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Cometary Delivery of Organic Molecules to the Early Earth

CHRISTOPHER F. CHYBA, PAUL J. THOMAS,* LEIGH BROOKSHAW,† CARL SAGAN

It has long been speculated that Earth accreted prebiotic organic molecules important for the origins of life from impacts of carbonaceous asteroids and comets during the period of heavy bombardment 4.5×10^9 to 3.8×10^9 years ago. A comprehensive treatment of comet-asteroid interaction with the atmosphere, surface impact, and resulting organic pyrolysis demonstrates that organics will not survive impacts at velocities greater than about 10 kilometers per second and that even comets and asteroids as small as 100 meters in radius cannot be aerobraked to below this velocity in 1-bar atmospheres. However, for plausible dense (10-bar carbon dioxide) early atmospheres, we find that 4.5×10^9 years ago Earth was accreting intact cometary organics at a rate of at least $\sim 10^6$ to 10^7 kilograms per year, a flux that thereafter declined with a half-life of $\sim 10^8$ years. These results may be put in context by comparison with terrestrial oceanic and total biomasses, $\sim 3 \times 10^{12}$ kilograms and $\sim 6 \times 10^{14}$ kilograms, respectively.

A SIGNIFICANT FRACTION OF EARTH'S VOLATILE INVENTORY may have been acquired as a late-accreting veneer from impacts of C-type asteroids (1) and comets (2, 3) during the period of heavy bombardment of the inner solar system 4.5×10^9 to 3.8×10^9 years ago. In addition to simple volatile molecules such as H_2O and short-chain hydrocarbons, C-type asteroids and comets are also rich in complex organics. In the case of asteroids, this is known from direct analysis of carbonaceous chondrite meteorites (4, 5), which are spectroscopically similar to C-type asteroids (6), their presumptive parent bodies. As long ago as 1908, this organic component in carbonaceous meteorites led Chamberlin and Chamberlin (7) to suggest that infalling "planetesimals" may have been an important source of prebiotic organic material on early Earth. In 1961, Oró (8) suggested, on the basis of spectroscopic observations of carbon- and nitrogen-containing radicals in cometary comae, that comets may have played a similar role. Since then, the possible relevance of cometary organics to the terrestrial origins of life has received considerable attention (9–11).

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Over the last decade, this potential cometary source of prebiotic organics has taken on new importance, as an emerging consensus in planetary science has replaced earlier models of a primordial reducing terrestrial atmosphere rich in methane (CH_4) and ammonia (NH_3) with that of a neutral one rich in carbon dioxide (CO_2) and molecular nitrogen (N_2). Such early CO_2 -rich atmospheres are implied by "hot" accretion scenarios for Earth, in which core formation takes place quickly, leaving the upper mantle (and hence, outgassed carbon) in an oxidized state (10, 12). The short photodissociation lifetimes of CH_4 and NH_3 in model paleoatmospheres reinforce this conclusion (13). If subduction-resistant continental platforms were largely or entirely absent on Earth before 3.8×10^9 years ago, the ~ 60 bars of CO_2 currently sequestered in continental platforms would have led to a dense, 10- to 20-bar CO_2 early terrestrial atmosphere (14), a conclusion that is consistent with solutions to the early faint sun "paradox," and with arguments based on comparative inner solar system planetology (15). Early Earth atmospheres with CO_2 pressures as high as 100 bars appear to be stable against a runaway greenhouse effect and are therefore consistent with oceans of liquid water (16).

Syntheses of key prebiotic molecules [such as hydrogen cyanide (HCN) and formaldehyde (H_2CO), precursors to purines, pyrimidines, and amino acids, and to sugars, respectively] would have been much more difficult in CO_2 atmospheres than in reducing ones (10). Experiments with CO_2 gas mixtures demonstrate that, relative to atmospheres rich in CH_4 or carbon monoxide (CO), yields of HCN and H_2CO , as well as amino acids themselves, drop precipitously by many orders of magnitude as the H_2/CO_2 ratio falls below unity (17). However, although these results are suggestive, there is certainly at present no requirement to invoke impactor-delivered organics to account for the evolution of life on Earth. Many other speculative mechanisms for terrestrial prebiotic synthesis have been proposed, including production of HCN by photolysis of N_2 and CH_4 in a hypothesized weakly reducing atmosphere (18), reduction of CO_2 to CO by impactor-delivered iron (19), volcanic production of H_2 by H_2O decomposition, or reduction of CO_2 in solution or in the presence of clays [see (10) for a review]. The goal of investigators at present must be to quantify as well as possible prebiotic organic production from the various proposed sources, so that their comparative importance may be weighed. Our purpose here is to extend this compilation to the case of cometary delivery of organics.

Pyrolysis of Cometary Organics by Impact

A long-standing objection to cometary delivery of intact organic molecules to Earth is that these compounds would be totally dissociated by the heat of cometary atmospheric passage and the ensuing impact. This has led Clark to suggest "an improbable,

the origin of life (11, p. 209). Although such unlikely events cannot be ruled out, they are also extremely difficult to quantify. However, a closer examination reveals that the claim that cometary organics will be pyrolyzed at impact is uncertain. Consider a comet colliding with Earth at a velocity of 18 km s^{-1} . [Some $\sim 25\%$ of short-period (SP) comet-Earth collisions should occur at or below this velocity (3).] If we assume that upon impact all of the comet's kinetic energy goes into heating the comet, treat the comet as composed of water ice, and choose a specific heat of water appropriate to the resulting high temperatures and pressures [$\sim 4 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (20)], we find the comet to be shocked to an average temperature of $\sim 40,000 \text{ K}$. This temperature is certainly too high to permit any organics to survive. However, it is too high by only a factor of 20 to 40. Because much of the kinetic energy of a comet with a density of 1 g cm^{-3} will be partitioned not into heating the impactor but into kinetic energy of ejecta and target heating (21), it is possible that aerobraking (slowing by atmospheric drag) and uneven distribution of shock energy throughout the impacting projectile will conspire to yield some region of the comet for which temperatures remain low enough to allow at least the hardier organics to survive. This possibility can only be quantified by detailed numerical modeling of cometary atmospheric passage and surface collision. But before pursuing such models, we must first review what is known about the abundance and volatility of cometary organics.

