

Amino acid survival in large cometary impacts

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Abstract—A significant fraction of the Earth's prebiotic volatile inventory may have been delivered by asteroidal and cometary impacts during the period of heavy bombardment. The realization that comets are particularly rich in organic material seemed to strengthen this suggestion. Previous modeling studies, however, indicated that most organics would be entirely destroyed in large comet and asteroid impacts. The availability of new kinetic parameters for the thermal degradation of amino acids in the solid phase made it possible to readdress this question.

We present the results of new high-resolution hydrocode simulations of asteroid and comet impact coupled with recent experimental data for amino acid pyrolysis in the solid phase. Differences due to impact velocity as well as projectile material have been investigated. Effects of angle of impacts were also addressed. The results suggest that some amino acids would survive the shock heating of large (kilometer-radius) cometary impacts. At the time of the origins of life on Earth, the steady-state oceanic concentration of certain amino acids (like aspartic and glutamic acid) delivered by comets could have equaled or substantially exceeded concentrations due to Miller–Urey synthesis in a CO₂-rich atmosphere. Furthermore, in the unlikely case of a grazing impact (impact angle ~5° from the horizontal), an amount of some amino acids comparable to that due to the background steady-state production or delivery would be delivered to the early Earth.

INTRODUCTION

The suggestion that a substantial fraction of the Earth's prebiotic inventory of organic molecules may have been delivered by infalling comets and asteroids is now nearly a century old (Chamberlin and Chamberlin, 1908; Lederberg and Cowie, 1958; Oró, 1961). This idea acquired greater importance after spacecraft missions to comet Halley revealed it to be ~25% organic by mass, which is consistent with its cosmic abundances of the elements (Krueger and Kissel, 1987; Delsemme, 1988; Chyba *et al.*, 1990). But a decade ago, Chyba *et al.* (1990) conservatively concluded that, apart from certain especially thermally hardy compounds such as polycyclic aromatic hydrocarbons (PAHs), most organics would probably be entirely destroyed in large comet and asteroid impacts (although this does not preclude the possibility of substantial postimpact organic synthesis in the expanding impact plume; Oró, 1961; Oberbeck and Aggarwal, 1992; McKay and Borucki, 1997). These authors suggested that small (≤ 100 m) comets could have been sufficiently aerobraked in a possible dense early CO₂ atmosphere for some organic delivery to have occurred. However, we now understand that objects in this size range would instead explode in the atmosphere in the manner of the Tunguska projectile (Chyba *et al.*, 1993; Chyba, 1993). Chyba and Sagan (1992) concluded that the dominant source of exogenous organics to early Earth would have been interplanetary dust particles (IDPs), which appear to be ~10% organic by mass, and which decelerate gently in the atmosphere and so can deliver their organics intact (Anders, 1989).

EVIDENCE FOR ORGANIC SURVIVAL IN BIG IMPACTS

Empirical and theoretical work over the past decade requires that these conclusions be reexamined. It was announced in 1989 that apparently extraterrestrial amino acids, α -aminoisobutyric acid and racemic isovaline, had been discovered immediately above and below the Ir-rich Cretaceous–Tertiary (K/T) boundary sediments at Stevns Klint, Denmark (Zhao and Bada, 1989). It was suggested

that dust evolved from a large comet may have been the source of these amino acids (Zahnle and Grinspoon, 1990), or that they might have resulted from postimpact quench synthesis (Chyba *et al.*, 1990; Oberbeck and Aggarwal, 1992). The former explanation was proposed to account for the amino acids' presence immediately above and below the boundary layer, but not within it—a distribution that seemed to exclude amino acid survival in the impact itself. This explanation now seems moot, in light of the discovery (T. Bunch, pers. comm.) of α -aminoisobutyric acid within the boundary layer at the K/T Sussex and Raton Basin sites, which suggests that the peculiar Stevns Klint distribution reflects processes unique to the geology of that site. In addition, Becker *et al.* (1996) announced the discovery of extraterrestrial He trapped in fullerenes at the Sudbury impact site that they argued requires these fullerenes to have experienced temperatures below 1000 °C throughout the impact, which also suggests that delivery of intact organics in large impacts might be possible.

Subsequent laboratory and numerical simulations have been ambiguous. In hypervelocity impact experiments at velocities of 1 to 2 km/s using samples of the Murchison meteorite, Tingle *et al.* (1992) found little loss of organic matter for pressures below ~20 GPa. But Peterson *et al.* (1997) found a steep decline (over 3 orders of magnitude) in the abundances of various amino acids for shock pressures increasing from 3 to 30 GPa, and the formation of secondary amino acids, especially at the higher pressures. As shown in our high-resolution simulations below, a fraction of large comets experiences shock pressures lower than ~35 GPa, even in impacts as fast as 20 km/s.

Further numerical work points to the possible significance of effects not considered in detail by Chyba *et al.* (1990). These authors' smoothed particle hydrodynamics (SPH) simulations were restricted to two dimensions; subsequent three-dimensional simulations (Thomas and Brookshaw, 1997) suggested that two-dimensional simulations overestimate impact temperatures by up to

an order of magnitude (although the effect of introducing the additional dimension must be disentangled from the effect of the lower resolution used in these three-dimensional simulations). More recent high-resolution three-dimensional hydrocode simulations suggest, when compared to similar two-dimensional simulations with equivalent resolution, that the temperature overestimation in two-dimensions is less than a factor of 2, with a comparable underestimation of shock pressure (Pierazzo and Melosh, 2000). Angle of impact is another factor that can contribute to increased organic survival in large impacts. Impacts at decreasing angles (measured from the horizontal) are characterized by weaker shocks and, therefore, increase the chance for organic survival (Chyba *et al.*, 1990; Thomas and Brookshaw, 1997; Blank and Miller, 1997; Pierazzo and Melosh, 2000). It has also been suggested that high pressures may offset the effects of shock temperatures and reduce the pyrolysis of organic material (Blank and Miller, 1997). Another potentially significant effect that could increase organic survival is the association of organics with dust particles embedded within the cometary ice matrix (Peterson *et al.*, 1997; Blank and Miller, 1997).

Numerical simulations have suffered from the lack of appropriate laboratory data for organic pyrolysis. Chyba *et al.* (1990) reluctantly considered kinetic parameters for five amino acids derived from their thermal degradation in solution, while explicitly warning that solution data were of questionable applicability to the shock pyrolyses being modeled; the authors' results suggested that amino acids would not survive most cometary impacts. Subsequent to that work, Rodante (1992) published kinetic parameters for the thermal degradation in the solid phase of 19 of the biological protein amino acids. The availability of these data, the empirical and theoretical hints that the earlier work may have overestimated organic pyrolysis in impacts, and the higher resolution now available in impact simulations suggest it is time to reconsider the importance of organic delivery in cometary impacts. To be as quantitative as possible, we focus on amino acid survival in particular.

We therefore present new two-dimensional high-resolution hydrocode modeling of asteroid and comet impact events and use the resulting thermodynamic histories of the projectiles to reconstruct the survival history of amino acids. We model spherical asteroid and comet projectiles 1 to 5 km in radius, impacting the surface at 15, 20, and 25 km/s. Temperature histories calculated *via* tracer particles are then used with known kinetic parameters for amino acids in the solid phase (Rodante, 1992) to estimate amino acid survival during the impact event.

