Biomolecule formation by oceanic impacts on early Earth

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Intense impacts of extraterrestrial objects melted the embryonic Earth, forming an inorganic body with a carbon-dioxide- and nitrogen-rich atmosphere[1,2]. Certain simple organic molecules have been shown to form under conditions resembling meteorite impacts, although the link between these events and the development of more complex molecules remains unclear[3]. Ordinary chondrites, the most common type of meteorite, contain solid carbon, iron and nickel—elements essential to the formation of organic chemicals[4,5]. Here we use shock experiments to recreate the conditions surrounding the impact of chondritic meteorites into an early ocean. We used a propellant gun to create a high-velocity impact into a mixture of solid carbon, iron, nickel, water and nitrogen. After the impact, we recovered numerous organic molecules, including fatty acids, amines and an amino acid. We suggest that organic molecules on the early Earth may have arisen from such impact syntheses. As the natural impacts that were frequent on the early Earth are more sustained and reach higher pressures than our experiments[6,7], they may have resulted in the synthesis of a greater abundance, variety and complexity of organic compounds.

Miller's synthesis of organic molecules from atmospheric gases—CH_4, NH_3 and H_2O—is well known. It spurred many studies using energy sources including impact energy[8–10]. However, the early atmosphere is thought to have been moderately oxidative, composed mostly of CO_2 and N_2 (refs 1,2), from which synthesis of organic molecules such as amino acids is difficult[11,12]. How and when organic molecules appeared in abundance in the inorganic world of the early Earth are therefore fundamental questions related to the origin of life on Earth.

Accretion of proto-planets and planetesimals formed the Earth about 4.5 Gyr ago; the collision energy of this process melted the Earth[13]. When the accretion slowed and the Earth's surface temperature decreased, atmospheric water condensed, forming the early ocean about 4.3 Gyr ago[14]. Rocks of sedimentary origin in Isua, Greenland, show that the Earth was widely covered by oceans from 3.8 Gyr ago at the latest[15]. Furthermore, lunar crater records suggest that impacts of extraterrestrial objects occurred with great frequency during those periods[6,7].

Average chemical compositions of such extraterrestrial objects are likely to have resembled those of terrestrial planets and ordinary chondrites. More than 85% of recovered meteorites are classified as ordinary chondrites[16], comprising mostly olivine, metallic iron and small quantities of solid carbon[4,5]. A laser shock experiment designed to simulate a terrestrial impact of an ordinary chondrite synthesized simple molecules such as hydrogen

cyanide, acetaldehyde and some simple hydrocarbons[3]. These factors lead us to suggest a working hypothesis: the bulk of organic molecules necessary for life's origins were generated by oceanic impacts of extraterrestrial objects containing metallic iron and solid carbon. This could have occurred through reactions of those minerals, together with oceanic water and atmospheric gases at high pressures and temperatures[17,18]. Previous results of shock recovery experiments support this hypothesis: such impacts can synthesize high yields of ammonia[19]. Metallic iron reduces water, thereby forming a hydrogen-rich locally reduced atmosphere. Furthermore, iron catalyses surrounding materials for both Haber–Bosch and Fischer–Tropsch type reactions, forming ammonia and hydrocarbons. Substantial amounts of solid carbon were probably supplied by extraterrestrial objects of chondrite compositions[20]. Such abundant solid carbon cannot be ignored as a carbon source of the organic compounds in the early Earth. To the best of our knowledge, no previous study has examined oceanic impacts of ordinary chondrite, which occurred frequently on the early Earth, as a process of producing organic molecules necessary for life's origin.

This letter presents a facile synthesis of various organic molecules in shock recovery experiments targeting mixtures of solid carbon (^{13}C), metallic iron, metallic nickel, water, gaseous nitrogen and ammonia, thus demonstrating the plausibility of our hypothesis (Table 1). For the experiments, we used a single-stage propellant gun in a previously reported system[19,21,22]. Starting materials were encapsulated in a stainless-steel sample container and were subjected to shock compression by hypervelocity impact (see the Methods section; Supplementary Information, Fig. S1) under the conditions presented in Table 1. For the experiments described herein, the shock pressure and duration have respective upper limits of about 6 GPa and about 0.7 μs because of experimental restrictions[19,21]. The shock pressure corresponds approximately to that of an impact of ordinary chondrite to an ocean with velocity of about 2 km s^{-1} (see Supplementary Information). The post-shock temperature is estimated as about 2,900–5,000 K assuming ideal gas behaviour (see Supplementary Information).