Cometary Organics: Results from the Halley Apparition

Laboratory analysis of CI and CII carbonaceous chondrite meteorites reveals them to be 3 to 5% by mass organic heteropolymer (4). In situ mass spectroscopy in the coma of comet Halley by the Giotto and Vega spacecraft revealed Halley dust to be fully one-third organic by mass (22). The volatile (gas) fraction of the comet appears to be $\sim 14\%$ by mass organic (23); assigning a standard gas/dust mass ratio of 1:1 gives an overall cometary organic component of $\sim 25\%$ by mass. This may seem extraordinary, but it should be remembered that Halley has approximately cosmic abundances of carbon and nitrogen—elemental abundances higher by more than an order of magnitude than those of CI chondrites (23, 24). Spectroscopic observations of comet Halley suggest that the production rate of H_2CO is about 2% by mass that of H_2O (25). In situ ion mass spectrometry for comet Halley (26) and spectroscopy of comet Wilson (27) suggest that CH_4 is present at 1 to 4% H_2O by mass. We therefore take H_2CO and CH_4 to account for 4 and 5% by mass of cometary organics, respectively. Perhaps $\sim 7\%$ by mass is HCN (23). Such estimates should be treated as rough at best.

Approximately 3% of the organic carbon in carbonaceous chondrites is in the form of amino acids (5). It is not known if comets contain comparable (or indeed any) amounts of such compounds. However, the discovery that amino acids from the Murchison meteorite are as a group highly enriched in deuterium ($\delta\text{D} = 1370\%$) strongly suggests that the amino acids or their precursors were formed at low temperatures in interstellar clouds (5, 28). If amino acids formed in interstellar clouds, they should be at least as abundant in comets as in carbonaceous chondrites. However, this conclusion need not hold if only amino acid precursors are present in interstellar dust. Despite dedicated searches, free amino acids remain undetected in interstellar clouds (29), although amino acids in dust would remain undetectable.

Finally, although we cannot entirely rule out the possibility that cometary organics are biological in origin (30), we believe that there is no persuasive evidence for this claim, and that much more

whether abiotic cometary organics may have played a role in stocking the terrestrial prebiotic inventory. We do not concern ourselves in the following with panspermia theories.

Volatility of Cometary Organics

Most organic material in carbonaceous chondrites is in the form of high molecular weight, "intractable" heteropolymer (4, 5). Laboratory experiments under conditions meant to simulate radiation processing of interstellar dust and cometary ices suggest that cometary organics are similar (32, 33), a result supported by the success of such materials in modeling organic spectral features in a number of comets (34). As a well-investigated analog to such intractable organics, we use terrestrial kerogens, which are both compositionally similar to meteoritic carbonaceous material (4) and provide reasonable spectroscopic fits to certain asteroids and outer solar system objects (35). The optical constants of type II kerogens and an organic extract from the Murchison carbonaceous chondrite are also in good mutual agreement (36). Terrestrial kerogens are biological in origin; our use of them as structural analogs to [presumably abiotic (31)] cometary organics carries no implication of a biological origin for the latter.

Kinetic parameters from pyrolysis experiments with type I and II kerogens indicate that such material can survive temperatures of $\sim 850 \text{ K}$ for 1 s (37). (As described below, in the impacts of relevance to this discussion, 1 s is an overestimate for the duration of the most intense shock heating that cometary organics will endure. Well before this time, shock temperatures will have peaked and begun quickly to decline.) However, about 50% of the resulting kerogen pyrolyzate is composed of *n*-alkanes up to C_{30} , as well as such aromatics as benzene, toluene, and *m,p*-xylene (38). Therefore, to understand the ultimate fate of kerogen-like organics in the impactor, we must examine the fate of their components, for example, short-chain hydrocarbons and simple aromatics (and their oxygen and nitrogen analogs and substitutions). Kinetic parameters derived from shock-tube pyrolysis of such compounds (for example, ethane or benzene) at temperatures of ~ 1000 to 3000 K , the best laboratory analog we have to organic destruction in large impacts, show that these basic organic units will survive at $\sim 1200 \text{ K}$ for 1 s (39, 40).

These temperatures are probably severe underestimates of the thermal stability of at least the hardiest of cometary organics. Thermogravimetric analyses of the involatile organic residue produced by electron, spark, or ultraviolet irradiation of cosmically abundant gases show that the residues are typically 50% stable at temperatures ranging from 600 to 1200 K ; time scales for such analyses are far in excess of 1 s (32). Similar material produced in analogous ice irradiation experiments provides a good match to observed cometary organic emission features (34). Therefore, we expect that there is some (probably polycyclic) component of cometary organics that is much more thermally stable than the compounds being explicitly considered here.

Kinetic parameters from shock-tube experiments with CH_4 show that it survives temperatures of $\sim 1500 \text{ K}$ for 1 s (41). Numerous shock-tube experiments with H_2CO (42) and HCN (43) have been performed; we estimate from these results that these compounds will withstand shock temperatures of ~ 1200 and $\sim 1800 \text{ K}$, respectively (44).

To our knowledge, kinetic parameters for the pyrolysis of amino acids have been measured only in solution. The results of such experiments are of questionable applicability to shock pyrolysis, but, until gas-phase results become available, we approximate impact

temperatures of ~ 700 K for 1 s (45), whereas amino acids should withstand temperatures in the range of 600 to 800 K (46).