HYDROCODE SIMULATIONS

We model spherical asteroid and comet projectiles 1 to 5 km in radius impacting both a continental crust and a 3 km deep ocean, using the two-dimensional, axis-symmetric Eulerian-Lagrangian hydrocode CSQ developed at Sandia National Laboratories (Thompson, 1990). The hydrocode makes use of the semianalytical equation of state ANEOS, a FORTRAN code designed for use with a number of hydrocodes (Thompson and Lauson, 1972). Utilizing valid physical approximations in different regimes, ANEOS uses the Helmholtz free energy to construct thermodynamically consistent pressures, temperatures, and densities. A major advantage of ANEOS over other analytical equations of state (*e.g.*, the Tillotson EOS; *e.g.*, see Melosh, 1989) is that it offers a limited treatment of phase changes. An important drawback of CSQ is that it allows the modeling of only vertical impacts, whereas 45° is in fact the most likely impact angle (Gilbert, 1893; Shoemaker, 1962). Because impact-

shock heating declines with increasing angle to the vertical (Chyba *et al.*, 1990; Thomas and Brookshaw, 1997; Pierazzo and Melosh, 2000), CSQ will underestimate the survivability of organic molecules in impacts. It is, however, possible to correct our results to take into account the effect of impact angle (Pierazzo and Melosh, 2000).

One hundred Lagrangian tracer particles were regularly distributed in half of the projectile (taking advantage of axial symmetry). The tracers allow us to record the trajectories and thermodynamic histories of the projectile during the impact. Resolution plays an important role in the thermodynamic evolution of the impact event (Pierazzo *et al.*, 1997); consequently, we kept the resolution of the Eulerian mesh to 50 cells (2%) per projectile radius in all the simulations, substantially higher than that used in earlier simulations (Chyba *et al.*, 1990; Thomas and Brookshaw, 1997). The thermodynamic state of the tracers was recorded every 0.01 s of simulation time. Asteroid impacts were modeled using granite (Pierazzo *et al.*, 1997) and dunite (Benz *et al.*, 1989) projectiles with an impact velocity of 15 km/s, the median asteroid impact velocity with Earth (Chyba, 1991). Comet impacts were modeled using ice projectiles (Tonks *et al.*, 1998, unpubl. data) with impact velocities of 15, 20, and 25 km/s. (The latter is just above the median short-period comet impact velocity with Earth; Chyba, 1991.) To model continental crust, we used the granite ANEOS equation of state (Pierazzo *et al.*, 1997). In the oceanic impact simulations, a 3 km deep ocean (using the equation of state for water; Tonks *et al.*, 1998, unpubl. data) overlaid a granite crust (we used granite because an ANEOS equation of state is not yet available for basalt). The simulations extended over a normalized time $\tau = D_i/v_i$ (where D_i is the diameter of the impactor and v_i its velocity) of ~40, long enough for the projectile material to be released from the shock state.

SURVIVABILITY OF AMINO ACIDS

Too little is known about the potential effects of shock loading on the modification of organic material. Laboratory experiments have shown that high stresses and elevated temperatures typical of shock waves may cause organic matter to decompose, to racemize, or to recombine into secondary products (Peterson *et al.*, 1997). Here we model the effect of shocks on amino acid degradation as due to thermal degradation from impact-shock heating. Impact-related temperature histories (from tracer particles) were extracted from the hydrocode simulations. A good resolution of the shock wave generated by the impact is guaranteed by the temporal resolution of these histories. The temperature history determines organic survival *via* the Arrhenius equation:

$$dM = -MA e^{-E_a/RT(t)} dt \quad (1)$$

where E_a (cal/mol) and A (1/s) are the activation energy and pre-exponential constant, respectively, for the organic molecule; $R = 1.987$ cal/mol is the gas constant; $T(t)$ is the time dependent temperature of the tracer (in K); and M is the mass of the organic material. New experimental values in the solid phase for E_a and A for the biological protein amino acids (Rodante, 1992) differ substantially from previously available kinetic parameters for thermal degradation in solution (Vallentyne, 1964). Neither case provides the best simulation of impact shock heating. We believe, however, that Rodante's kinetic parameters in the solid phase are more appropriate for impact simulations than those from solution, where hydrolysis will occur (Bada, 1991). The ideal kinetic parameters for these simulations would derive from shock-tube or impact gun experiments, but such data are not currently available. Our results will need to be reconsidered once such data are reported.

Effects of Projectile Type

Differences in the thermodynamic evolution for comet and asteroid impacts at the same velocity are due to the different projectile compositions. Figure 1 shows the spatial (a), temperature (b), and pressure (c) evolution of tracers from various parts of a 1 km-radius comet impacting the ocean at 20 km/s. The comet does not penetrate into the oceanic crust (it is stopped by the 3 km deep ocean) and ends up mostly vaporized (due to the high shock pressures, shown in Fig. 1c); whereas an asteroid impacting at 15 km/s reaches and penetrates the oceanic crust. Comet material enters the expansion plume and emerges from the opening crater relatively early in the impact; whereas melted asteroid material remains compressed inside the crater for a longer time, resulting in significantly higher temperatures and pressures over the length of the simulation. Figure 1b shows that comet tracers descend to a temperature below 1000 K relatively early (~2.5 s after impact); asteroid tracers, however, experience temperatures above 2000 K as long as 4 s after the impact.

Effects of the Kinetic Parameters

Amino acid survival depends strongly on the kinetic parameters E_a and A . In particular, for amino acids with large values of A , such as alanine and leucine, the survival fraction is virtually zero in vertical impacts. For intermediate values of A the survival fraction is low; this is the case, for example, for glycine, lysine, and valine. Only for low values of A (as for aspartic acid, glutamic acid, phenylalanine, and asparagine) is the survival rate nonnegligible for cometary vertical impacts. Figure 2 shows the temporal evolution of the surviving fraction of various amino acids in projectile locations corresponding to the tracers shown in Fig. 1. Asteroid simulations produce temperatures too high for significant survival of any amino acid at impact speeds ≥ 15 km/s.

