

# A Hitchhiker's Guide to Early Earth

*Icy comets crashing  
into a young Earth  
may have brought  
the basic ingredients  
for life.*



**H**OW on Earth did life begin? Or, more precisely, how did life on Earth begin? Theories abound, but all require the existence of basic building blocks such as amino acids to construct the earliest forms of life. One of the most exciting possible sources of these raw materials may have been the comets and asteroids that rained heavily upon Earth during its first billion years. Consequently, while life itself likely arose on Earth, the building blocks of life may well have had an extraterrestrial origin. If this cosmic origin of life's building blocks is correct, the hitchhiking organic molecules would have had to withstand the extreme pressures and temperatures of a fiery crash onto Earth's surface.

Ironically, answers to these questions about the origins of life are intimately connected to questions related to what would happen to the organic molecules of missile-borne chemical weapons if the attacking missile were intercepted by another missile. Like so many seemingly disparate subjects in science, these two are connected at a fundamental level, in this case by questions concerning the fate of organic liquids subjected to strong shock compression.

Past investigators have depended on computer modeling to determine whether the molecules could survive or be destroyed. But the limited success of these computational and theoretical approaches has underscored the long-standing need for experimental answers. Only recently have laboratory experiments been able to explore the chemistry of the extreme shock regimes associated with the delivery of amino acids to early Earth by comets or the fate of missile-borne chemical weapon agents following missile interception.

At Livermore, a team of scientists led by physicist-geochemist Jennifer Blank is conducting a series of shock experiments to explore the viability of

extraterrestrial delivery and to determine what happens to a chemical weapon's payload when intercepted by another missile. Blank says, "These experiments are the closest we can come in the laboratory to investigating the role these primordial ice balls may have played in bringing the building blocks of life to our planet or of testing the effects of missile interdiction on an incoming chemical warhead's payload."

### The Livermore Connection

Blank and her team are using Livermore's 6.2-meter-long, two-stage, light-gas gun to conduct their shock experiments on organic liquids. They are focusing initially on cometary impacts. For decades, Livermore has used its gas guns to perform shock experiments on solid materials. Working with liquids in shock and recovery experiments is much more difficult than working with solids and has not been done before. "Our high-pressure-shock organic chemistry experiments are defining a new area of scientific exploration," Blank notes.

The team's experiments generate impact velocities approaching

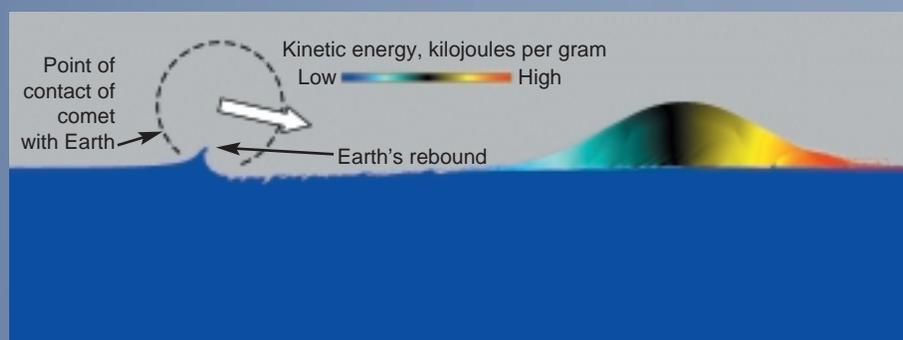
2 kilometers per second, yield temperatures of 500 to 800°C, and produce a maximum impact pressure of 40 gigapascals (about 400,000 times atmospheric pressure). At Mach 6 speed, the gas gun's impactor smashes into a small metal capsule filled with mixtures of amino acids in water, mimicking the supersonic collision of a comet with the rocky surface of Earth.

"Right from the beginning, we knew that something had happened," says Blank. "The solution that went into the capsule was clear, and what came out was golden yellow." Through subsequent chemical analysis, the team discovered that the initial amino acids in the mixture had linked together to form peptides, from which proteins can be formed.

### Cometary Matters

Life as we know it requires three essential ingredients: water, organic matter, and energy. An icy comet carrying organic material that crashes into Earth could potentially supply all of these ingredients in a single, tidy package.

