a major source of formaldehyde (H_2CO) in Earth's atmosphere (*1*). The presence of CH_4 and other reduced gases, in abundances greatly exceeding those expected in thermochemical equilibrium, arises from biological activity (*2*). This report is concerned with the production of H_2CO, by photochemical reactions in the atmosphere, at an early stage in Earth's history before life has originated; H_2CO is one of the simple molecules that might have played a key role in the abiotic synthesis of complex organic molecules on the primitive Earth.

The laboratory synthesis of H_2CO and other important organic molecules has been carried out by a number of workers. The initial mixtures used to simulate the composition of the primitive atmosphere have ranged from highly reducing (*3*) to slightly oxidizing (*4*) materials. Although the oxidation state of Earth's atmosphere before life had originated is still highly uncertain, it is generally agreed that it would have been determined by the outgassing history and the composition of volcanic gases. There is strong indirect evidence for a geologically rapid initial degassing of volatiles, rather than a continuous release over the history of the terrestrial planets. Supporting arguments for this view have been presented by Fanale (*5*) for Earth, by Walker (*6*) for Earth and Venus, and by McElroy *et al.* (*7*) for Mars. It is also unlikely that free iron would have been present in the upper mantle for more than 5×10^8 years after Earth had formed (*8*). Once native iron had been removed from the upper mantle by differentiation of the core and mantle, volcanic emissions of CH_4 would have been negligible and the composition of volcanic gases would not differ significantly from that of the present (*8*). However, the outgassed volatiles may have contained a small fraction (a few percent) of reduced compounds such as H_2 and CO, in amounts slightly greater than those observed today (*6*). It has been implicitly assumed by earlier workers that the reduced materials was lost solely through the escape of H_2 from the exosphere. Our study raises the possibility of the production of reduced organic carbon from this material.

The major atmospheric constituents after Earth had differentiated should be CO_2, N_2, and H_2O (*8*), with smaller amounts of reduced gases such as H_2 and CO. For the purposes of this investigation, we have assumed that the abundances of CO_2, N_2, and H_2O are the same as today's and that the abundance of H_2 was governed by the balance between volcanic release, the escape of hydrogen atoms, and photochemical reactions. The mixing ratio of H_2 in the atmosphere was calculated to be of the order of 10^{-3} (*9*). Except for the absence of a stratospheric thermal inversion, the thermal structure was also taken to be the same as the present. The reactions and rate coefficients used in the photochemical model are presented in Table 1 (*10*).

In the absence of shielding by O_2, CO_2 and H_2O are photolyzed in the troposphere according to the reactions

$$CO_2 + h\nu \rightarrow CO + O \quad \text{(J1)}$$

$$H_2O + h\nu \rightarrow H + OH \quad \text{(J2)}$$

Hydrogen atoms, formed in reaction J2 react with CO to yield formyl radicals (HCO) by

$$H + CO + M \rightarrow HCO + M \quad \text{(R7)}$$

The HCO radicals are removed by the following paths (*11*)

$$HCO + H \rightarrow H_2 + CO \quad \text{(R8)}$$

$$HCO + h\nu \rightarrow H + CO \quad \text{(J3)}$$

$$HCO + HCO \rightarrow H_2CO + CO \quad \text{(R9)}$$

The production of H_2CO from CO_2 is described by the following reaction sequence

$$2(CO_2 + h\nu \rightarrow CO + O) \quad \text{(J1)}$$

$$2(H_2O + h\nu \rightarrow H + OH) \quad \text{(J2)}$$

$$2(H + CO + M \rightarrow HCO + M) \quad \text{(R7)}$$

$$HCO + HCO \rightarrow H_2CO + CO \quad \text{(R9)}$$

$$CO + OH \rightarrow CO_2 + H \quad \text{(R5)}$$

$$2(O + H_2 \rightarrow OH + H) \quad \text{(R2)}$$

$$3(OH + H_2 \rightarrow H_2O + H) \quad \text{(R1)}$$

$$3(H + H + M \rightarrow H_2 + M) \quad \text{(R6)}$$

which may be summarized as

$$CO_2 + 2H_2 \rightarrow H_2CO + H_2O$$

In our standard photochemical model, the abundances of the major atmospheric gases are as follows: N_2, 0.8 bar; H_2O, 0.012 bar; CO_2, 2.4×10^{-4} bar; CO, 2.4×10^{-7} bar; and H_2, 8.0×10^{-4} bar (*12*). Vertical profiles of important minor