Effects of Impact Speed

The higher the impact speed, the stronger is the shock and resulting temperature experienced by the projectile. The peak shock temperature distribution is reflected in the survival of amino acids

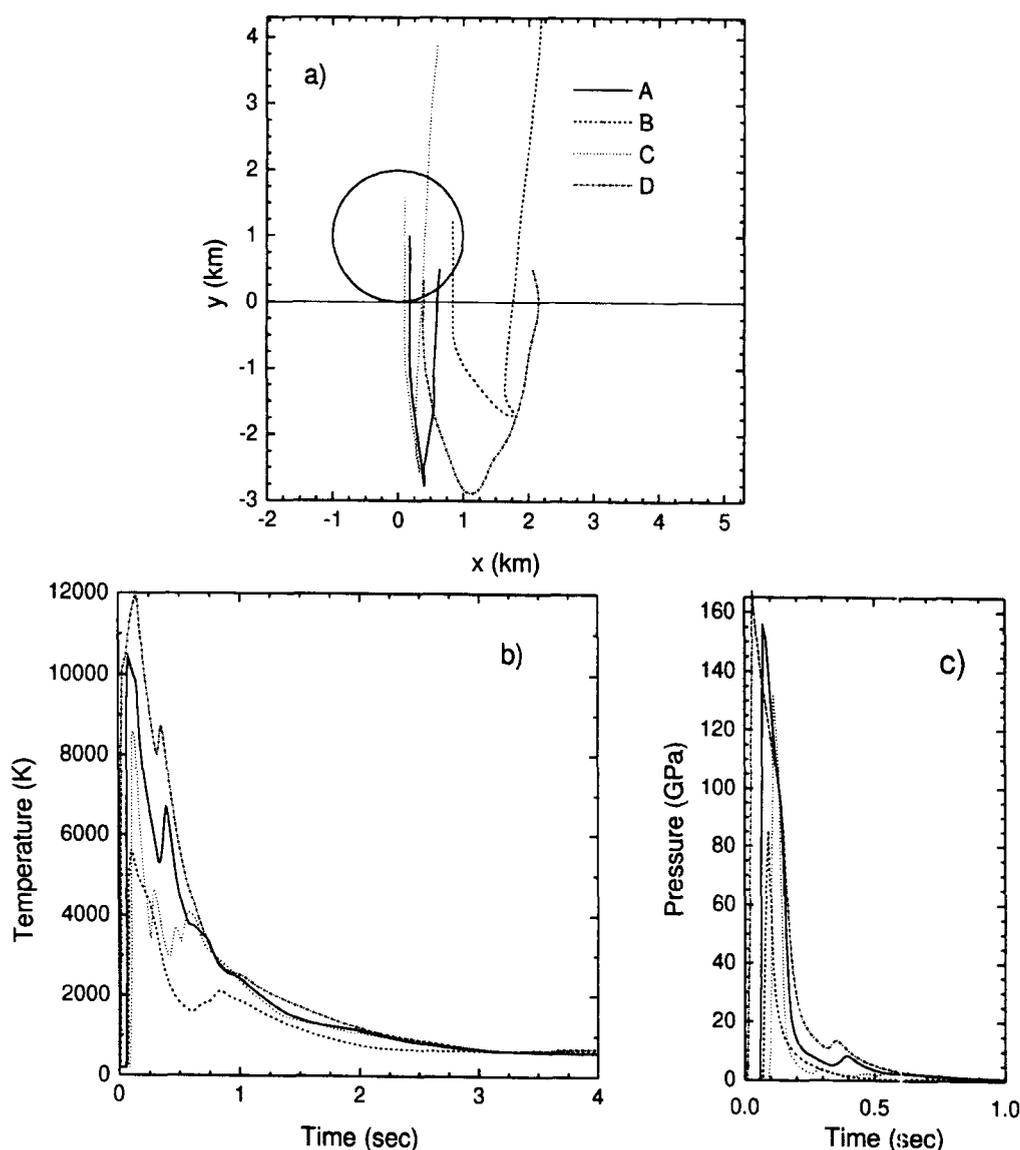


FIG. 1. Spatial (a), temperature (b), and pressure (c) evolution of selected tracer particles from a comet 1 km in radius impacting a 3 km deep ocean at 20 km/s.

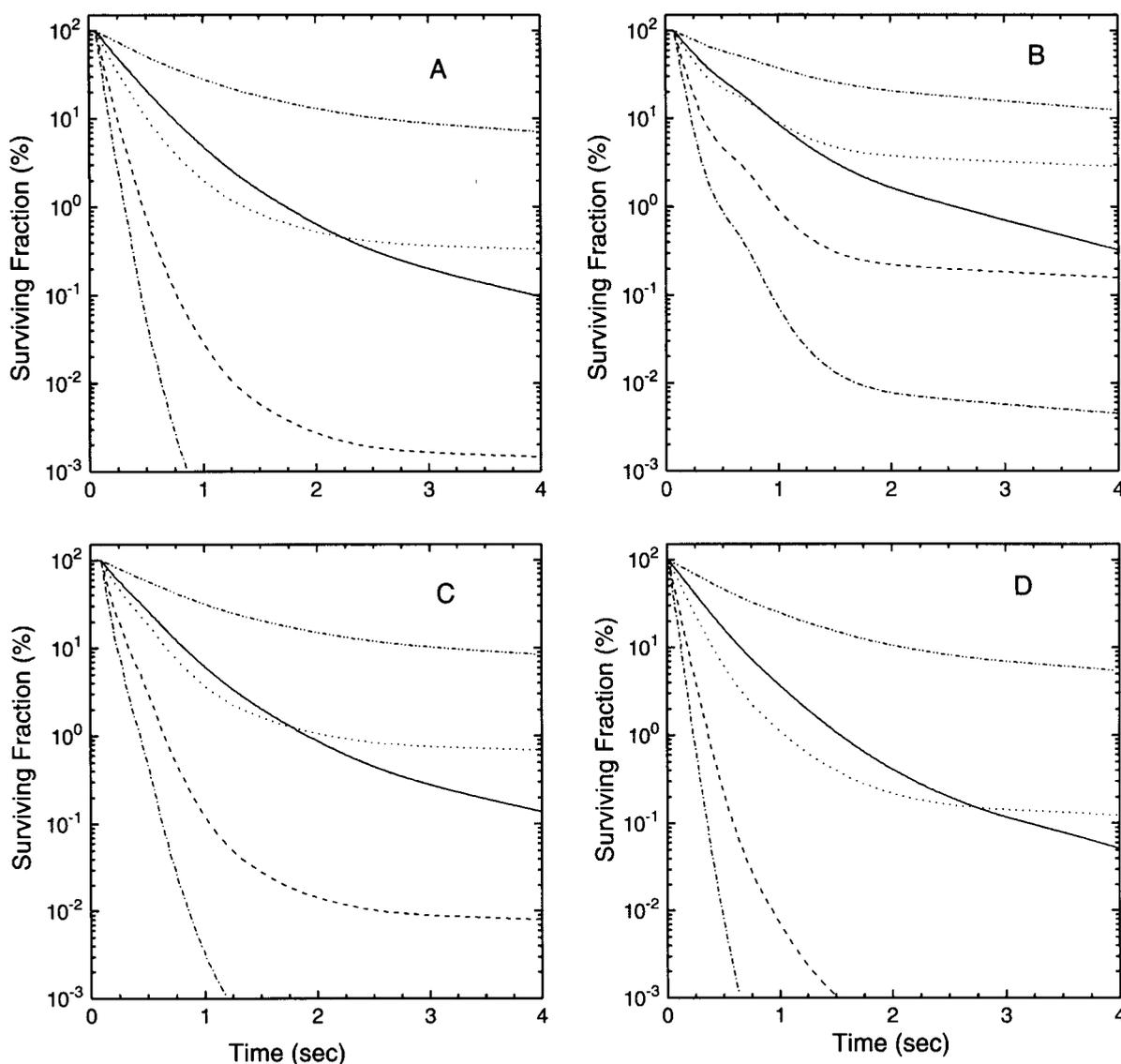


FIG. 2. Survival of selected amino acids for the tracers of Fig. 1. The amino acids are: aspartic acid (solid line), glutamic acid (dashed line), phenylalanine (dotted line), glycine (dot-dashed line), and asparagine (dot-dot-dashed line). Letters A through D correspond to the tracers shown in Fig. 1.

for the various impact velocities. In Fig. 3, the amino acid surviving fraction is calculated by averaging over amino acid survival throughout the body of the impacting projectile, using the 100 tracers and Eq. (1).