Impact Environment of Early Earth

The existence of complex terrestrial microorganisms by 3.5×10^9 years ago and evidence for biologically mediated carbon isotope fractionation in 3.8×10^9 year Isua metasediments (47) suggest choosing the period before 3.8×10^9 years ago to assess cometary delivery of organics. Attempts to estimate the impact environment of early Earth typically begin with an analytical fit to the lunar cratering record. The impactor flux thus derived can then be scaled to Earth's larger gravitational cross section. Following such a procedure for several published lunar cratering data sets and choices of time constant for the decay of the early impactor flux, Chyba (3) found three possible values, spanning the current uncertainties:

$$M(t) = 0.76[t + 4.57 \times 10^{-7} (e^{t/\tau_A} - 1)] (m_2^{1-b} - m_1^{1-b}) \text{ kg}^b \text{ km}^{-2} \quad (1)$$

$$M(t) = 0.99[t + 2.3 \times 10^{-11} (e^{t/\tau_B} - 1)] (m_2^{1-b} - m_1^{1-b}) \text{ kg}^b \text{ km}^{-2} \quad (2)$$

$$M(t) = 0.40[t + 5.6 \times 10^{-23} (e^{t/\tau_C} - 1)] (m_2^{1-b} - m_1^{1-b}) \text{ kg}^b \text{ km}^{-2} \quad (3)$$

for the total mass $M(t)$ that has been incident in impactors with masses in the range m_1 to m_2 on a lunar surface of age t . Here $b \approx 0.47$, t is in 10^9 years, $\tau_A = 220 \times 10^6$, $\tau_B = 144 \times 10^6$, and $\tau_C = 70 \times 10^6$ years. If we perform the appropriate gravitational scaling, Eqs. 1 through 3 yield a total cometary mass incident on Earth since 4.5×10^9 years ago of $M_{\text{tot}} = 1 \times 10^{21}$, 3×10^{21} , or 7×10^{23} α kg, respectively, where α is the fraction of the ancient impacting mass flux that was cometary (3). Nearly all of this mass was collected before 3.8×10^9 years ago, that is, during the period of heavy bombardment, which is also the time of interest for the origins of life.

The parameter α is not well constrained. Estimates of current asteroidal and cometary cratering rates suggest that comets account for 10 to 30% of the recent production of terrestrial impact craters >10 km in diameter, although "extinct" comets or possible comet showers could raise this fraction to over 50% (48). How to extrapolate this result back to the early solar system is not clear, however. Although none of the data pertaining to this question are conclusive, it seems likely that $\alpha \approx 10$ to 20% (2). For definiteness, we set $\alpha = 0.1$ in the following. Our results scale linearly, so the effect of a different choice of α will be evident.

Comets are $\sim 18\%$ carbon by mass (23), so Eqs. 1, 2, and 3 imply that Earth has collected 2×10^{19} , 6×10^{19} , or 1×10^{22} ($\alpha/0.1$) kg of cometary carbon, respectively, which may be compared to the total terrestrial surface (ocean, atmosphere, and sedimentary column) carbon inventory of $\sim 9 \times 10^{19}$ kg (14, 49). Clearly, there is a discrepancy between the terrestrial carbon inventory predicted by Eq. 3 and that actually present on Earth. A similar discrepancy exists for H_2O (3). Impact erosion by sufficiently large and fast-moving comets and asteroids could reduce this discrepancy for carbon (which may have been eroded as atmospheric CO_2) but appears incapable of doing so for condensed volatiles such as H_2O (3). It therefore appears that the volatile flux predicted by Eq. 3 for $\alpha = 0.1$ is too large by a factor of ~ 100 .

Conversely, the mass flux predicted by Eqs. 1 and 2 is probably too small. Sleep *et al.* (50) have used lunar highland iridium and nickel abundances to calculate the total amount of material impact-

$\times 10^7$ years ago. Scaling to Earth yields a value $M_{\text{tot}} = 5 \times 10^{21}$ α kg as a lower limit for the total cometary mass incident on Earth subsequent to 4.5×10^9 years ago (3).

Taking these limits into account and recalling that comets are about 25% organic by mass suggests that $\sim 10^{20}$ kg of cometary organics have impacted Earth over geological time. Clearly, as many investigators have noted, Earth may have acquired a vast quantity of extraterrestrial organics. The key question, however, is what fraction of these organics actually survived atmospheric passage and impact shock heating. We now turn to models of these two processes.

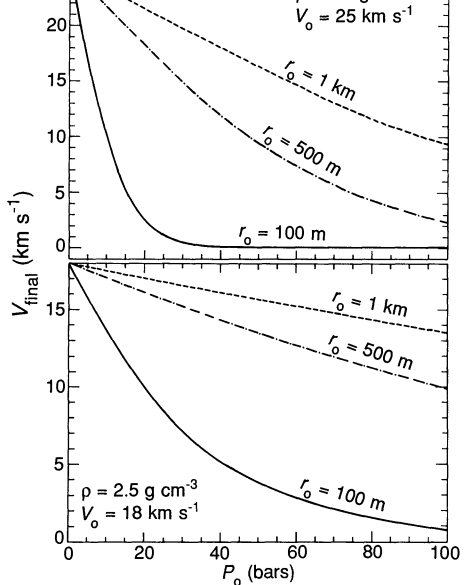
Atmospheric Entry and Ablation

We model atmospheric entry by a finite difference numerical scheme that incorporates aerobraking and ablation. In this model, both atmospheric drag and ablation rate are functions of cross-sectional area, which in turn changes as a result of ablation (51, 52). As a conservative assumption, we treat all organic molecules in ablated material as completely pyrolyzed.

Impactor ablation is determined by the drag coefficient C_D , the heat of ablation ζ , and the heat transfer coefficient C_H . These parameters are functions of impactor shape, composition, mass, and velocity. From aerodynamic theory of hypervelocity impactors in the terrestrial atmosphere, we set $C_H = 0.01$ (21, 53) and $C_D = 0.92$ (21). These values are consistent with typical estimates (52). The exact value of ζ is a function of material type and the specific process of ablation. Passey and Melosh (54) suggested taking ζ for an iron meteorite to be the average of the heats of fusion and vaporization, 5 MJ kg^{-1} . The same procedure, if we use the heats of fusion and vaporization of ordinary chondrites (55), also yields 5 MJ kg^{-1} . Given this chondritic value for ζ , we scale to cometary and carbonaceous chondritic values using observed ablation coefficients $\sigma = C_H/C_D \zeta$ for cometary, carbonaceous chondritic, and ordinary chondritic meteors, taking C_H/C_D to be the same for all three types. [Values of σ for different meteor types have been determined from luminosity observations of some 3000 small meteors of varying compositions, densities, and orbital elements (56).] We find ζ for carbonaceous chondrites and comets to be 3.2 and 1.6 MJ kg^{-1} , respectively. This cometary value is within 25% of the average of the heats of vaporization and fusion of ice (57), a remarkable agreement between observations of cometary meteors and laboratory data. Even models with detailed self-consistent calculations of the above parameters (55) produce values that are nearly constant throughout atmospheric passage.

