Synthesis of glycine-containing complexes in impacts of comets on early Earth

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Delivery of prebiotic compounds to early Earth from an impacting comet is thought to be an unlikely mechanism for the origins of life because of unfavourable chemical conditions on the planet and the high heat from impact. In contrast, we find that impact-induced shock compression of cometary ices followed by expansion to ambient conditions can produce complexes that resemble the amino acid glycine. Our ab initio molecular dynamics simulations show that shock waves drive the synthesis of transient C–N bonded oligomers at extreme pressures and temperatures. On post impact quenching to lower pressures, the oligomers break apart to form a metastable glycine-containing complex. We show that impact from cometary ice could possibly yield amino acids by a synthetic route independent of the pre-existing atmospheric conditions and materials on the planet.

Origins-of-life research focused initially on the production of amino acids from organic materials already present on the planet. In addition to protein production, amino acids and short peptides probably played a significant role in the chemical evolution that led to the emergence of life. Peptide nucleic acids, which consist of a backbone of achiral poly(N-(2-aminoethyl)glycine), were proposed as a precursor to ribonucleic acid (RNA) on early Earth. Polypeptides were shown to catalyse the formation of RNA in an energetically favoured reaction in which activated mononucleotides were used. Seminal experiments observed amino-acid synthesis in a vaporized reducing (H$_2$- and CH$_4$-rich) mixture subjected to electrical discharges to simulate hypothetical conditions on the early planet. However, the actual composition of early Earth’s atmosphere is not known, and the current view is that the atmospheric conditions were more oxidizing, consisting mainly of CO$_2$, N$_2$ and H$_2$O, with only small amounts of CO and H$_2$. Shock-heating experiments and calculations on aqueous mixtures found that synthesis of the organic molecules necessary for amino-acid production does not occur in a CO$_2$-rich environment.

The possibility exists of the production and/or delivery of prebiotic molecules from extraterrestrial sources. Cometary ices are predominantly water, but contain many small molecules important to prebiotic aqueous chemistry, such as CO$_2$, NH$_3$ and CH$_3$OH (ref. 9). Recent analysis of dust samples from comet Wild 2 showed the presence of glycine in the captured material. Interplanetary dust particles accrete icy layers that consist of H$_2$O, CO, CO$_2$, CH$_3$OH and NH$_3$ (ref. 12). The flux of organic matter to Earth from comets and asteroids during periods of heavy bombardment may have been as high as $10^{13}$ kg yr$^{-1}$, delivering up to several orders of magnitude greater mass of organics than probably pre-existed on the planet.

The median nucleus radius of short-period comets was measured as 1.61 km, and long-period comets can have nucleus radii up to 56 km (ref. 14). A comet of such sizes that passes through Earth’s atmosphere will be heated externally, but will remain cool internally. On impacting the planetary surface, a shock wave will be generated because of the sudden compression. The shock wave travelling through the comet will compress a small section of material on a timescale limited by the rise time of the shock wave (<10 ps). A shock wave causes a reactive material to visit numerous thermodynamic states during the course of compression. Shock waves can create sudden, intense pressures and temperatures, which could affect chemical pathways and reactions within a comet before interactions with the ambient planetary atmosphere can occur. Until now, the overall delivery and/or production of amino acids from these impact events was thought to be improbable because of the extensive heating (thousands of K) from the impact, which would cause pyrolysis of organic compounds. However, an oblique collision in which an extraterrestrial ice impacts a planetary atmosphere with a glancing blow would generate much lower temperatures. Shock compression followed by rarefaction wave and subsequent expansion would occur over the course of several seconds. Under this scenario, organic materials could potentially be synthesized within the interior of the comet during shock compression and survive the high pressures and temperatures. On expansion, stable materials, such as amino acids, could survive interactions with the planetary atmosphere or ocean. These processes would result in large concentrations of organic species being delivered to Earth from exogenous sources. Shock-compression experiments on comet mixtures showed that a high percentage of pre-existing amino acids survived relatively low pressure conditions (412–870 K and 5–21 GPa; 1 GPa = 10 kbar) and that mixtures resembling carbonaceous chondrites can produce a variety of organic material at pressures of ~6 GPa (ref. 20). The production of amino acids by ultraviolet irradiation of interplanetary dust particles and amino-acid condensation in the presence of a catalyst were investigated. Hydrodynamic simulations of large comet impacts indicated the release of large quantities of gas by carbonaceous rock. Nonetheless, to date few studies are reported on the production of prebiotic molecules at both the extreme temperatures and pressures (for example, >1,000 K and 20 GPa) that result from the impact of a large icy body such as a comet.