Effects of Projectile Size

The size of the impactor also influences the survivability of amino acids. To quantify this effect, we carried out comet impact simulations using projectiles 1, 3, and 5 km in radius at impact speeds of 20 km/s. The peak shock temperature experienced by the projectile does not differ much in the three cases. However, the larger the projectile the longer the shock wave takes to propagate to the rear end of the projectile, where it is reflected back as a rarefaction wave that unloads the material from the shocked state. (Material near the rear of the projectile will experience a shorter shock pulse than material close to the impact point.) At constant impact speed, τ (for the 3 and 5 km projectiles) is 3 and 5 \times higher than for the 1 km projectile. Because the material stays in the shocked

state longer, amino acid thermal degradation increases. Projectile size dependence of amino acid survival is shown in Fig. 4 for several amino acids.

Survival Maps

The application of Eq. (1) to all the tracers' temperature histories provides a map of survival of amino acids in the projectile. Integration over the volume of the projectile gives the fraction of surviving amino acids after the impact event. The final survival map for the various amino acids depends strongly on both the peak shock temperature and the aftershock, or decay, temperature in the projectile.

As an example, Fig. 5 shows a contour map of (a) peak shock, and (b) decay temperature (4 to 4.5 s after impact) in the projectile. The resulting surviving fraction for the amino acid aspartic acid is shown in Fig. 6. The peak shock temperature decreases away from the impact point with maximum values around the axis of impact, whereas the decay temperature shows off-axis maximum values.

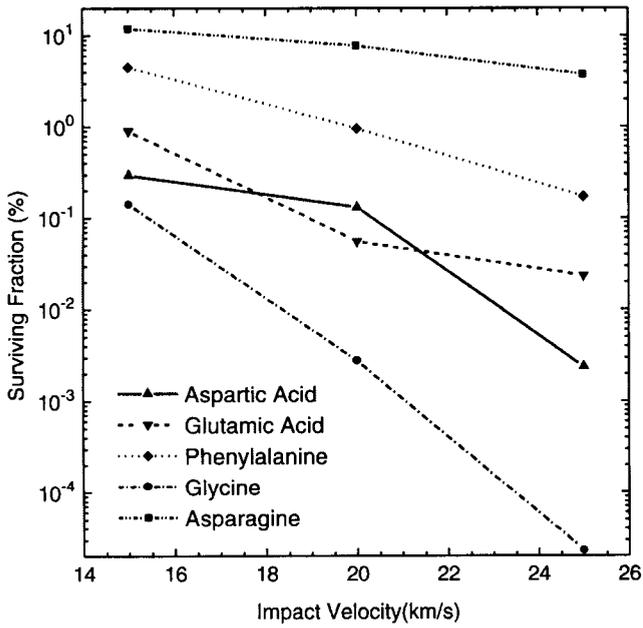


FIG. 3. Amino acid survival in vertical impacts of a 1 km radius comet as function of impact speed.

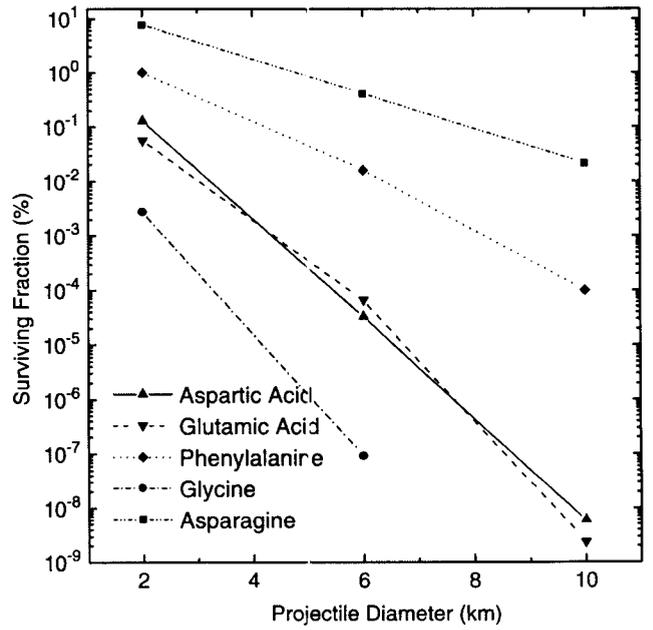


FIG. 4. Amino acid survival in cometary vertical impacts at 20 km/s as function of comet diameter.