As initial conditions for atmospheric entry, we need typical cometary impact velocities with Earth. Statistics for SP comet velocities and impact probabilities may be used to calculate the percentage of cometary collisions with Earth that occur at a given velocity (3). Some 25% of SP cometary collisions with Earth occur with velocities at or below 18 km s^{-1} , and another 50% occur with velocities between 18 and 23 km s^{-1} . Because models of the early cometary bombardment of the inner solar system (58) indicate that the flux of comets scattered directly from the Uranus-Neptune region (that is, following SP-like orbits) dominated by several orders of magnitude the flux of those (long-period) comets first scattered out to the Oort cloud, we may use SP velocities as typical for cometary collisions with Earth during the heavy bombardment.

Calculations based on the use of our atmospheric entry model show that, for a cometary impactor (density $\delta = 1 \text{ g cm}^{-3}$, an initial velocity of 23 km s^{-1} , and $\zeta = 1.6 \text{ MJ kg}^{-1}$), even impactors of initial radius $r_0 \approx 100$ m have their speeds reduced $\leq 10\%$ by aerobraking, if we assume an atmospheric density similar to that of



present-day Earth (pressure $P_0 = 1$ bar). Impactors with $\delta = 2.5$ g cm^{-3} , an initial velocity of 18 km s^{-1} , and $\zeta = 3.2$ MJ kg^{-1} [parameters appropriate for chondritic asteroids (3, 6)] are aerobraked less than cometary impactors of the same size, because of their greater density. Large objects, with $r_0 \geq 1$ km, impact Earth's surface with their speeds essentially unchanged.

However, aerobraking in a primordial dense CO_2 terrestrial atmosphere may have been much more effective than in the present one. For a primordial atmosphere with $P_0 = 10$ -bar CO_2 (14–16), with consequent (16) greenhouse-enhanced surface temperature and H_2O abundance (0.6 bar), 0.8-bar N_2 , and resulting scale height (7.3 km), 100-m comets striking the atmosphere at a typical incidence angle of 45° with initial velocities V_0 of 23 or 18 km s^{-1} are aerobraked to final impact speeds of 5.9 km s^{-1} . (For comparison, at an incidence angle of 0° , a comet with $V_0 = 18$ km s^{-1} would be aerobraked under such conditions to a final velocity of 8.1 km s^{-1} .) Asteroidal impactors are not slowed to below ~ 10 km s^{-1} . Mass loss due to ablation is 65 to 83% for cometary impactors and $\leq 25\%$ for chondrites with $r_0 = 100$ m (59). Larger objects will be less ablated, because of their smaller ratio of area to volume. In a primordial atmosphere with $P_0 = 20$ -bar CO_2 , final velocities for 100-m comets at 45° and 23 km s^{-1} are ~ 1 km s^{-1} . Although the results of these self-consistent 10- and 20-bar early atmospheres will be used for all subsequent calculations, we have used a simplified model in Fig. 1 to provide graphic intuition of cometary and chondritic aerobraking in terrestrial atmospheres ranging from 1 to 100 bars, for impactors with radii of 100, 500, and 1000 m.

Throughout the calculations presented here, we have taken the cometary density $\delta \equiv 1.0$ g cm^{-3} . Calculations of the density of comet Halley based on nongravitational forces suggest a large range of possible densities, 0.2 to 1.5 g cm^{-3} (60). How will a different choice for δ affect the above results? In the aerobraking model used here (51, 52), both deceleration and ablation in the atmosphere are, to a good approximation, proportional to $\rho/\delta r$, where ρ is the atmospheric density, and δ and r are the density and radius of the impactor, respectively. Thus, for a given r , the results found above for aerobraking a comet with a density of 1 g cm^{-3} in a 10-bar atmosphere will be approximately the same as those for a comet with a density of 0.5 g cm^{-3} in a 5-bar atmosphere. This approximation is imperfect, as a 5-bar CO_2 atmosphere will not have exactly the same greenhouse temperature or proportional H_2O abundance (and

as a function of surface atmospheric pressure for generic cometary and chondritic impactors at an incidence angle of 0° with radii of 100, 500, or 1000 m. In this illustrative model, the atmosphere is equivalent to the contemporary terrestrial one, with a surface pressure increased to P_0 .

reasonable values for SP comets: Using a cometary radius–absolute magnitude (H_{10}) relation derived from comet Halley, Hughes (61) found that about 6, 45, and 75% of SP comets have radii $r < 0.1$, 0.5, and 1.0 km, respectively. Provided Halley's r - H_{10} relation is roughly representative, SP comets with radii of several hundred meters are not uncommon.

We have not attempted to model the effects of impactor fragmentation due to aerodynamic stresses. At present, our understanding of this process is incomplete, and existing models make many simplifying assumptions (54, 55). Neglecting this process renders our estimates of survivable organic material conservative, as fragmentation greatly increases the effective surface area of an impactor, enhancing aerobraking and reducing impact velocity. This effect, of importance only for impactors with radii ≤ 1 km, will be discussed further below. Catastrophic fragmentation of a comet or comet fragment appears to have occurred in Tunguska, Siberia, in 1908 (62). Fragmentation of a CI carbonaceous chondrite occurred over Revelstoke, Canada, in 1965; photomicrographs of resulting fragments up to 0.5 cm in size showed no heat damage within an exterior layer ≤ 0.7 mm thick (63), suggesting that such airbursts would indeed allow organic inclusions to survive. Fragmentation of “sun-grazing” and “Jupiter-grazing” comets, presumably due to tidal stresses, also suggests that some comets are loosely cohesive [tensile strengths of $\leq 10^3$ to 10^5 dyne cm^{-2} (64)] and subject to fragmentation upon entry into Earth's atmosphere.