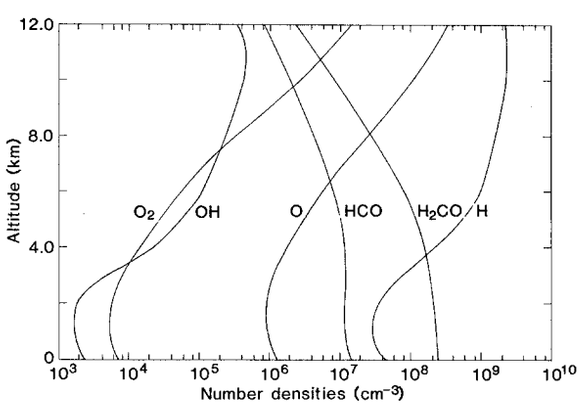

Fig. 1. Concentrations of important minor species in the standard model. The surface mixing ratios of N_2, H_2O, CO_2, CO, and H_2 are 1, 1.5×10^{-2}, 3×10^{-4}, 3×10^{-7}, and 1×10^{-3}, respectively. Except for H_2O, these gases are well mixed throughout the troposphere. The height-independent eddy diffusion coefficient is 10^6 cm^2 sec^{-1}.

0036-8075/80/1010-0183$00.50/0 Copyright © 1980 AAAS

constituents are shown in Fig. 1. Production and loss rates of HCO radicals and H_2CO are given in Fig. 2. Most of the H_2CO ($\approx$ 99 percent) is destroyed by photolysis (reactions J4 and J5). However, a small fraction is incorporated into rain droplets and delivered to the oceans. We calculated the rate of removal of H_2CO from the atmosphere by precipitation, using the scavenging coefficients of Wofsy (*13*) for H_2CO in the present atmosphere. For the standard model the rainout rate of H_2CO was 2.8×10^8 molecule cm^{-2} sec^{-1}. A variety of models were also constructed to study the sensitivity of our results to the choice of the essential input parameters (*14*).

The atmospheric abundance of CO_2 was controlled by a number of processes, including volcanic release, the weathering of surface rocks, and dissolution in the oceans. It is most likely (*15*) that the partial pressure of CO_2 in the primitive atmosphere was buffered at about 2×10^{-4} bar by the latter two processes. However, recent work (*16*) suggests a possibly higher concentration of CO_2 in the primitive atmosphere. In this case, the production and subsequent rainout rate of H_2CO could greatly exceed that calculated in our standard model (*14*). Our results are also somewhat sensitive to the thermal structure. Knauth and Epstein (*17*) have suggested that surface temperatures could have reached 340 K during the early Archean (3.7×10^9 years ago). In this calculation, the distribution of relative humidity was held fixed at 50 percent (*14*).

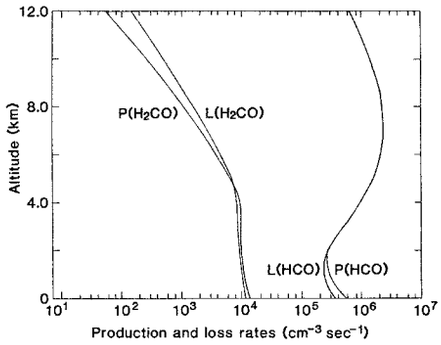

Fig. 2. Production (*P*) and loss (*L*) rates of HCO and H_2CO in the standard model.

For the case of an H_2 mixing ratio of 10^{-3}, the concentration of O_2 is exceedingly small. The tropospheric profile of O_2 is governed, in this case, by photochemical equilibrium. Later evolutionary stages may be represented by the models, in which the H_2 abundance has decreased. In addition, the emergence of O_2, perhaps because of photosynthesis (*18*), would have curtailed the production of H_2CO. This would have occurred through reactions such as

$$O + HCO \rightarrow OH + CO \qquad (R12)$$

$$O_2 + HCO \rightarrow HO_2 + CO \qquad (R13)$$

The value given for the wet removal of H_2CO, in the standard model, is sufficient to fill the oceans, at their present volume, to a $10^{-3}M$ solution in 10×10^6 years. At this concentration, H_2CO in solution may polymerize (*19*). The results of Ponnamperuma (*20*) indicate that, in the presence of ultraviolet radiation of wavelengths near 2800 Å, polymerization may take place in a $3 \times 10^{-4}M$ solution of H_2CO. Other processes may also have occurred (*4*). However, this does not alter the conclusion that simple organic molecules could have been delivered to the oceans from photochemical reactions in the atmosphere under weakly reducing conditions. Further laboratory studies should be performed to assess the factors governing the production and stability of H_2CO in conditions appropriate to the primitive Earth.