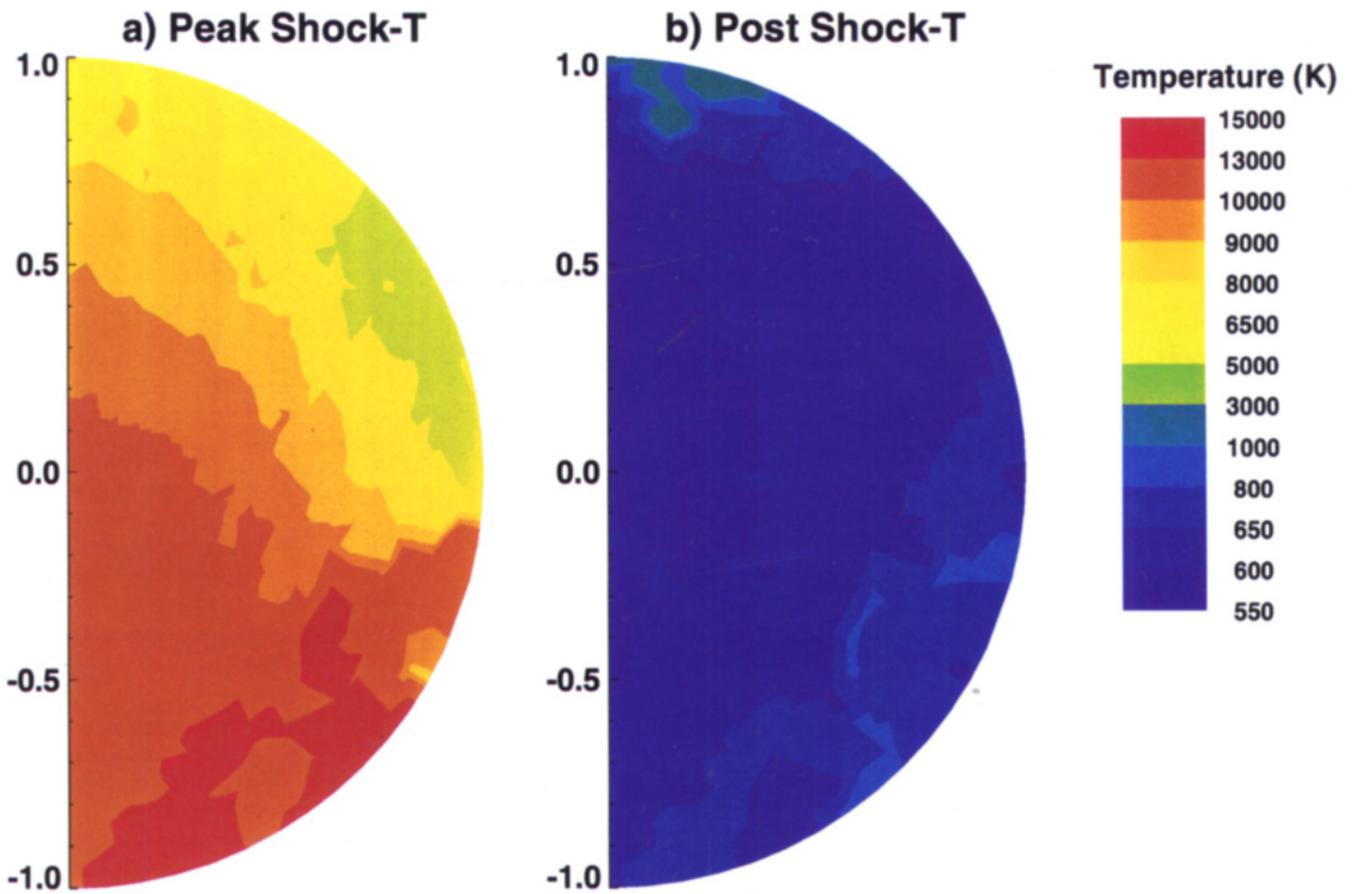


FIG. 5. Temperature map of (a) peak shock temperature and (b) postshock (after 4 s) temperature inside the projectile for a 1 km radius comet impacting at 20 km/s.

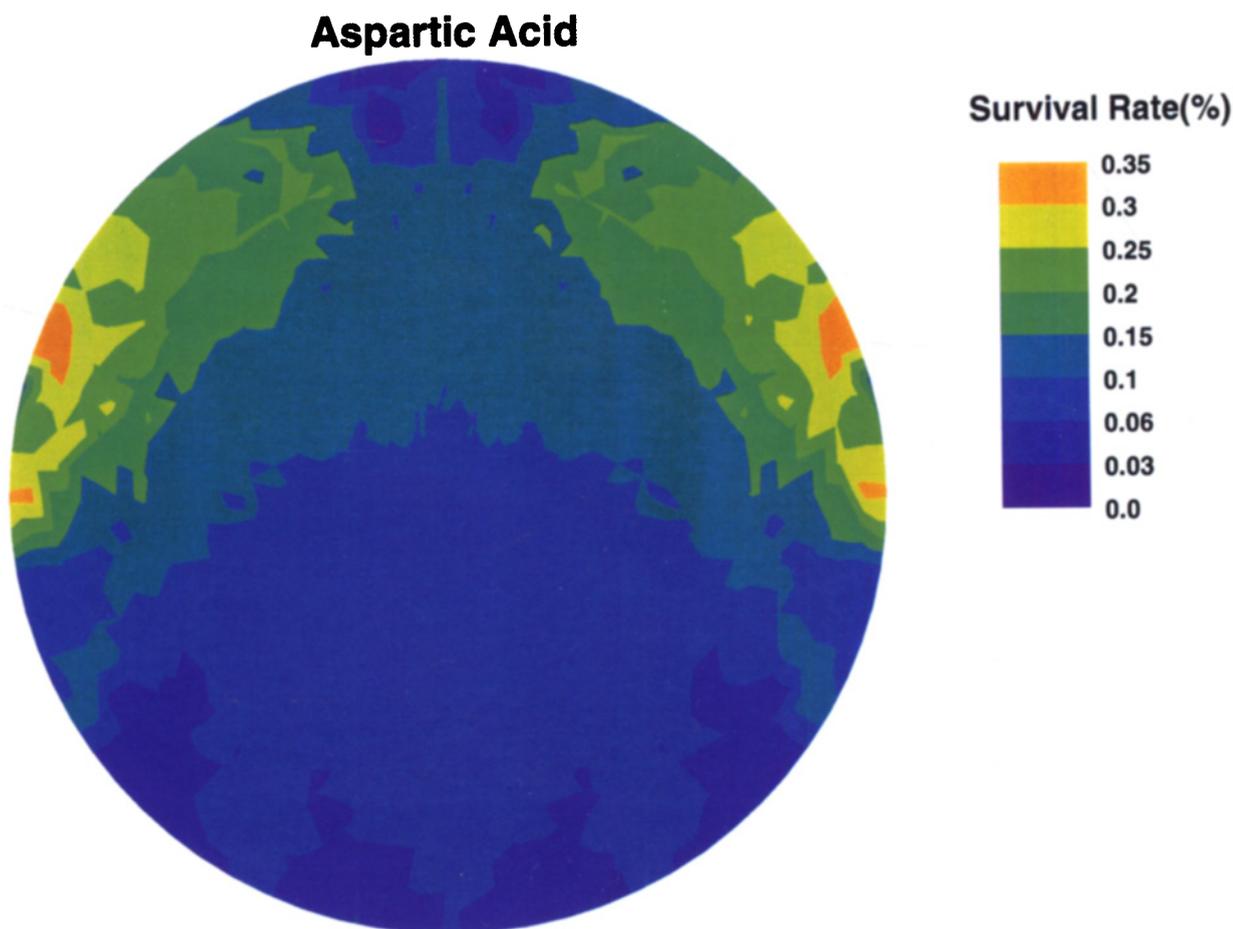


FIG. 6. Survival map for aspartic acid within the comet, subsequent to the impact characterized by the peak and postshock temperatures of Fig. 5.

Figure 6 suggests lower survival near the incident face of the projectile, where the shock temperatures are highest, and maximum survival away from the axis of impact, with a peak at about two o'clock.

Effects of Impact Angle

Pierazzo and Melosh (2000) show that it is possible to correct results from hydrocode simulations of vertical impacts to take into account the angle of impact. They find that the peak shock temperature of the projectile scales like the sine of the angle of impact (θ) to the $3/2$ power, whereas the postshock temperature scales with the sine to the 0.8 power for a series of high-resolution three-dimensional hydrocode simulations. Correspondingly, a linear correlation of the shock pressure with $\sin \theta$ was found. To correct for the angle of impact, we scaled our results for vertical impacts by multiplying each temperature history of the tracers inside the projectile by $(\sin \theta)^{0.8}$ and then followed the procedure described above to obtain the survival rate of amino acids. This is a conservative correction because, according to the results of Pierazzo and Melosh (2000), it overestimates the peak shock temperature for oblique impacts (therefore decreasing the probability of amino acid survival). Figure 7 shows the survival of selected amino acids for a 2 km diameter comet impact at 20 km/s as function of θ . At 45° , the

most probable angle of impact (Gilbert, 1893; Shoemaker, 1962), survival has increased over that for vertical impacts by a factor of 3 for aspartic acid and by a factor of 5 for glutamic acid.