Hydrodynamic Simulation of Cometary Impact

Given appropriate post-aerobraking collision speeds with Earth, we then calculate resulting shock temperatures throughout the impactor, via a numerical scheme called the smoothed particle hydrodynamics (SPH) method (65). A hydrodynamic model is acceptable because typical shock pressures ($\sim 10^{12}$ to 10^{13} dyne cm^{-2} or $\sim 10^2$ to 10^3 GPa) are much higher than the material strengths of rock or ice (~ 1 GPa). The advantage of SPH in impact simulations is that motion of material is represented by motion of mass points; this avoids problems with complex or tangled grids, boundaries, or multiple materials. SPH allows us to calculate (via equations for continuity, momentum, and energy, applied at the mass points) the density, pressure, their derivatives, and the internal energy of the material, using known statistical methods based on smoothing kernels (66). As each point has a mass and a smoothed density, it may be viewed as a particle. The calculation is advanced forward in time by calculating pressure forces at each mass point and moving the points accordingly.

The SPH formulation allows one-, two-, or three-dimensional simulations to be done with almost equal facility. For constant resolution, however, the number of mass points increases as the power of the dimension. As a result of computing constraints, the SPH simulations reported here are two-dimensional, with a resolution of 8% of the radius of the comet.

An important problem in modeling shock transitions with particle schemes is particle interpenetration at the shock interface. Simple dimensional arguments show that particle interpenetration will occur when the relative velocity of particles is on the order of the local sound speed. To overcome this difficulty when modeling supersonic flows, we have added an artificial viscosity to the momentum equation. In the continuum limit, the artificial viscosity terms reduce to standard viscous terms in the Navier-Stokes equation. The effect of these terms is to broaden the shock front while reducing postshock oscillations. The magnitude of the viscous coefficients is

reduced to the minimum consistent with ensuring that particle penetration will not exceed the resolution of the calculation (67).

With SPH we are able to calculate the density and internal energy of every particle at each time step. We ignore radiative heat transfer in our calculations, as it has a negligible effect on calculated temperatures ($\approx 0.01\%$). To calculate pressures and particle tem-

peratures, we need an equation of state (EOS) for each material. We use two independent methods to calculate temperature and pressure from density and internal energy, the Tillotson EOS (TEOS) (68) and the Los Alamos Sesame II EOS database (69).

The TEOs is based on a set of analytic equations that can be used over a wide range of pressures, densities, and materials. The parameters incorporated in the analytic equations are fixed for each material by experimental data. TEOs has been widely used (21, 70), although it is incapable of representing material strength (by negative pressures) and does not adequately represent two-phase media (70). The advantages of TEOs are its computational simplicity and its calculation of pressure as a function of density and internal energy, both, in turn, easily calculable in SPH. The major disadvantage of TEOs is that temperature is not explicitly determined. Fortunately, the specific heat of H_2O is known over a wide range of thermodynamic parameters (20). For our purposes, it is adequate to take the specific heat of water to be a constant [$4 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (20)], as we will use TEOs only as a check on results given by the Sesame II database.

The latter is a library of some 100 materials. Pressures and thermal energies for each material are tabulated over a wide range of densities and temperatures; programs are supplied to invert and interpolate from these tables, so that pressure and temperature can be found as a function of density and thermal energy. We have used Sesame II together with our SPH code to trace the evolution of temperature throughout the bodies of comets and asteroids during impact on basalt and ocean surfaces. A wide variety of impact velocities and angles, as well as impactor sizes, has been investigated. Throughout, we have been guided by the conservative requirement that only those collisions that result in some fraction of the impactor remaining heated to a temperature $T \lesssim 1800 \text{ K}$ for $\leq 1 \text{ s}$ are possible contributors to the terrestrial organic inventory. (For projectiles small enough to be sufficiently aerobraked for temperatures to remain below $\sim 2000 \text{ K}$, shock temperatures peak and begin to decline in well under 1 s; in calculating organic survivability, we conservatively treat the peak temperature reached by any given particle to extend for this length of time.) For both chondrites and comets impacting basalt surfaces at all plausible impact speeds for bodies with $r_0 > 100 \text{ m}$, none of the impactor experiences $T < 1800 \text{ K}$. However, comets impacting the ocean surface at velocities of $\leq 10 \text{ km s}^{-1}$ do have some fraction heated to a maximum temperature below this level. [For example, comets with impact speeds of 5.9 km s^{-1} , as found above for aerobraking in a 10-bar CO_2 atmosphere, have 100, 87, and 40% of their mass exposed to temperatures < 1800 , 1200, and 1000 K, respectively (71). Substantial quantities of HCN, CH_4 , H_2CO , and even kerogen-like