Table 1. Reactions and rate coefficients used in the photochemical model. Units for two- and three-body rate constants are cubic centimeters per second and centimeters raised to the sixth power per second, respectively. Globally averaged photodissociation rate constants (per second) are given for 0 and 12 km, respectively. Numbers are values used in the standard model; T, absolute temperature; P_{atm}, atmospheric pressure.

Reaction	Rate constant		Source in (*10*)
	0 km	12 km	
J1 $CO_2 + h\nu \rightarrow CO + O$	2.3×10^{-12}	3.5×10^{-11}	a
J2 $H_2O + h\nu \rightarrow H + OH$	9.3×10^{-15}	1.4×10^{-9}	a
J3 $HCO + h\nu \rightarrow H + CO$	1.0×10^{-2}	1.0×10^{-2}	b
J4 $H_2CO + h\nu \rightarrow H + HCO$	1.8×10^{-5}	1.8×10^{-5}	c
J5 $H_2CO + h\nu \rightarrow H_2 + CO$	2.5×10^{-5}	2.5×10^{-5}	c
J6 $H_2O_2 + h\nu \rightarrow OH + OH$	5.5×10^{-5}	5.7×10^{-5}	a
J7 $O_2 + h\nu \rightarrow O + O$	4.1×10^{-10}	4.7×10^{-10}	a
J8 $O_3 + h\nu \rightarrow O_2 + O$	2.3×10^{-4}	2.3×10^{-4}	a
R1 $H_2 + OH \rightarrow H_2O + H$	$1.2 \times 10^{-11} \exp(-2200/T)$		d
R2 $H_2 + O \rightarrow H + OH$	$7.0 \times 10^{-11} \exp(-5000/T)$		e
R3 $O + OH \rightarrow O_2 + H$	1.7×10^{-11}		f
R4 $OH + OH \rightarrow H_2O + O$	$1.0 \times 10^{-11} \exp(-500/T)$		d
R5 $CO + OH \rightarrow CO_2 + H$	$1.3 \times 10^{-13} (1 + P_{atm})$		d
R6 $H + H + M \rightarrow H_2 + M$	$2.6 \times 10^{-33} \exp(375/T)$		g
R7 $H + CO + M \rightarrow HCO + M$	$2.0 \times 10^{-33} \exp(-850/T)$		h
R8 $H + HCO \rightarrow H_2 + CO$	3.0×10^{-10}		i
R9 $HCO + HCO \rightarrow H_2CO + CO$	6.3×10^{-11}		i
R10 $OH + HCO \rightarrow H_2O + CO$	5.0×10^{-11}		h
R11 $O + HCO \rightarrow H + CO_2$	1.0×10^{-10}		j
R12 $O + HCO \rightarrow OH + CO$	1.0×10^{-10}		j
R13 $O_2 + HCO \rightarrow HO_2 + CO$	5.0×10^{-12}		d
R14 $HO_2 + HCO \rightarrow H_2O_2 + CO$	1.0×10^{-11}		k
R15 $H + H_2CO \rightarrow H_2 + HCO$	$2.8 \times 10^{-11} \exp(-1540/T)$		d
R16 $OH + H_2CO \rightarrow H_2O + HCO$	$1.7 \times 10^{-11} \exp(-100/T)$		d
R17 $O + O + M \rightarrow O_2 + M$	$9.6 \times 10^{-34} \exp(480/T)$		e
R18 $O + O_2 + M \rightarrow O_3 + M$	$9.9 \times 10^{-29} T^{-2.1}$		d
R19 $O + O_3 \rightarrow O_2 + O_2$	$1.5 \times 10^{-11} \exp(-2218/T)$		d
R20 $H + O_2 + M \rightarrow HO_2 + M$	$1.6 \times 10^{-28} T^{-1.4}$		d
R21 $O + HO_2 \rightarrow OH + O_2$	3.5×10^{-11}		d
R22 $H + HO_2 \rightarrow H_2 + O_2$	1.4×10^{-11}		ℓ
R23 $H + HO_2 \rightarrow OH + OH$	3.2×10^{-11}		ℓ
R24 $H + HO_2 \rightarrow H_2O + O$	9.4×10^{-13}		ℓ
R25 $OH + HO_2 \rightarrow H_2O + O_2$	4.0×10^{-11}		d
R26 $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2.5×10^{-12}		d
R27 $H_2O_2 + O \rightarrow OH + HO_2$	$2.8 \times 10^{-12} \exp(-2125/T)$		d
R28 $H_2O_2 + OH \rightarrow H_2O + HO_2$	$1.0 \times 10^{-11} \exp(-750/T)$		d
R29 $H + O_3 \rightarrow OH + O_2$	$1.4 \times 10^{-10} \exp(-470/T)$		d
R30 $OH + O_3 \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-940/T)$		d
R31 $HO_2 + O_3 \rightarrow OH + 2O_2$	$1.1 \times 10^{-14} \exp(-580/T)$		d