Molecular dynamics (MD) simulations provide an accurate description of shock compression, which can greatly facilitate experimental design and interpretation. Simulating the breaking and forming of chemical bonds behind a shock front frequently requires the use of a quantum theory such as density functional theory (DFT).
for example, see Gygi and Galli23). DFT has been shown to reproduce accurately the high pressure–temperature properties of a number of systems, including deuterium24, nitrogen25, carbon26 and the solid and liquid phases of water26–28. Here, we report DFT–MD simulations of amino-acid synthesis in a shock-compressed prototypical astrophysical ice mixture. DFT–MD simulations can access readily the picosecond timescales associated with the rise time of a shock wave25,28. To perform simulations of the unique thermodynamic conditions of a shock25,29 and minimize the usual system–size issues37, we used the multiscale shock-compression simulation technique (MSST)28–31. MSST allows for an approximate treatment of the hydrodynamic effects in cometary impact, combined with a realistic description of the chemistry at extreme conditions. MSST is a simulation methodology based on MD and the Navier–Stokes equations for compressible flow. Instead of simulating a planar shock wave within a large computational cell with many atoms, the MSST computational cell follows a Lagrangian point through the shock wave. MSST does not include non-planar shock waveforms. MSST was shown to reproduce accurately the shock Hugoniot (thermodynamic end states) of a number of systems25,28, as well as the sequence of thermodynamic states throughout the reaction zone of shock-compressed explosives31. MSST can reproduce the same shock-wave profiles, physics and chemistry as found in direct, multi-million particle simulation of shock compression32 (see Supplementary Information for more details).

Amino acids contain both amine (–NH₂) and carboxyl (–COOH) functional groups, and require the formation of C–N bonds for their synthesis. Protein synthesis is driven by peptide bond formation, that is C–N bonds formed between –COOH and –NH₂ groups from different amino acids with an H₂O group eliminated. Hence, our goal is to create a more fundamental understanding of C–N bond formation and the survivability of such species as a function of elevated temperatures and pressures caused by shock compression. Similar to previous experiments32, our studies contained a mixture of H₂O, CH₃OH, NH₃, CO and CO₂ in a molar ratio of 2:1:1:1:1, respectively. Our simulations (706–4,083 K, 10–59 GPa) far exceeded the pressure–temperature ranges of previous shock-compression studies13,20. Simulations at higher temperatures and pressures resulted in excitations beyond the electronic ground state, similar to those of a plasma. Our computed shock Hugoniot results show correspondence with previous experimental33,34 and theoretical28 results for liquid water (see Supplementary Information).

Astrophysical ice with an initial velocity of 29 km s⁻¹ (approximate median encounter velocity of Earth13) would have to impact the Earth at an angle of 8° to achieve a shock velocity of 5 km s⁻¹, and at 24° for 10 km s⁻¹. For a shock velocity of 10 km s⁻¹, the impact angle distribution model of Shoemaker35 gives a cumulative probability of 17%. Shock velocities from previous studies12,20 correspond to probabilities of impact of about 0.5% and 2%, respectively. Inset: computed impact angles for our simulated shock velocities.

**Results and discussion**

A constant-pressure state was achieved within 0.4–3.0 ps in all shock-compression simulations. The time over which cometary 10.11 km would be held in this hot, compressed state before the arrival of a rarefaction wave and subsequent decompression is approximately 0.4 seconds (see Supplementary Information). However, previous results show the rise time of the shock wave (the viscosity-induced width of the shock front) in polycrystalline materials to be <10 ps (refs 15,16). Shock-compression studies of materials with micrometre-sized grains (similar to grain sizes found in comets9) found sharply focused shock waves that traversed across each individual grain37. Our shock-compression simulations (up to 11 ps in length) thus span the relevant timescales that correspond to the initial chemistry behind the shock wave within an ice grain in a comet. These timescales are amenable to study by laser shock-compression experiments39.

After compression, our simulations formed a series of new compounds (Fig. 2). At 47 GPa (shock velocity of 9 km s⁻¹, Hugoniot temperature of 3,141 K) almost none of the starting materials remained, aside from small mole fractions of H₂O and NH₃. We observed a number of complex C–N bonded species and H⁺ ions. Our results showed that the C–N bond kinetics achieved a steady state after several picoseconds (see Supplementary Information). The quantity and complexity of C–N bonded species grew rapidly as a function of pressure. We have analysed the chemical species prevalent in the shock-compressed astrophysical ice at these conditions.