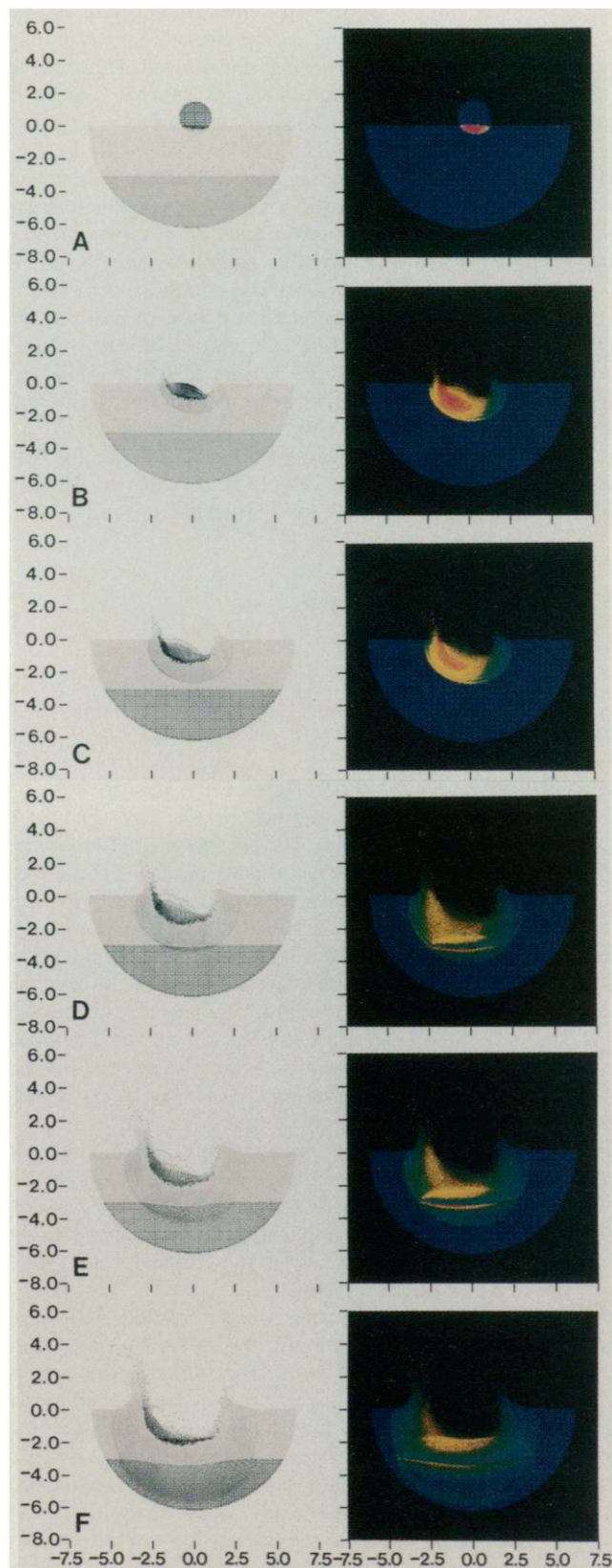


Fig. 2. Step-by-step evolution of an oblique cometary impact at 7.5 km s^{-1} onto an ocean 3 km deep underlain by a basaltic sea floor. To demonstrate the effects of an underlying seabed, we have given the comet a radius of 1 km, although aerobraking would only reduce impact velocity to this extent for a much smaller comet. In the color images, red represents temperatures in the range 1800 to 2300 K, yellow 1300 to 1800 K, green 800 to 1300 K, and blue 300 to 800 K. The accompanying monochrome images identify particles from the comet, ocean, and basaltic sea floor. The images are spaced at intervals of 0.2 s. Note that, despite the oblique impact (A), the shock front is circular (B and C). Distortion of the shock after it reaches the sea floor (D-F) is due to the fact that the density of basalt is greater than that of water. A secondary shock is reflected off the seabed (E and F) but does not heat the comet significantly. The higher temperatures generated as the shock front passes into the sea floor are due to the fact that the specific heat capacity of basalt is less than that of water. The coolest fraction of the cometary material is found in the region surrounding that part of the comet opposite the point of impact and in the ejecta sheet. Our simulations show that this material is ejected from the vicinity of the impact without significant further heating.

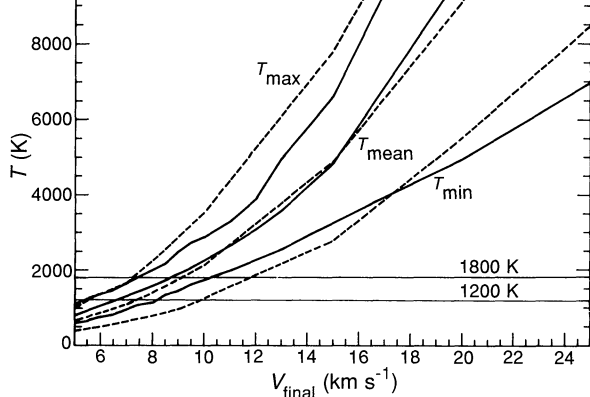


Fig. 3. Maximum, minimum, and mean temperatures for a comet impacting an ocean 3 km deep. The results here are independent of comet radius, provided the ocean is at least several cometary radii deep. The dotted lines denote temperatures obtained from the Tillotson EOS with an assumed constant specific heat capacity for ice. The solid lines represent temperatures from Sesame EOS. The temperatures 1800 and 1200 K are the temperatures for which HCN and simple organics (such as short-chain aliphatics, benzene, and H₂CO), respectively, survive shock heating for time scales comparable with those of impact. For impact velocities ≤ 10 km s⁻¹, a significant fraction of the organic inventory survives impact.

heteropolymers and amino acids would survive this impact intact.] This is so because the greater specific heat and lower density of water result in a smaller fraction of the kinetic energy of the impactor being converted into impactor thermal energy. In these calculations, neither the depth of the ocean nor the absolute size of the impactor is important, provided the ocean is at least several impactor radii deep. These results are essentially independent of impact angle for the cases calculated (up to 45° to the normal). Figure 2 illustrates the step-by-step evolution traced by our code for an ocean-impacting comet. Figure 3 shows the resulting maximum, mean, and minimum temperatures experienced as a function of impact velocity.

Cometary Delivery of Organics to Early Earth

To determine the flux of cometary organics delivered intact to early Earth, we must convolve the incident cometary mass flux, the cometary organic mass fraction, ablative loss during atmospheric passage, and pyrolysis of organics on impact. The relevant incident cometary mass flux is that corresponding to objects 100 to 200 m in size, because our simulations show that, in a 10-bar CO₂ atmosphere, only these will be aerobraked to impact velocities low enough to permit organics to survive.

Equations 1, 2 and 3 will yield the total mass incident on Earth in comets in a given size range since time t . A much more useful quantity is the mass flux (in kilograms per year) at a particular time in Earth's past, which both facilitates comparison with photochemical or other production rates of prebiotic organics (10, 72–74) and allows us to state our conclusions contingent on particular models for early terrestrial atmospheric evolution and the origin of life, for example, “if the time of interest for stocking the prebiotic inventory was 4.2×10^9 years ago and if the atmospheric density at that time was 10 bars, then the flux of intact cometary organics was \dot{m}_{org} kilograms per year.” [For example, it may be that delivery of organic molecules before some time t was useless to the origins of life, because of subsequent surface pyrolysis of organics by giant impacts (50).] In order to present our results in this form, we find

to Earth. We calculate ablation, aerobraking, and subsequent shock-heating and pyrolysis over mass bins for m_1 and m_2 corresponding to comets with radii from r_1 and r_2 , taking radial bin sizes of 50 m.