JOSEPH P. PINTO
Goddard Institute for Space Studies, New York 10025
G. RANDALL GLADSTONE
YUK LING YUNG
California Institute of Technology, Pasadena 91125

References and Notes

1. S. C. Wofsy, J. C. McConnell, M. B. McElroy, *J. Geophys. Res.* **77**, 447 (1972).
2. J. E. Lovelock and L. Margulis, *Tellus* **26**, 2 (1974).
3. S. L. Miller and H. C. Urey, *Science* **130**, 245 (1959).
4. J. S. Hubbard, J. P. Hardy, N. H. Horowitz, *Proc. Natl. Acad. Sci. U.S.A.* **68**, 574 (1971); P. H. Abelson, *ibid.* **54**, 1490 (1965).
5. F. P. Fanale, *Chem. Geol.* **8**, 279 (1971).
6. J. C. G. Walker, *Evolution of the Atmosphere* (Macmillan, New York, 1977).
7. M. B. McElroy, T. Y. Kong, Y. L. Yung, *J. Geophys. Res.* **82**, 4379 (1977).
8. H. D. Holland, in *Petrologic Studies—A Volume in Honor of A. G. Buddington*, A. E. J.

Engle, H. L. James, B. F. Leonard, Eds. (Geological Society of America, Boulder, Colo., 1962), p. 447. However, according to the preliminary results of J. S. Lewis (personal communication), the composition of degassed volatiles could have been the following: H_2O, 20 percent; CO_2, 50 percent; CO, 20 percent; and H_2, 10 percent by volume. This composition is much more reducing than that used in the calculation.
9. M. B. McElroy, *Chemical Processes in the Solar System: A Kinetic Perspective* (Butterworths, London, 1975); Y. L. Yung and M. B. McElroy, *Science* **203**, 1002 (1979). Analyses of the ratio of deuterium to hydrogen by Y. L. Yung and M. B. McElroy [*Bull. Am. Astron. Soc.* **9**, 497 (1977)] and H. Craig and J. E. Lupton [*Earth Planet Sci. Lett.* **31**, 369 (1976)] indicate that large quantitites of H_2 could have escaped from Earth's atmosphere in the past. These results are consistent with an H_2 mixing ratio of $\sim 10^{-3}$ in the primitive atmosphere. The production and subsequent removal of H_2CO represents an additional loss of H_2. However, it is unlikely that such a calculation would yield results outside our current range of estimates for the H_2 mixing ratio.
10. Sources of rate coefficient data are as follows: (a) See Yung and McElroy (*9*). (b) Estimated. A a mean cross section of 3×10^{-19} cm^2 was derived for the visible band from the theoretical study of P. J. Bruna, R. J. Buenker, S. D. Peyerimhoff [*J. Mol. Struct.* **32**, 217 (1976)]. A. A. Borisov, V. T. Galochkin, S. A. Mulenko, A. N. Oraevskii, E. F. Starodubtsev, A. F. Suchkov [*Sov. J. Quantum Electron.* **8**, 1094 (1978)] have estimated mean cross section of 1×10^{-20} cm^2 for the same band. The values of Bruna *et al.* have been used here. (c) J. G. Calvert, J. A. Kerr, K. L. Demerjian, R. D. McQuigg, *Science* **175**, 751 (1972). (d) W. B. DeMore, *Jet Propulsion Lab. Publ. 79-27* (1979). (e) J. A. Logan, M. J. Prather, S. C. Wofsy, *Philos. Trans. R. Soc. London* **290**, 187 (1978). (f) R. T. Watson, personal communication. (g) S. C. Liu and T. M. Donahue, *J. Atmos. Sci.* **31**, 1118 (1974). (h) D. L. Baulch, D. D. Drysdale, J. Duxbury, S. J. Grant, *Evaluated Kinetic Data for High Temperature Reactions* (Butterworths, London, 1976), vol. 3. (i) J. P. Reilly, J. H. Clarke, C. B. Moore, G. C. Pimentel, *J. Chem. Phys.* **69**, 4381 (1978). (j) R. F. Hampson and D. Garvin, Eds., *Reaction Rate and Photochemical Data for Atmospheric Chemistry 1977* (Special Publication 513, National Bureau of Standards, Washington, D.C., 1978). (k) Estimated. (l) W. Hack, H. G. Wagner, K. Hoyermann, *Ber. Bunsenges. Phys. Chem.* **82**, 713 (1978); W. Hack, A. W. Preuss, H. G. Wagner, K. Hoyermann, *ibid.* **83**, 212 (1979).