We defined molecular species using a pre-established methodology of optimal bond cutoff distances and lifetimes38–40. At 10 GPa (5 km s⁻¹, 706 K) we observed the formation of NH₂COO⁻ (namely, carbamate, the simplest molecule that contains both amine and carboxyl groups). The carbamate anion (unstable under ambient aqueous conditions) formed within 2 ps of shock compression, and survived through the remainder of the simulation. On achieving a steady pressure state, approximately 76% of the starting material remained, and the lifetime of H₂O was calculated as 1.65 ps, many orders of magnitude shorter than its lifetime at ambient conditions (~10 hours41). Water at extreme conditions was shown to catalyse chemical reactivity in C–N–O–H materials42. At 24 GPa (7 km s⁻¹, 1,590 K), we observed that 53% of the starting material remained, and that the H₂O lifetime decreased to 360 fs. Thus, we expected a high degree of chemical reactivity at these conditions. At this pressure and temperature we observed a mole fraction of 0.05 for many different C–N bonded species with lifetimes between 65 and 120 fs, and an additional mole fraction of 0.03 for C–N bonded species with lifetimes <50 fs. In addition, we calculated an H⁺ mole fraction of 0.11. The free hydrogen ions created a localized reducing environment that could drive C–N bond formation in otherwise oxidizing conditions. Shock compression to 47 GPa (9 km s⁻¹, 3,141 K) and 59 GPa (10 km s⁻¹, 4,083 K) both yielded a similarly high degree of reactivity.
of chemical reactivity and molecular ionization throughout the simulations. We discuss the trajectory at 47 GPa in detail here.

At 47 GPa, the highly transient nature of covalent bonding in the hot, compressed system produced a large number of short-lived species, which yielded a computed mole fraction of C–N bonded species of 0.03. The atomic fraction of C–N bonded species (number of atoms in C–N bonded species divided by the total number of atoms in the simulation) was approximately 24%. The mole fraction of H\textsuperscript{+} increased to 0.35. Only 16% of the starting material remained, and the H\textsubscript{2}O lifetime decreased to \textless 80 fs. At this point it became difficult to describe the system as having molecular species because the calculated lifetimes were all roughly equal to the chosen cutoff. Under these extreme conditions, we observed a large number of exotic C–N bonded species (Fig. 3a). NH\textsubscript{2}COO\textsuperscript{−} was observed to react with organics such as HCOOH to form larger, transient species. Some species showed the formation of C–C bond chains by reactions with CO\textsubscript{2} and HCO\textsuperscript{−} moieties, indicative of a mechanism that could form complex amino acids.

To approximate the expansion that occurs immediately after planetary impact and shock compression, we expanded the system from 47 GPa in discrete constant pressure–temperature (NPT) steps along the water isentrope. Each step was between 2 and 4 ps in duration, for a total expansion simulation time between 15 and 28 ps. The water isentrope was computed from a recent equation of state\textsuperscript{43} (see Supplementary Information). Cometary ice with a radius of 1.61 km and a speed of sound similar to that of water (1.482 km s\textsuperscript{−1} at 20 °C) takes over two seconds to expand. It is not possible to model this timescale by MD simulation. However, the expanding comet visits approximately the same locus of thermodynamic states as our expansion simulations. Calculations have shown that the chemical reactions within expanding cometary materials quench at temperatures between 2,000 and 3,000 K (ref. 7). After expanding to a pressure of 0.5 GPa and a temperature of 1,550 K, the system remained largely unreactive on the timescales...
of our simulations. Longer timescale effects of elevated post shock temperatures on chemical products are the subject of future work. Further expansion along the isentrope would yield a low-density gas, which would be difficult to simulate with our plane-wave-based DFT method. To test the stability of compounds formed during our simulations, we quenched the system temperature in three sequential steps to 300 K. After expanding the simulation cell, NPT simulations were run at 300 K for an additional 10–20 ps. The longest of our simulations of the adiabatic expansion covered approximately 50 ps in total. A single expansion–cooling cycle required ~80,000 central processing unit hours, which limited the rate at which the cycle could be performed. Determination of the chemistry after adiabatic expansion as the material interacts with the planetary environment was beyond the scope of this study.

Several quenches were performed with varying numbers of NPT steps and at different points in time along the shock-compressed trajectory, all of which exhibited the survival of several stable C–N bonded species (Fig. 3b). In particular, we observed consistently a synthetic route to complexes that resembled the amino acid glycine through the decomposition of large C–N bonded oligomers. Glycine is the simplest proteinogenic amino acid and has a chemical formula of NH₂CH₂COOH. We observed a possible mechanism for its ‘shock synthesis’ which began with the formation of its C–N backbone during shock compression (Fig. 4a). The high pressures and temperatures allowed for the rapid formation of the C–N bonded oligomers, which contain sequences of carbon and nitrogen atoms that resemble those of several amino acids. Isentropic expansion caused the oligomer to break apart into smaller fragments (Fig. 4b). These fragments were highly reactive and had lifetimes between 50 and