An obvious question remains: Are there amino acids in comets to begin



A two-dimensional simulation of an icy comet hitting the rocky Earth. This image represents the distribution of kinetic energy 678 microseconds after impact, sufficient time for the primary shock wave to pass completely through the comet. The wide distribution of energy in the comet indicates that the comet's trailing portion should be cooler—and experience lower velocity—than the front end. Thus, the rear part of the comet could arrive as a puddle of liquid water, with a high concentration of organic compounds, ready to host further chemical evolution. (Simulation by Greg Miller, Lawrence Berkeley National Laboratory.)

with? Recent experiments conducted at the National Aeronautics and Space Administration's Ames Research Center in Mountain View, California, and at a number of European research centers found that dehydrated amino acids are easy to form in laboratory simulations of interstellar clouds. Scientists do not yet know whether comets incorporate these molecules, but spectroscopic studies of comets suggest that 20 percent of their tails are organic material. Additionally, analysis reveals that meteorites landing on Earth are replete with a variety of complex organic compounds, including more than 70 different amino acids.

What has remained a mystery is the manner in which cometary organic building blocks could survive their journey to the early Earth's surface.

The figure on p. 5 shows a model of a comet smashing obliquely into a rocky Earth. As the collision occurs, the energy of the impact is distributed throughout the comet, splashing jets of material in all directions. A backward splash will have the lowest velocity relative to Earth, so this slower-moving portion would have the greatest chance of surviving as an intact puddle. The temperatures and pressures of these backward jets are also those most readily achievable in laboratory experiments.

The high temperatures created when a comet collides with Earth would certainly cause the breakdown of organic compounds trapped in the collision. However, in the fraction of the second of a strong shock impact, the extreme high pressures can impede or even prevent molecules from breaking down. A predictive theory of the organic chemistry under these extreme conditions does not exist, so

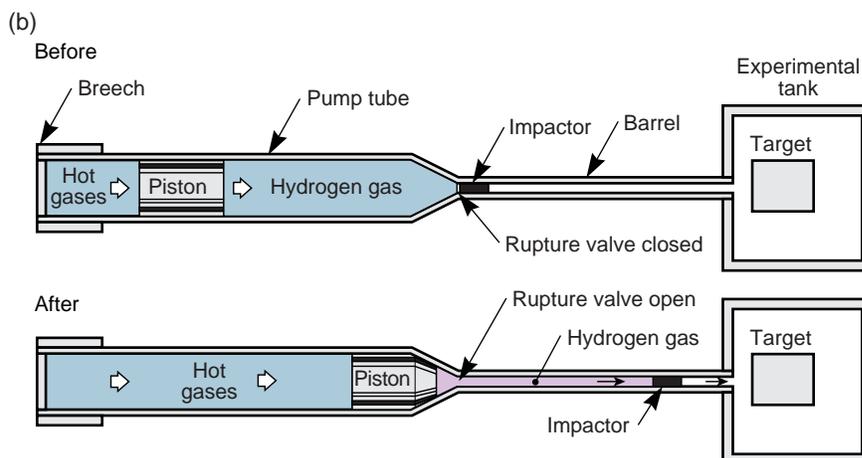
Blank and her team are exploring these uncharted regimes in the laboratory.

### Shock and Recovery

The proxy for a comet in these experiments is a few drops of water and organic material contained in a 2.5-centimeter-diameter stainless-steel capsule. The team's biggest challenge has been to design a capsule capable of keeping its liquid cargo intact during the high-pressure shock loading and release.

Another challenge was to extract the material from the container after it has been smashed by a supersonic projectile. After the still warm capsule is removed from the gas-gun experiment tank, it is machined down on one side to within about 15 micrometers of the liquid inside. The capsule is then pierced with a special drill bit, and the contents are removed with a syringe.

Samples are characterized using liquid chromatography and mass spectrometry (LCMS). A portion of the sample is pushed through a chromatographic column, and as the liquid travels through the column,



(a) A liquid sample is loaded into a capsule, which in turn will be placed into the chamber of Livermore's 6.2-meter-long light-gas gun. (b) A schematic of the gas gun in operation. A gunpowder explosion on the left pushes the piston, which pushes helium gas to open the rupture valve. The projectile then flies down the barrel of the gun to hit the target inside the gun's chamber.

different compounds separate out. (See the [figure on p. 8](#).) Mass spectrometry is then used to determine the mass of each component.