Other Effects

Among other factors that can influence the survival of organics in impacts are projectile inhomogeneities and shape effects. Porosity is an important factor in generating inhomogeneities inside the impactor. For a porous material, extra work must be done to close the pores. Therefore, during an impact, more energy must be partitioned to a porous projectile, resulting in higher peak and postshock temperatures. A simulation with a 40% porous comet impacting at 25 km/s showed an increase of 50 to 75% in the average temperature of the projectile during the impact relative to the nonporous case. This, in turn, results in a decrease in survival of amino acids. This decrease varies between $\sim 15\%$ for asparagine and 40–50% for aspartic and glutamic acid.

The effect of the shape of the impactor on the survival of amino acids has never been addressed before, although we are planning to investigate it in a future study. A preliminary study (Pierazzo, 1999), however, suggests that the irregular projectile shape might enhance the survival of organics by increasing the volume of the projectile subjected to lower shocks.

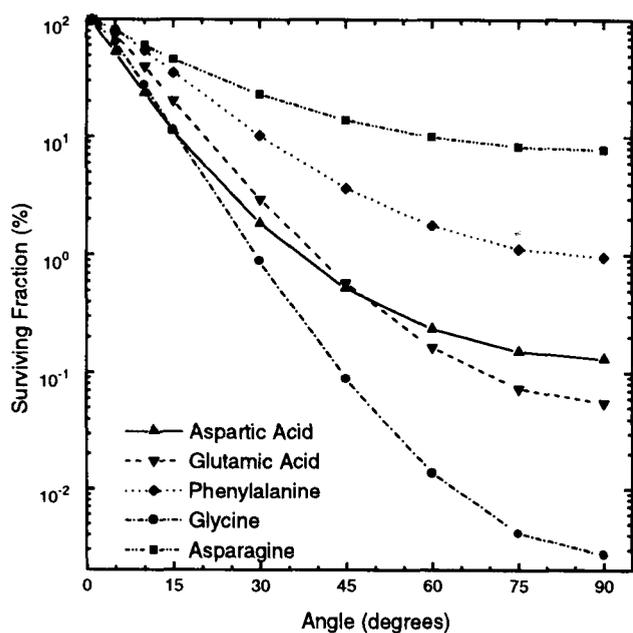


FIG. 7. Survival fractions for selected amino acids as a function of the angle of impact from the horizontal. Survivability increases at low-impact angles.

COMPARISON WITH MILLER–UREY SYNTHESIS

The conclusion that certain amino acids would survive even large cometary impacts is itself a remarkable result. To determine the quantitative importance of the potential cometary source, we compare these results with those from endogenous sources of amino acids. As a convenient way of framing this comparison, we compare resulting concentrations within the global ocean for certain amino acids resulting from Miller–Urey synthesis and cometary input. These concentrations are very low in both cases; to be credible for the origin of life, both cases must therefore appeal to concentration mechanisms in evaporating ponds or other special environments.

First consider amino acids synthesized *via* the standard electrical discharge Miller–Urey syntheses (Schlesinger and Miller, 1983; Stribling and Miller, 1987). Although these were originally demonstrated in reducing, methane-rich atmospheres, it is now thought unlikely that such an atmosphere ever existed (Walker, 1986), though this conclusion remains a lively topic of debate (Sagan and Chyba, 1997). It seems most likely that Earth's atmosphere at the time of the origins of life was rich in CO_2 , probably with a number ratio of H_2 to CO_2 much less than unity (Walker, 1986; Kasting, 1993). Stribling and Miller (1987) find the HCN yield in an atmosphere with $[\text{H}_2]/[\text{CO}_2] = 4$ to be 4 nmol/cm²/year, and a net amino acid yield 10% of the HCN yield. These calculations assume no loss of HCN in the atmosphere prior to entering the ocean (Stribling and Miller, 1987; Chang, 1993). Moreover, for $\text{CO}_2/\text{H}_2/\text{N}_2$ atmospheres, amino acid yield falls by a factor of $\sim 10^3$ as $[\text{H}_2]/[\text{CO}_2]$ drops from 4 to 0.1 (Bada, 1991). The latter ratio on the early Earth may have been much lower than 0.1; Kasting (1993) suggests a value of $\sim 10^{-2}$. For definiteness, we choose $[\text{H}_2]/[\text{CO}_2] = 0.1$ for our comparisons, possibly overestimating Miller–Urey synthesis.

Calculating analogously to Stribling and Miller (1987), we find net amino acid yields of about 4×10^{-4} nmol/cm²/year from electrical discharges in a realistic $\text{CO}_2/\text{H}_2/\text{N}_2$ atmosphere. However, this is an overestimate, because these authors relied on lightning and

coronal discharge rates suggested by Miller and Urey (1959) that derived from measurements made prior to Earth-orbiting satellites. These values have subsequently been updated using modern data (Chyba and Sagan, 1991). Total (coronal plus lightning) discharge rates on Earth appear to be $\sim 50\times$ lower (Chyba and Sagan, 1991) than those used by Stribling and Miller (1987), giving a net amino acid yield from electrical discharge of 8×10^{-6} nmol/cm²/year. Schlesinger and Miller (1983) have experimentally determined mole ratios of amino acids produced in a variety of model atmospheres for various molecular ratios. For $[\text{H}_2]/[\text{CO}_2] = 0.5$, the lowest ratio for which they report amino acid mole ratios, they find detectable abundances of alanine, aspartic acid, glutamic acid, and serine relative to glycine ($\equiv 100$) of 7.0, 0.22, 0.06, and 0.40.

These ratios provide a source term for endogenous production of various amino acids on early Earth. Resulting amino acid concentrations in the ocean (in the absence of concentrating mechanisms) are given by

$$d[C]/dt = S/V - k[C] \quad (2)$$

where $[C]$ is the concentration (mol/l), S is the source term (mol/year), V is the ocean volume (1.4×10^{21} l), and k is the destruction rate (1/year) for the amino acids. Equation (2) is readily integrated; in the limit of large t , $[C]$ attains a steady-state value $[C]_{\infty} = S/(Vk)$. For Miller–Urey synthesis, S for various amino acids is as calculated above. A variety of sinks can be considered, including destruction by ultraviolet light (Dose, 1974), adsorption onto clays (Hedges and Hare, 1987; Oberbeck and Aggarwal, 1992; Chang, 1993), thermal decomposition (Vallentyne, 1964), and passage through hydrothermal vents (Stribling and Miller, 1987). Following Stribling and Miller (1987), we will take the 10^7 -year timescale for the circulation of the volume of the entire ocean through submarine vents at 300 °C (Edmond *et al.*, 1982) to be the dominant sink for amino acids. The effects of adsorption on clays are difficult to quantify (Stribling and Miller, 1987); organics and salts in seawater could provide an effective shield against ultraviolet photodissociation of dissolved organics (Cleaves and Miller, 1998); and most amino acids for which thermal decomposition parameters in solution are known (excluding serine; Vallentyne, 1964; Bada and Miller, 1968) have lifetimes at 273 K much longer than 10^7 year. (The half-life for the deamination of aspartic acid at 0 °C between pH 5 and 8 is 3×10^7 year; Bada and Miller, 1968.) In any case, the ratio of concentrations resulting from Miller–Urey synthesis to those derived from cometary input will not change as long as the same sink timescale is used for both. Taking half the ocean to circulate through 300 °C vents in 5 Ma gives $k = 1.4 \times 10^{-8}$ /year, yielding values for $[C]_{\infty}$ for aspartic acid, glutamic acid, and glycine shown in Table 1 (we include only those amino acids that are produced in detectable quantities in CO_2 atmospheres (Schlesinger and Miller, 1983) that also should be present in comets, by analogy with the Murchison meteorite (Cronin and Pizzarello, 1983; Shock and Schulte, 1990) and would have a nonnegligible survival in cometary impacts).