11. Note that R7 and R8 constitute an effective cycle for the catalytic recombination of atomic hydrogen. This cycle also accounts for the difference in the computed atomic hydrogen densities at low altitudes between this model and that of J. F. Kasting, S. C. Liu, T. M. Donahue, *J. Geophys. Res.* **84**, 3097 (1979).
12. The one-dimensional model extends from 0 to 120 km with a vertical resolution of 2 km, based on the numerical scheme developed by M. Allen, Y. L. Yung, and J. W. Waters (in preparation). The equations of continuity are solved for all species. Vertical transport of long-lived species is described in terms of eddy diffusion. For the standard model, a uniform value of the eddy diffusion coefficient (K) of 10^6 cm^2 sec^{-1} was chosen. Concentrations of the major species H_2O, CO_2, and H_2 were fixed at the lower boundary, and a zero flux was specified for CO. Concentrations of radical species were determined on the basis of their photochemical production and loss rates. A flux of reduced material of $\sim 10^{10}$ cm^{-2} sec^{-1} (mostly as H_2) is required at the lower boundary, in order to maintain the steady state.
13. S. C. Wofsy, *Annu. Rev. Earth Planet. Sci.* **4**, 441 (1976).
14. For H_2 mixing ratios of 10^{-4}, 3×10^{-4}, and 3×10^{-3}, the H_2CO rainout rate is 1.7×10^7, 4.4×10^7, and 1.0×10^9 molecule cm^{-2} sec^{-1}, respectively. For CO_2 mixing ratios of 6×10^{-4}, 1.2×10^{-3}, and 3×10^{-3}, the rainout rate is 4.8×10^8, 1.2×10^9, and 3.1×10^9 cm^{-2} sec^{-1}. Adjusting the value of k_8 to 1×10^{-10}, 2×10^{-10}, and 5×10^{-10} leads to rainout rates of 1.9×10^9, 4.5×10^8, and 1.4×10^8 cm^{-2} sec^{-1}. Adopting a uniform value for K of 10^5 cm^2 sec^{-1} leads to a rainout rate of 2.3×10^8 cm^{-2} sec^{-1}, and raising the surface temperature by 10 percent to 317 K leads to a rainout rate of 8.8×10^7 cm^{-2} sec^{-1}.
15. F. P. Fanale, personal communication.
16. T. Owen, R. D. Cess, V. Ramanathan, *Nature (London)* **277**, 640 (1979).
17. L. Knauth and S. Epstein, *Geochim. Cosmochim. Acta* **40**, 1095 (1976).
18. L. V. Berkner and L. C. Marshall, *J. Atmos. Sci.* **22**, 225 (1965).
19. Perhaps the most important question concerning the fate of H_2CO, once it had been precipitated into the primitive oceans, is its interaction with solar ultraviolet radiation. Preliminary results of G. L. Kok (private communication) indicate that H_2CO in solution does not exhibit the same absorption spectrum as gaseous H_2CO. Photolysis for H_2CO in solution is therefore unlikely, as it undergoes a rapid and almost complete hydrolysis to methylene glycol, $CH_2(OH)_2$, and to other products by processes such as the Cannizzaro reaction [J. F. Walker, *Formaldehyde* (Reinhold, New York, 1964)]. These data imply a certain degree of stability for H_2CO in solution. This question should be investigated further with attention being paid to factors such as pH, the oxidation-reduction state, and the presence of other ultraviolet absorbers in the primitive oceans.
20. C. Ponnamperuma, in *Origin of Prebiological Systems and of Their Molecular Matrices*, S. W. Fox, Ed. (Academic Press, New York, 1965), p. 221.
21. One of us (J.P.P.) thanks J. C. G. Walker for many helpful discussions. We also thank M. Allen, F. P. Fanale, G. L. Kok, C. B. Moore, J. S. Lewis, and J. J. Morgan for their useful comments. J.P.P. is a NASA National Research Council resident research associate. This work was also supported in part by NASA contract NSG-7376 under the Planetary Atmospheres Program. Contribution 3357 of the Division of Geological and Planetary Sciences, California Institute of Technology.