Figure 4 | Mechanism for glycine–CO₂ complex synthesis on expansion and cooling. a, The high pressures and temperatures from shock compression (47 GPa (9 km s⁻¹)) caused a large C–N bonded oligomer to form. In this species, we observed a sequence of carbon and nitrogen atoms that corresponded to that of glycine (only the atomic sites that eventually form the complex ⁻OCO–NH–CH₂–COOH are shown here and in (b) and (c)). b, During isentropic expansion (16.6 GPa, 2,673 K), the large C–N bonded chain in (a) broke apart to form several fragments. The C–N sequence that corresponds to glycine remained intact during the expansion. A significant quantity of H⁺ ions remained in the system, although we also observed an increase in the number of H₂O molecules. c, On cooling to the initial conditions (0.5 GPa, 300 K), we observed the formation of several stable and metastable C–N bonded species, including HCN, NH₂–COOH and a more complex molecule with several C–N bonds. A single CO₂ molecule was observed also. Smaller moieties, such as H and OH, are eliminated from the C–N backbone that forms ⁻OCO–NH–CH₂–COOH. This species can react with a proton source, such as H₃O⁺, to form glycine.
200 fs, although their C–N backbone could remain intact. Cooling then caused the fragments to eliminate smaller moieties (for example, OH and H) to form species such as the anion $\text{OCO–NH–CH}_2$–COOH (Fig. 4c). This glycine–CO$_2$ complex requires a one-step protonation reaction to form glycine. We computed significant mole fractions of H$_2$O$^+$ (0.03) and NH$_4^+$ (0.07) in our cooled and expanded simulations. Calculations with a quantum-chemical solvation model$^{44}$ showed that protonation of $\text{OCO–NH–CH}_2$–COOH either by H$_2$O$^+$ or NH$_4^+$ in a solvent environment representative of the shock-mole, cooled simulation, was thermodynamically favourable. The glycine–formation reaction of $\text{OCO–NH–CH}_2$–COOH + H$_2$O$^+$ ↔ CO$_2$ + H$_2$O + NH$_4$–CO$_2$–COOH has a Gibbs free energy of reaction ($\Delta G_m$) of $\pm 24.2$ kcal mol$^{-1}$. The reaction of $\text{OCO–NH–CH}_2$–COOH + NH$_4^+$ ↔ CO$_2$ + NH$_4$ + NH$_2$–CH$_2$–COOH has a $\Delta G_m$ of $\pm 2.2$ kcal mol$^{-1}$ (see Supplementary Information for more details). Thus, the complex C–N bonded oligomers could form glycine given realistic timescales of the isentropic expansion model$^{44}$. We performed simulations at shock velocities (km s$^{-1}$) for all elements in the system. We employed Goedecker–Teter–Hutter pseudopotentials$^{47}$ with the Becke–Lee–Yang–Parr exchange correlation functional$^{48,49}$. We returned by stardust.$^{319,320}$

Conclusions

Our simulations provide a possible mechanism for the ‘shock synthesis’ of prebiotic molecules on early Earth that is independent of the atmospheric conditions and materials already present on the primitive planet. Novel experiments capable of monitoring complex time-dependent chemical reactivity in shock-compressed systems$^{48}$ hold promise to verify this synthetic route. On shock compression, we observed a high degree of chemical reactivity at extreme, reduced environments. This reactive environment helps induce the formation of C–N bonded oligomers that contain sequences of C–N bonds equivalent to those of alpha amino acids. On quenching to lower pressures and temperatures, the oligomers break apart to form more stable complexes. Many of these complexes can react easily with H$^+$ to form glycine. Other exotic, metastable C–N species that we observed in our quenched simulations could conceivably form more complex amino acids or even peptide chains that resemble the proteins needed for the formation of life.

Methods

DFT-MD simulations. All simulations were performed with the CP2K molecular simulation software suite,$^{4,6}$ using the Born–Oppenheimer approximation to maintain the system in its electronic ground state. Interatomic potentials were thus calculated on the fly from directly solving the Schrödinger equation. We used a plane-wave cutoff of 400 Ry and an optimized double zeta valence polarized basis set for all elements in the system. We employed Goedecker–Teter–Hutter pseudopotentials$^{47}$ with the Becke–Lee–Yang–Parr exchange correlation functional$^{48,49}$. We performed simulations at shock velocities (km s$^{-1}$) for all elements in the system. We employed Goedecker–Teter–Hutter pseudopotentials$^{47}$ with the Becke–Lee–Yang–Parr exchange correlation functional$^{48,49}$. We returned by stardust.$^{319,320}$

References

A method for tractable dynamical kinetics in dynamically compressed amorphous carbon.


A transient semimetallic layer in detonating nitromethane.


A study of graphite under shock compression.


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