TABLE 1. Estimated oceanic amino acid concentrations (10^{-12} mol/l) four billion years ago.

Source	Glycine	Aspartic acid	Glutamic acid
Electrical discharge, $[\text{H}_2]/[\text{CO}_2] = 0.1$	2000	5	1
Steady-state cometary input	400	10	70
Low-angle 5 km-radius comet impact	30	0.7	4

COMETARY DELIVERY OF AMINO ACIDS

We now need to determine S for Eq. (2) in the case of cometary delivery of amino acids. To do so, we must estimate the amino acid abundances in comets and then follow the fate of these molecules in cometary impacts.

Although it is known that comets are rich in organic molecules (Krueger and Kissel, 1987; Delsemme, 1988; Chyba *et al.*, 1990), we are unlikely to know for certain whether they contain amino acids prior to an *in situ* analysis or sample return mission. However, carbonaceous chondrites, the most volatile-rich meteorites, contain amino acids; the Murchison meteorite is known to contain well over fifty different amino acids (Cronin, 1976; Cronin and Pizzarello, 1983; Shock and Schulte, 1990) (including about half of the twenty biological protein amino acids; no cometary delivery is assumed for protein amino acids not present in Murchison). Evidence for the amino acid glycine in the interstellar medium remains ambiguous (Snyder, 1997); if amino acids do exist in the interstellar medium, comets may inherit them directly during accretion.

The Murchison amino acids occur in laboratory meteorite extract as both free amino acids and as derivatives of precursors converted to amino acids by acid hydrolysis (Cronin, 1976; Cronin and Pizzarello, 1983). The amino acid abundances used in our calculations include only those for free amino acids; in particular we take initial concentrations in the Murchison meteorite for glycine, aspartic acid, and glutamic acid to be 37.8 (~3 ppm by mass), 1.5, and 3.9 nmol/g, respectively (Cronin, 1976). Note that these numbers are much lower than those listed in typical compilations of Murchison amino acid abundances (Cronin and Pizzarello, 1983; Shock and Schulte, 1990). In effect, we make the conservative assumption that amino acid precursors in comets do not contribute to amino acids in Earth's oceans (nor do we consider delivery of HCN by comets and any possible subsequent amino acid synthesis; the abundance of HCN is ~10% by number that of H₂O in comets; Irvine, 1998). We also note that some of the free glutamic acid may have been present in the meteorite as pyroglutamic acid, for which we have no thermal decomposition data (Shock and Schulte, 1990). We multiply the Murchison amino acid concentrations by 10 to scale crudely for the fact that the overall organic fraction of comets is ~10× that found in carbonaceous chondrites (Chyba *et al.*, 1990).

We then estimate how much total cometary mass may have been incident upon the Earth ~4 Ga in the size ranges relevant to our calculations. Based on the lunar cratering record, the mass flux of objects with masses between m_{min} and m_{max} impacting Earth 4 Ga is given in Chyba and Sagan (1992)

$$\dot{m}(t = 4 \text{ Ga}) = 1.8 \times 10^3 (m_{max}^{1-b} - m_{min}^{1-b}) \quad (3)$$

where $b = 0.54$, and \dot{m} is in units of kg/year, provided m_{max} and m_{min} are in units of kg. In Eq. (3), we consider a mass range corresponding to asteroids with radii between 0.5 km (large enough to pass through the atmosphere unaffected; Chyba *et al.*, 1993; Chyba, 1993) and 6 km (much above which our simulations show amino acid survival to be minimal). We take 10% of this predominantly asteroidal (Chyba, 1991) mass flux to have been due to short-period comets, a choice consistent with previous modeling (Chyba *et al.*, 1990). Equation (3) gives a total cometary mass accreted by the Earth of 9×10^{11} g/year, taking into account that about half of the mass from impacting comets would be lost from the atmosphere (Chyba, 1991; Melosh and Vickery, 1989). Integrated over 10^9 year, this rate would give $\sim 5 \times 10^{20}$ g of

cometary water delivered to Earth, which is well below the upper limit of $\sim 10^{23}$ g now seemingly permitted by three observed cometary D/H ratios (Bockelée-Morvan *et al.*, 1998). Were all cometary glutamic acid, for example, to survive these impacts, the steady-state oceanic concentration would be $\sim 2 \times 10^{-9}$ mol/l, $\sim 10^3$ times that provided by Miller–Urey synthesis. Glutamic acid impact survival at >0.1% level would therefore dominate Miller–Urey glutamic acid production. If comets were a smaller (or larger) part of the impacting flux in the radial range 1 to 5 km, our results may be scaled linearly to the appropriate value. We must now calculate the fraction of cometary amino acids that actually would survive impact.

We performed simulation runs for comets of radii 1, 3, and 5 km and with impact velocities of 15, 20, and 25 km/s. Within a given cometary radius bin (0.5 to 2, 2 to 4, and 4 to 6 km), we calculate amino acid input to Earth's oceans weighted over the range of possible impact angles and velocities.

Weighted averages over impact angle θ were performed using the scaling of temperature with $(\sin \theta)^{0.8}$ previously described, and the result that impact angle probability is proportional to $\sin \theta \cos \theta d\theta$ (Gilbert, 1893; Shoemaker, 1962). Figures 8 and 9 show resulting amino acid survival as a function of impact velocity (Fig. 8) and impactor diameter (Fig. 9) after weighting over the range of possible impact angles. Statistics for Earth impact velocities for short-period comets are poor but suggest that ~30% of impacts occur with velocities between 15 and 20 km/s and ~30% of impacts occur at velocities between 20 and 25 km/s. The surviving fraction of amino acids in each velocity bin was calculated by averaging survival for the velocity extrema of the bin. Impacts at velocities >25 km/s are taken to give zero contribution, as they may lead to impact blowoff from the atmosphere, preventing accretion of cometary material (Chyba, 1991; Melosh and Vickery, 1989).