Equations 4 through 6 then give $\dot{m}_{\text{org}}(t)$, the rate of organic accretion by Earth, as a function of time:

$$\dot{m}_{\text{org}}(t) = 420 (1 + 2.1 \times 10^{-6} e^{t/\tau_A}) (\alpha/0.1) \text{ kg year}^{-1} \quad (4)$$

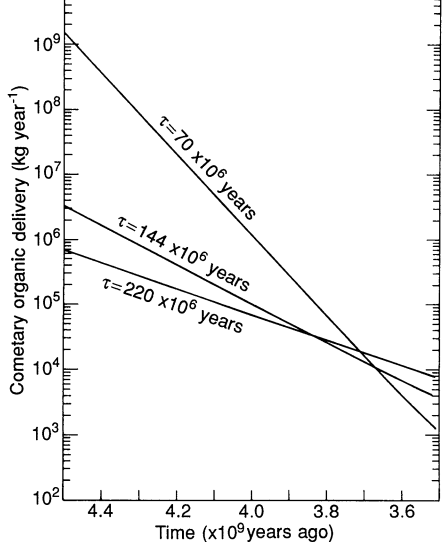
$$\dot{m}_{\text{org}}(t) = 540 (1 + 1.6 \times 10^{-10} e^{t/\tau_B}) (\alpha/0.1) \text{ kg year}^{-1} \quad (5)$$

$$\dot{m}_{\text{org}}(t) = 220 (1 + 8.0 \times 10^{-22} e^{t/\tau_C}) (\alpha/0.1) \text{ kg year}^{-1} \quad (6)$$

These equations require a choice of α only for objects with radii ~ 100 m; because larger objects do not contribute to $\dot{m}_{\text{org}}(t)$, the cometary percentage of these impactors is irrelevant to our results. Equations 4 through 6 imply that, in a 10-bar CO₂ atmosphere 4.5×10^9 years ago, Earth was accreting organics at the rate of 7×10^5 , 3×10^6 , and 1×10^9 kg year⁻¹, respectively. (The 25% lowest velocity comets account for $\geq 50\%$ of these.) This flux thereafter declined with time constants τ_A , τ_B , or τ_C (Fig. 4). Using the empirical constraints on the impact record described above, we find that the most likely range of organic accretion is $\sim 10^6$ to 10^7 kg year⁻¹. (Or course, both ultraviolet photolysis of organics settling and raining out of the atmosphere and thermal and cosmic-ray decomposition of those accumulating on the surface would lower this total.) Intact heteropolymer and its pyrolyzates each represented $\sim 40\%$, and HCN, CH₄, and H₂CO represent about 9, 6, and 4%, respectively, of this surviving organic mass fraction. Amino acids, if present at carbonaceous chondrite abundances, were $\sim 1\%$ of the total. (There is a kind of impact selection of the thermodynamically most stable species, but significant amounts of comparatively labile organics also survive impact.) For a 20-bar atmosphere 4.5×10^9 years ago, Earth would have accreted only several times as many cometary organics, although these would have experienced considerably less shock heating. These results may be put in context by comparison with terrestrial oceanic and total biomasses, $\sim 3 \times 10^{12}$ kg and $\sim 6 \times 10^{14}$ kg, respectively (49).

We have not treated the possibility of the delivery of intact organics by efficient fragmentation or airburst. We estimate the magnitude of this effect in the following way. A bolide will undergo airburst when the differential pressure between its leading and trailing hemispheres exceeds its tensile strength. But for comets with radii $r_0 \geq 1$ km, an atmospherically induced pressure wave would not have time to traverse the comet before terrestrial impact, so that only impactors with $r_0 \leq 1$ km may undergo airburst (75). From Eqs. 1 through 3, the incident mass ratio between comets in the ranges 200 to 1000 m and 50 to 200 m is about 13. If all comets in the range 200 to 1000 m were to undergo airburst and if all their organics were to reach the surface intact, then our previous estimates of terrestrial organic accretion would be too low by a factor of ~ 50 (76).

Zhao and Bada (77) have recently identified large quantities of apparently extraterrestrial nonprotein amino acids, α -aminoisobutyric acid (AIB) and racemic isovaline, in Cretaceous-Tertiary (K/T) boundary sediments. Because iridium abundances require the K/T bolide (assuming a single object was responsible) to have been ~ 10 km in radius, according to our results amino acids (or any other organics) could not have survived the resulting impact in a presumptive 1-bar atmosphere 65×10^6 years ago. As just argued, neither would a 10-km-diameter bolide have undergone airburst, so it appears that the claimed extraterrestrial amino acids cannot be the result of intact delivery by a comet or asteroid. It has been suggested that dust evolved from a large comet trapped in the inner solar system may have provided the source (78). Alternatively, the K/T amino acids may be the result of post-impact quench synthesis. Barak and Bar-Nun (73) have found efficient production of AIB (at



ery of organics to Earth as a function of time (from Eqs. 4 through 6), for a 10-bar CO₂ atmosphere and a typical cometary density δ of $\sim 1 \text{ g cm}^{-3}$. If comets instead have a density of $\sim 0.5 \text{ g cm}^{-3}$, the results shown would correspond approximately to 5-bar CO₂ atmospheres.

levels $\sim 10\%$ that of glycine and alanine) in shock tube experiments with initial mixtures of 10% ethane (C₂H₆) + 10% NH₃ in argon + air + H₂O. Production efficiency seems to be unaffected by the background air, at least up to O₂/C₂H₆ ratios of 2.5. Therefore, the quench synthesis explanation for K/T amino acids is not yet ruled out.

Anders (79) recently suggested that interplanetary dust may have been an important source of prebiotic organics for early Earth. He calculates the current infall rate of organic carbon in interplanetary dust to be $f \approx 3 \times 10^5 \text{ kg year}^{-1}$. If we assume that f scales proportionally to the impactor flux in the inner solar system, the time dependencies of Eqs. 4 through 6 may be used to extrapolate f into the past. We then find a terrestrial infall rate 4.5 $\times 10^9$ years ago of organic carbon from interplanetary dust of $\sim 10^8$ to $10^{10} \text{ kg year}^{-1}$.