In the few dozen gas-gun experiments performed to date, from 40 to 95 percent of the initial amino acids survived. The fraction of survival depends on the impact pressure, the projectile thickness, the starting concentration of amino acids, and the structure of the amino acids.

An exciting and unanticipated discovery was the nature of the reaction products created by the impact. The dominant products are all possible pairs of the original amino acids joined together by a peptide bond, which implies that some of the energy of the impact has been harnessed to create larger organic molecules. Peptide chains composed of more than two amino acids are also produced in the experiments, though to a lesser degree.

To provide a comparison for the experimental results, Livermore physicist Nick Winter is simulating the pressure dependence of peptide formation on shock loading. Using quantum chemistry methods, Winter is developing computational models that will allow calculation of the pressure dependence of reaction rates.

### Intercepting a Chemical Weapon

An allied series of experiments was performed to determine if missile-borne chemical warfare agents might survive the impact from an intercepting missile. During a missile intercept, portions of the liquid payload of chemical agent would be subjected to strong shock waves. Currently, no information is available about the chemical stability of these compounds in such a scenario. Specifically, nothing is known of the extent to which the payload might be altered as a consequence of the intercept. A substantial portion of the lethal load could be altered chemically

to nontoxic compounds by the shock, reducing the threat posed by the weapon, or the shock could increase the toxicity of the chemicals. A precise knowledge of the chemistry that would occur in an intercept is critical to the design of interception strategies and technologies.

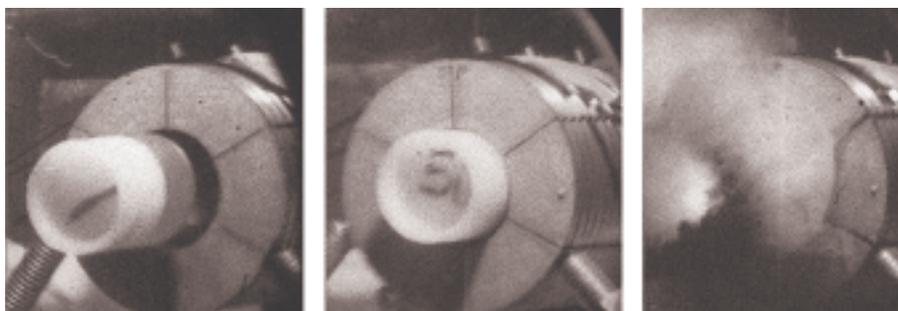
Livermore's gas-gun experiments with simulants of various chemical warfare agents are the first of their kind. The goal is to provide laboratory evidence of whether chemical agents

might survive a missile intercept. Additionally, unique reaction products from such experiments, detectable by remote sensing methods, would constitute a simple means of determining successful intercepts.

To extract a solution after a gas-gun experiment involving chemical weapon simulants, analytical chemists Armando Alcaraz and Pete Nunes of the Forensic Science Center at Livermore use solid-phase microextraction (SPME) methods.



Two 2.5-centimeter-diameter experimental capsules, one (left) filled with a solution of approximately 125 microliters of liquid (amino acids in water) and ready for a shock experiment, the other open to reveal the hollow volume in the center to contain the liquid.



Three still images of the supersonic impactor hitting the stationary test capsule. The projectile's velocity is 0.81 kilometers per second, which is about 2,000 miles per hour. The capsule is inside the cylindrical "pig."

Using gas chromatography–mass spectrometry to characterize the solution before and after an experiment, the chemists have begun to obtain results.

“Again, we knew that something had definitely happened,” says Blank. “The solution that went in was pale yellow, and what came out looked like used motor oil.”

