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Comment on "Prebiotic Chemistry within a Simple Impacting Icy Mixture"

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In a recent paper appearing in this Journal, Goldman and Tambllyn (GT) applied quantum molecular dynamics simulations of the shock compression of water ice containing CH_3OH , NH_3 , CO_2 , and CO to the modeling of oblique cometary collisions with prebiotic Earth.¹ The study utilized an impact model incorporating maximum pressures and temperatures, respectively, of 60 GPa and 4600 K with decay times to ambient conditions extending over hundreds of picoseconds. It yielded a "sweet spot" at 36 GPa and 2800 K where a range of C–C and C–N chain structures surfaced that upon expansion and cooling yielded complex organic substances including amino acids and precursors to other prebiotic organic substances, and the authors concluded that such impacts could have supplied early Earth with the molecular predecessors of life.

Provided here are comments comparing the GT results with those developed with a model for comet impacts described by Pierazzo and Chyba (PC).² That approach has been integrated with the rate parameters for the thermolysis of alkanes in an examination of impact survival from a kinetics perspective³ and operates over a set of conditions substantially different from those in the GT model. Most significantly, it incorporates characteristic relaxation times of hundreds of milliseconds over which periods the pressures decline far more rapidly than do the temperatures. Thus a shock interval 8–9 orders of magnitude greater than what was presumed in the GT model tied to a circumstance in which stabilizing high pressures vanish while temperatures remain at organic thermolysis levels over extended periods presents a somewhat different picture of survival likelihood.

A vertical impactor experiences shock conditions that are moderated in impacts with increasing obliquity, with the temperatures and pressures scaling respectively as $\sin^{0.8} \theta$ and $\sin \theta$ for an impact angle of θ degrees as measured from the horizontal.⁴ Figure 1 represents a PC approach to the impact of a 2 km body traveling at 20 km/s for both a vertical impact and an event at $\theta = 21^\circ$ for which conditions the GT model affords complex organic products. In the vertical case there is no question about survival of any organic compounds formed at impact; they would be destroyed more-or-less instantly at ~ 100 ms where the pressure has fallen to near ambient while the temperatures remain at 3000+ K for tens of milliseconds.

But as the figure shows it is clear that, although the conditions for the oblique impact are more modest, they are nonetheless fatal. Thus at ~ 100 ms any products created initially are exposed to temperatures of nominally 1500 K over hundreds of milliseconds. Table 1 lists half-life upper limits at

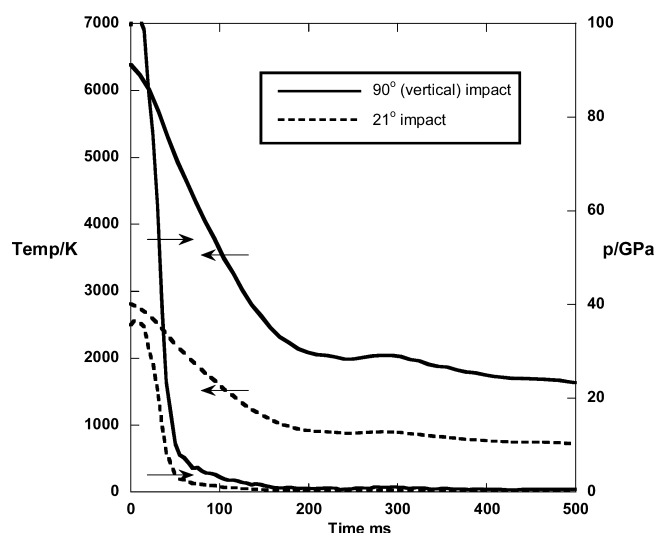


Figure 1. Pressure and temperature time records for the impact of a 2 km body traveling at 20 km/s, developed from the account of Pierazzo and Chyba² as described in ref 3.

Table 1. Half-Lives of Life-Related Organic Substances

| compound | class | half-life/ms ^a | | source |
|----------------------------|-------------------|---------------------------|-------|--------|
| | | 1500 K | 950 K | |
| thymine | nucleobase | 0.1 | 9.9 | 6 |
| glycine | amino acid | 7.0×10^{-5} | 0.2 | 7 |
| diethyl methyl phosphonate | phosphate ester | 2.5×10^{-4} | 1.6 | 8 |
| decane | alkane | 1.7×10^{-4} | 41.9 | 9 |
| isocyanic acid | organic precursor | 1.1 | 293.9 | 10 |

^aThe half-lives were developed in each case for a simple first-order decomposition by ignoring the possible introduction of rate-accelerating chain processes at high temperatures, and are thus viewed as upper limit values.

1500 and 950 K for materials for which pyrolysis rate parameters A and E_a are available and includes decane, isocyanic acid (HNCO), and compounds characterizing the classes of substances identified in the Murchison meteorite.⁵ They are all representative of the variety of complex organic substances that emerged in the GT simulations and were then presumed to be precursors to complex organic substances. It is

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seen that the half-lives at 1500 K extend over a broad range, but as a group they straightforwardly fall at periods well within the elevated temperature regime following pressure release in Figure 1. The compounds and those they represent are thus fully destroyed at that point, and any succession to complex organic molecules cannot take place.

More highly angular events will provide still lower shock temperatures, but at the same time the peak shock pressures are reduced and the issue remains. Therefore, though not shown in the figure, it emerges that at $\theta = 10^\circ$, for example, the temperature falls from about 1500 K at its peak to 950 K at the ambient pressure point. The values in Table 1 suggest that some degree of survival may be possible, but the peak pressure in that case is reduced to about 17 GPa and below the range covered by the GT simulations, and product formation itself could then be problematic.

It is notable that the carbonization of organic compounds is exoergic above 1300 K.¹¹ It becomes overwhelmingly prominent at impact temperatures,^a and impact craters themselves have provided evidence of carbonization with the recovery of C₆₀ at the crater sites.¹³ It has been suggested that the carbon allotrope is “frozen in” as the thermodynamically favored substance during the cool-down phase of an impact,¹⁴ but whatever the kinetic and thermochemical details its isolation in samples from impact sites substantiates the conclusion developed with the PC approach that organic survival in cometary impacts is highly unlikely.

Finally, it appears that exogenous organic sources may be unacceptable as a class as components of life's origins. Organic materials in micrometeorites and interplanetary dust particles, the largest single source of exogenous carbon by large margin,¹⁵ are converted to graphitic substances during atmospheric entry,¹⁶ and carbonaceous chondrites such as the Murchison meteorite represent an insignificant fraction of the total exogenous carbon supply.¹⁵ Endogenous production from CO₂, N₂, phosphate, and water (unquestionably abundant precursor substances on early Earth) is an appealing point of initiation, and their photochemical conversions to organics prompted by naturally occurring semiconductors is seen by many a promising route to the start of life.^{17–20}

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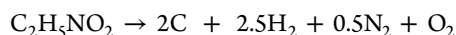
Notes

The authors declare no competing financial interest.

[‡]Retired.

ADDITIONAL NOTE

^aThe Gibbs energy for the carbonization of glycine, for example,



is −240 kJ/mol at 1500 K and falls to −740 kJ/mol at 2500 K. (The values were estimated from data provided in Johnson et al.¹²) It is not clear whether carbon was included as a possible product in the GT simulations, but these values suggest its formation could be the overwhelming chemical route in an impact.

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