Even in ~ 10 -bar early terrestrial atmospheres, this rate exceeds the conservative estimates we have derived here for ~ 100 -m comets. However, we have left almost entirely unquantified likely augmentations to the latter estimate, including those arising from ablated material, airbursts, lower temperatures implied by three-dimensional impact simulations [as opposed to the two-dimensional simulations used here (71)], a possible extremely thermally stable fraction of cometary organics, and a relaxation of our approximation that peak shock heating extends over the full 1 s of the impact simulation. Moreover, the role of (small) carbonaceous asteroids is yet to be determined. In any case, the nature of the organics provided by interplanetary dust and impacting comets would have been radically different. Comets could deliver extremely volatile molecules, such as CH₄ or nonpolymeric HCN and H₂CO, whereas the organics in interplanetary dust are almost certainly highly processed and refractory.

Finally, we emphasize that we have ignored a host of possible mechanisms for impact generation of organics, including production by shock waves in reducing or neutral atmospheres (72, 73) or even by vaporization and recombination of target material (80). Moreover, substantial organic recombination may take place by the quenching of the vaporized cometary projectile itself (81). However, efficient organic synthesis in dense background CO₂ atmospheres by means of such recombination is problematic.

Typical estimates of photochemical production rates for HCN and H₂CO in terrestrial CO₂ atmospheres (taking into account rainout efficiencies) are $\sim 10^9 \text{ kg year}^{-1}$ (74). But these rates drop precipitously as the H₂/CO₂ ratio falls below ~ 1 (17). It is

difficult, in which intact cometary organics would be delivered in large amounts.

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$$\langle f(\mathbf{r}, h) \rangle = \int_V f(\mathbf{r}') W(\mathbf{r} - \mathbf{r}', h) d\mathbf{r}' \quad (7)$$

so that derivatives of f are replaced by derivatives of W . If f is known at the points \mathbf{r}_i , where $i = 1, 2, \dots, N$, the equations above can be approximated by summations. The summation equations produced from the equations of motion of the particles are then easily solved by computer.

$$\left\langle \frac{\partial f}{\partial x} \right\rangle = - \int_V f \frac{\partial}{\partial x'} W(\mathbf{r} - \mathbf{r}', h) d\mathbf{r}' \quad (8)$$

67. The need to restrict the interpenetration of particles at a shock interface places a lower limit on the magnitude of the artificial viscosity. All results quoted here use this lower limit. No constraint is placed on the upper limit of the artificial viscosity. Tests done to examine the effect of increasing the artificial viscosity show that variations of $\sim 10\%$ occur in the results, insignificant relative to other uncertainties in the calculation. In most problems the inclusion of an artificial viscosity gives satisfactory results. However, spurious heating occurs when materials collide supersonically. This effect (called wall heating) has been shown to be greatly reduced, and the shock fronts sharpened [W. H. Noh, *J. Comput. Phys.* **72**, 78 (1987)], by the inclusion of an artificial thermal diffusion. We include an artificial thermal diffusion along the lines of that of J. J. Monaghan, "SPH Meets the Shocks of Noh" (personal communication, 1988).
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71. Preliminary three-dimensional models of cometary impacts indicate that our estimates of the fraction of the comet exposed to $T < 1200 \text{ K}$ may be underestimates, in some cases by as much as a factor of ~ 10 . This is consistent with work reported by W. T. Brown, in *Shock Waves in Condensed Matter*, W. J. Nellis, L. Seman, R. A. Graham, Eds. (AIP Conference 78, American Institute of Physics, New York, 1981), pp. 529–533, who found pressure reductions by factors of ~ 2 for three-dimensional codes over two-dimensional approximations. These differences will be further explored in future work (P. J. Thomas, L. Brookshaw, C. F. Chyba, C. Sagan, in preparation).
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75. This does not require all comets with radii $\leq 1 \text{ km}$ to undergo airburst, however. P. R. Weissman [*Nature* **314**, 517 (1985)] cited two terrestrial impact craters of diameters 8.5 and 14 km, for which impactor compositions are known to have been either carbonaceous chondritic or cometary. These craters are consistent with impacts by either intact bolides or tightly clustered fragments (54) but are certainly inconsistent with a Tunguska-like airburst. Applying a standard impactor mass-diameter scaling law (3) for either a C-chondrite or a comet impacting Earth at $\sim 20 \text{ km s}^{-1}$ yields radii of ~ 200 and 600 m for the two impactors.
76. A more careful examination would treat cometary fragments after an airburst according to the methods outlined in this article. One way to calculate the mass fraction of fragments in a given size range is to assume a power-law distribution of fragment sizes [D. L. Turcotte, *J. Geophys. Res.* **91**, 1921 (1986)]. One such distribution is $N(m) = Cm^{-D/3}$, where $N(m)$ is the number of fragments with mass $> m$, C is a constant fixed by the total mass, and D is a material-dependent constant. This equation can be used to calculate the mass fraction of fragments in the range 50 to 200 m, which may then be combined with Eqs. 1 through 3 to calculate the mass of surviving organics. For geological materials D is typically ~ 2.5 ; more fragile materials have smaller values. If D is in the range 2.2 to 2.8, we find that our neglect of fragmentation underestimates terrestrial organic accretion by a factor of 4 to 9.
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82. We thank H. Pongracic for advice on using SPH in impact calculations and for allowing us to read draft copies of her thesis (65), A. Burnham and D. Camp for helpful discussions and preprints on kerogen pyrolysis, and S. Lyon for help in implementing the Los Alamos Sesame database. We are especially grateful to E. Anders, B. Clark, K. Zahnle, and two anonymous referees for their comments on an earlier version of this manuscript. We have benefited greatly from discussions with S. L. Miller, J. Oró, G. Hoffman, C. P. McKay, J. Melosh, J. Kasting, J. L. Bada, A. Bar-Nun, S. Chang, P. Gierasch, and P. Schultz. This work was supported by National Aeronautics and Space Administration grants NGR 33-010-220, NGR 33-010-101 (C.S.), NGT-50302 (C.F.C.), NEGW-1023 (P.J.T.), Office of Naval Research grant N00014-B3-K-0610 (L.B.), and a grant from the Kenneth T. and Eileen L. Norris Foundation.