### The Challenges of Scale

Just how real are these laboratory simulations? “Closer than one might expect,” says Blank. “The impact conditions are right on target for simulating defense scenarios. In contrast, the impact temperature of a real ice ball hitting rock would be about 15 to 30 percent higher than the 500 to 800°C attained in our current suite of gas-gun experiments.” One might think that the higher temperatures of an actual impact would destroy more of the organic material. However, the temperatures achieved in the laboratory experiments are already much higher than the thermal

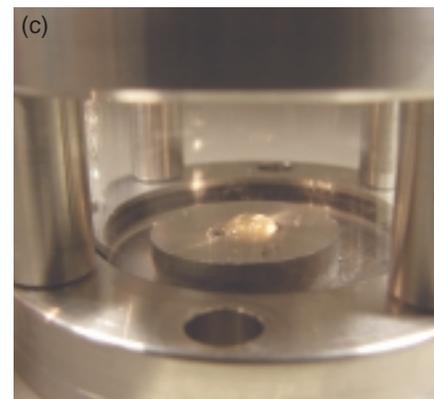
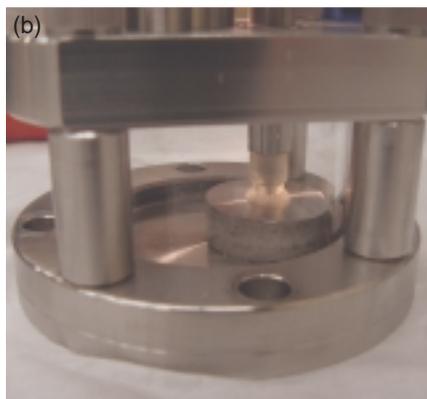
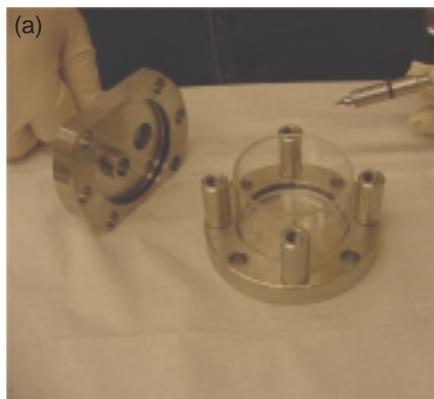
stability limits of amino acids under ordinary atmospheric pressure. Hence the high survival percentages of amino acids show clearly that the destructive effects of high temperatures are buffered by the accompanying high pressures in shock waves.

Another difference between laboratory shock experiments and an actual cometary collision is the duration of the impact shocks. In the experiments, materials are shocked for only a few microseconds, while a 1-kilometer-thick ice ball hitting Earth would experience a shock wave lasting 1 second, a time difference of six orders of magnitude. The experiments assume that the comet is a single dense ball of ice. In reality, comets are known to be aggregates of much smaller objects, so this apparent discrepancy in time scales is much less severe.

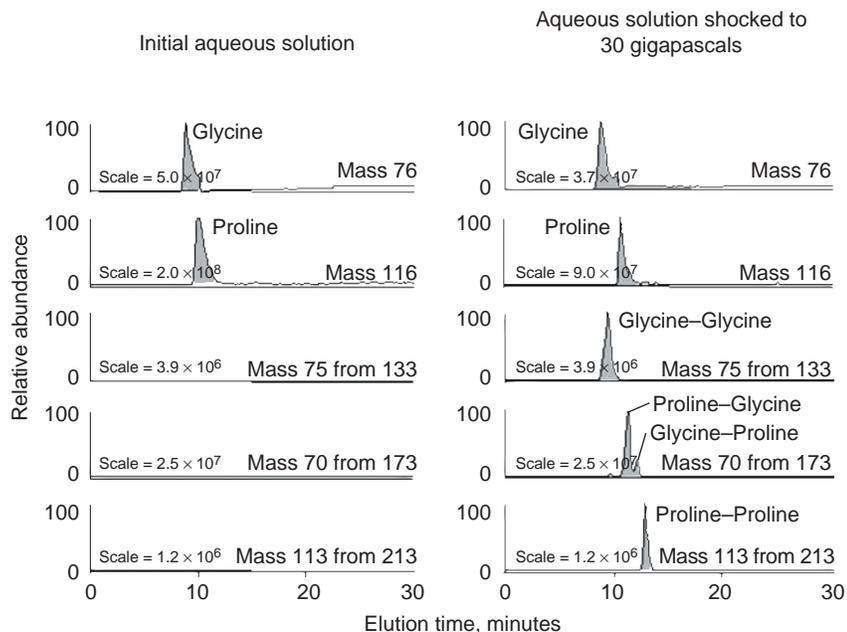
The ultimate in experimental understanding will be to perform real-time spectroscopic analysis of the liquids at 100-nanosecond intervals during the shock process itself. Such measurements

are a technical challenge but would provide a more complete understanding of the physical and chemical evolution of the different reaction pathways from their onset. Obtaining such measurements is a goal that Blank and her team hope to pursue in the future by relying on techniques developed by Laboratory physicist Neil Holmes.