7 February 1980; revised 17 June 1980

Ganymede: A Relationship Between Thermal History and Crater Statistics

Abstract. *An approach for factoring the effects of a planetary thermal history into a predicted set of crater statistics for an icy satellite is developed and forms the basis for subsequent data inversion studies. The key parameter is a thermal evolution-dependent critical time for which craters of a particular size forming earlier do not contribute to present-day statistics. An example is given for the satellite Ganymede and the effect of the thermal history is easily seen in the resulting predicted crater statistics. A preliminary comparison with the data, subject to the uncertainties in ice rheology and impact flux history, suggests a surface age of 3.8 × 10⁹ years and a radionuclide abundance of 0.3 times the chondritic value.*

Geomorphic evolution of impact craters on planetary surfaces, created over a wide range of geologic time and a wide spectrum of sizes, provides insight into the temporal behavior of endogenic modification processes. This report presents a simple architecture for generating a set of predicted cumulative impact crater curves reflecting endogenic modification processes on Ganymede. The study was motivated by Voyager spacecraft observations of a relative deficiency of large impact craters (Fig. 1).

A thermal history model is specified and related directly to the viscosity history, the functional forms being fairly well known in terms of flow laws for geologic materials (*1*). The mechanism of crater modification is viscous relaxation, dependent on crater size and the explicit behavior of viscosity with depth. A crater of size D on the surface of Ganymede will have a limited lifetime that depends explicitly on the time of crater formation. This initial model adopts a practical definition of lifetime in terms of a detectability limit based on a critical crater depth, $d_c(D)$. Craters shallower than $d_c(D)$ are not detectable; the specific value of this parameter is an empirical measure from any photograph and is based on resolution, lighting angle, and albedo variation. The lifetime of a crater, $L(t,D)$, is the time differential between creation at time t and the moment when crater depth is less than $d_c(D)$. A critical time $T_0(D)$ is that point in geologic history when $L(t,D)$ extends exactly to the present (*2*).

The predicted cumulative crater statistic, $\hat{\Sigma}(D,t)$, is written as the integral over a differential functional $N(D,t^*)$ such that

$$\hat{\Sigma}(D,t) \equiv \int_D^\infty N(D',t^*)\, dD' \qquad (1)$$

and is the number of craters of size $\geq D$ that exist on a surface formed at time t; the variable t^* is $\max[t,T_0(D)]$. The interpretation of t^* in $N(D,t^*)$ is clear if we envision a surface, formed at time t, that collects craters to the present. We count those craters in the present epoch, but it is clear that by definition if $t < T_0(D)$, craters of size D on the surface formed at t will not last to the present and be counted today. Conversely, if $t > T_0(D)$, craters of size D will persist and be counted.

For a thermal history we assume a scenario starting 4.6×10^9 years ago with a silicate core containing a chronditic complement of radiogenic heat sources, a liquid water mantle, and a surface temperature, T_0, of 100 K. At all times in the history of Ganymede, the Rayleigh number for the mantle is supercritical and convection is the dominant mode of heat transport. The freezing time of the liquid water mantle has been described (*3*). Us-

0036-8075/80/1010-0185$00.50/0 Copyright © 1980 AAAS