This procedure allows us to determine the cometary source term S in Eq. (2), and the corresponding oceanic concentrations $[C]_{\infty}$. The results are shown in Table 1, which compares the steady-state cometary input with Miller–Urey production rates. Table 1 also displays results for the unlikely case of a single 5 km-radius comet

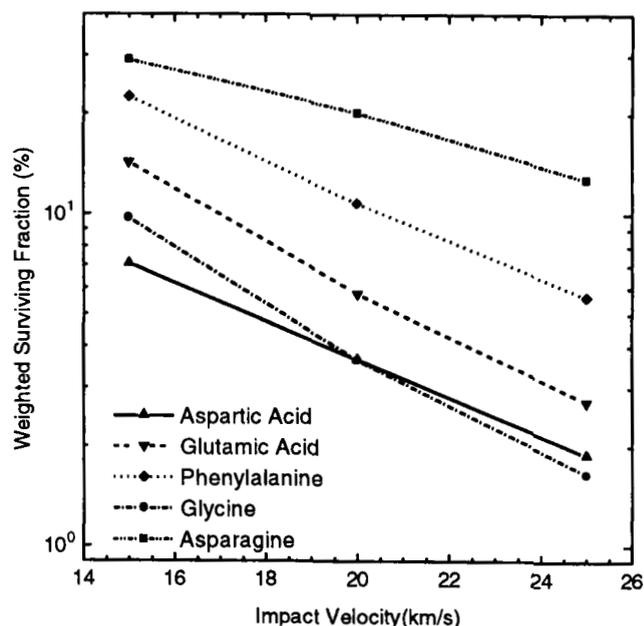


FIG. 8. Amino acid surviving fraction weighted over impact angle as a function of impact velocity for 1 km radius comets.

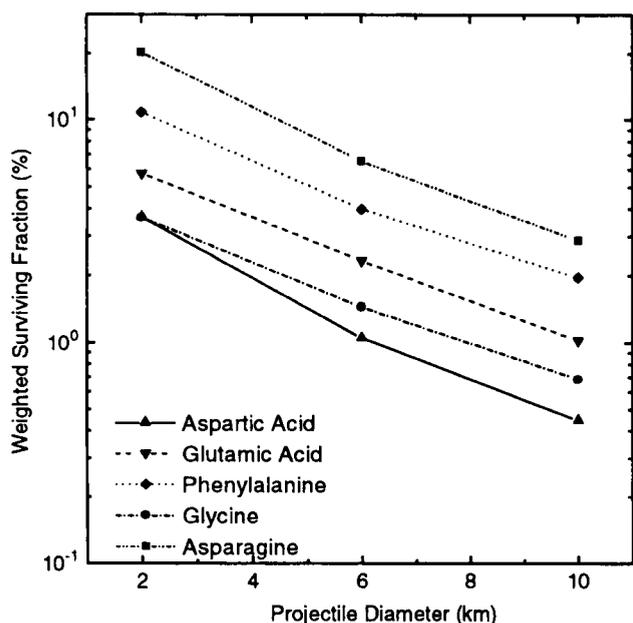


FIG. 9. Amino acid surviving fraction weighted over impact angle as a function of impactor diameter for 20 km/s impacts.

striking the surface of the ocean at 20 km/s with an inclination of 5° to the horizontal (~0.5% of all incident comets should have struck Earth at or below this inclination). This simulation of a special case is in the spirit of Clark's suggestion (Clark, 1988) that rare fortuitously low-angle cometary collisions may have been important for the origin of life. For this particular case, our simulations indeed show substantial amino acid survival, often in the tens-of-percent range; a single object may thereby itself deliver an abundance of certain amino acids comparable to that due to background production or delivery. (The results for the oblique comet shown in Table 1 simply assume that all surviving cometary amino acids are mixed into 1.4×10^{21} l of ocean water, giving a resulting amino acid molarity in the global ocean. It is possible, of course, that regional or local instantaneous concentrations could be considerably higher.) Thus, there may have been occasional periods of duration $\sim 10^7$ years with oceanic concentrations of certain amino acids above that of the steady-state cometary value.

Other mechanisms for the production or delivery of amino acids to the Earth may also have existed. Interplanetary dust particles 4 Ga ago may have been delivering 2×10^{12} g/year total mass to Earth. If these particles had Murchison-level concentrations of amino acids, and if these amino acids completely survived atmospheric entry, then resulting oceanic concentrations of glycine, for example, could be as high as 4×10^{-9} mol/l. However, atmospheric passage for a typical 50 μm IDP entering at 45° subjects the IDP to ~ 1 s of heating above 1200 °C and ~ 6 s above 500 °C (Love and Brownless, 1991). A rough calculation using Eq. (1) for glycine (Rodante, 1992) suggests that its survival would be $<0.1\%$ after atmospheric passage. More general conclusions will require modeling a broad suite of IDP sizes and entry angles.

Brinton *et al.* (1998) have reported concentrations of the amino acid α -aminoisobutyric acid in some Antarctic micrometeorites (in the 100–400 μm size range) that are substantially higher than in CM chondrites. They estimate that the flux of α -aminoisobutyric acid on Earth today may therefore be 3×10^5 g/year, corresponding (Chyba

and Sagan, 1997) to 6×10^7 g/year 4 Ga ago. Were all this to be mixed into the ocean, the resulting steady-state concentration of α -aminoisobutyric acid would (by Eq. (2)) be 3×10^{-8} mol/l. This source might therefore have dominated other sources of amino acids on early Earth. Note, however, that this calculation is based on an extrapolation from a single Antarctic sample (A91) with α -aminoisobutyric acid significantly above background levels (Brinton *et al.*, 1998).

Additional endogenous sources for amino acids may also have existed. For an early atmosphere with CO_2 concentrations about 100× the present atmospheric level, and a methane flux equal to the modern abiotic hydrothermal flux (Chang, 1993), the HCN rainout rate via the production of N from solar Lyman alpha photolysis of N_2 in the middle atmosphere could have been $\sim 1 \times 10^{-2}$ nmol/cm²/year, or about twice that produced by electrical discharge in a $[\text{H}_2]/[\text{CO}_2] = 0.1$ atmosphere (Chang, 1993; Zahnle, 1986). Substantially higher HCN production would have occurred for correspondingly higher CH_4 fluxes (Zahnle, 1986).

These results suggest the possibility that the apparently extraterrestrial amino acid α -aminoisobutyric found at K/T boundary sites could possibly have been directly delivered by the K/T impactor. The concentrations detected (Zhao and Bada, 1989) could be provided by a 10 km-diameter comet provided that much of the α -aminoisobutyric acid present within the object survived impact. (This assumes cometary amino acid levels at least 10× that of Murchison. Intriguingly, sample A91 suggests that some micrometeorites have α -aminoisobutyric acid concentrations $\sim 100\times$ higher than Murchison; Brinton *et al.* 1998.) In the absence of thermal degradation parameters in the solid state (Rodante, 1992) for α -aminoisobutyric acid, this problem cannot yet be addressed quantitatively. However, the results described here suggest that this scenario must now be considered possible.

It is clear that there are substantial uncertainties in estimates for both exogenous and endogenous sources of organics, as well as the dominant sinks. All of the likely mechanisms described here lead to extremely low global concentrations of amino acids, emphasizing the need for substantial concentration mechanisms—or for altogether different approaches to the problem of prebiotic chemical synthesis.

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