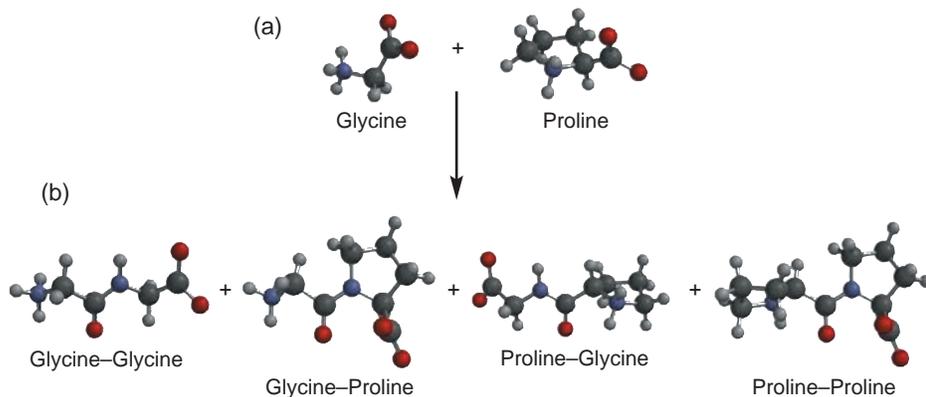
Such short time-scale measurements are also essential to more accurate computer models of the chemistry of high-pressure, high-temperature shock regimes. The quantity of data going into such simulations is so enormous that an accurate representation can cover only a brief period of time, typically a few nanoseconds. Thus, even the supercomputers at Livermore need another generation or two of development before these complex chemical and physical interactions over longer time periods can be simulated. Until then and until the accompanying computer codes can be developed, calibrated, and validated, scientists’



Livermore scientists have developed a new piercing device for extracting liquids under pressure in metal capsules following gas-gun shock experiments. (a) The piercing device consists of a clean glass chamber between two metal plates. The top plate has a connection for a drill bit and a silicon septum through which a needle can pass for sample collection. (b) A shocked capsule is positioned in the piercer under the drill. A Teflon sleeve around the drill bit will capture any spray that occurs when the capsule is punctured. (c) The capsule has been pierced and the drill retracted. Shocked liquid has beaded on the surface of the capsule awaiting collection.



Examples of liquid chromatography–mass spectrometry spectra for a sample solution of two amino acids, glycine and proline. Peaks corresponding to the major compounds are plotted for the sample before and after it was shocked. After the liquid was shocked, some glycine and proline persist and four new compounds are present: glycine–glycine, glycine–proline, proline–glycine, and proline–proline.



This model of dipeptide production shows that when (a) an aqueous solution bearing two amino acids, glycine and proline, is shocked, (b) four dipeptide products may result. The reaction of two amino acids to form a dipeptide is accompanied by production of a water molecule, using a hydrogen atom from one amino acid and an oxygen–hydrogen group from the other, hence the two possible forms of the glycine–proline dipeptide. (Model by Livermore physicist Nick Winter.)

knowledge and understanding depend on experiments such as those being done by Blank and her team.

### At the End Is the Beginning

The Livermore research on shocked organic liquids has been much in the news lately. After all, who doesn't want to know how it all began on Earth? And in a post–September 11 world, a chemical weapon threat is an uncomfortably real possibility that must be countered effectively.

Blank is quick to make clear that the Livermore work depends on the talents of her colleagues in engineering, analytical chemistry, biochemistry, and computer modeling of hydrodynamics and quantum chemistry. Together, this team is bringing a new understanding of how it all could have started. Simultaneously, this research is providing critical information that could help to counter the threat from missile-launched chemical weapons of mass destruction.

**Key Words:** amino acids, astrobiology, liquid chromatography–mass spectrometry (LCMS), origins of life, shock physics, solid-phase microextraction (SPME).

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