The most serious problem for this type of study is distinguishing synthetic organic molecules from those that are present adventitiously, although experiments and analyses are carried out very carefully to avoid contamination. In this study, solid ^{13}C-carbon was used as the carbon source. The products were identified using mass spectrometers coupled to gas or liquid chromatographs (GC–MS and LC–MS; see Supplementary Information, Methods). The detection of ^{13}C-enriched molecules verifies their experimental origin, as ^{13}C makes up only 1.1% of the total naturally occurring

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Table 1 | Experimental conditions and organic molecules produced.

Run No.		SA004	SA007	SA006	BL004	BL007
Samples	Fe (mg)	200	200	200	200	200
	Ni (mg)	20	20	20	20	20
	^{13}C (mg)	30	30	30	30	30
	H_2O (mg)	130	130	0	130	130
	NH_{3aq} (mmol)	1.95	0	0	1.95	0
	N_2 (μmol)	15	15	15	—	—
	Impact velocity (km s^{-1})	0.9	0.9	0.9	0	0
Products (pmol)	^{13}C-acetic acid	2,200	1,360	NA	ND (17,600)	ND (14,200)
	^{13}C-propanoic acid	1,020	440	NA	ND (tr.)	ND (tr.)
	^{13}C-butanoic acid	136	88	NA	ND	ND
	^{13}C-pentanoic acid	22	24	NA	ND	ND
	^{13}C-hexanoic acid	tr.	ND	NA	ND	ND
	^{13}C-2-methyl propanoic acid	D	D	NA	ND	ND
	^{13}C-methylamine	16,700	7,430	ND	ND (94)	ND (18)
	^{13}C-ethylamine	945	280	ND	ND (63)	ND (17)
	^{13}C-propylamine	89	12	ND	ND (2)	ND (2)
	^{13}C-butylamine	tr.	ND	ND	ND (tr.)	ND (tr.)
	^{13}C-glycine	24	ND	ND	ND (261)	ND (1,190)

NA, ND, tr. and D respectively represent not analysed, not detected, detected in trace amounts and detected. Amounts of ^{12}C-organic molecules in starting materials are listed in parentheses as references. Uncertainty is of the second order.

carbon (see the Supplementary Information for more information regarding contamination and possible isotopic exchange.

The recovered container's outer surface was cleaned after impact treatment. Several small holes were drilled in it after freezing with liquid nitrogen. The products, in wet powder form, were subsequently recovered through the holes. Extraction procedures for organic products are summarized in Supplementary Information, Fig. S2 and Methods. The extracted products were divided into three portions and subjected to respective analyses for carboxylic acids, amines and amino acids. Analyses using GC–MS and LC–MS required appropriate pre-treatment of samples, for example, derivatization of amino groups (see Supplementary Information, Methods). X-ray powder diffractometry analyses of the extraction residue confirmed reduction of water by metallic iron. The X-ray powder diffractometry analyses of the solid residue indicate that the iron in the starting materials was partially oxidized to magnetite and wüstite (see Supplementary Information, Fig. S3).

A total-ion chromatogram (TIC) of SA007, showing peaks of the ^{13}C-carboxylic acids from acetic to pentanoic acid, is presented in Fig. 1a. Mass spectra of respective carboxylic acids are presented in Fig. 1b–e, with numbered peaks attributable to fragments of the respective ^{13}C-carboxylic acids, as indicated in the inset molecule diagram. Similar TIC and mass spectra of SA004 are shown in Supplementary Information, Fig. S4. The TICs of a derivatized test solution containing ^{12}C-methylamine and ^{12}C-ethylamine, derivatized SA004 and derivatized SA007 are presented in Fig. 2a–c with mass spectra in the insets. Similar selected-ion chromatographs of propylamine are shown in Supplementary Information, Fig. S5. An amino acid, ^{13}C-glycine, was also identified in SA004 using selected-ion chromatography and mass spectroscopy (Fig. 3). These spectra prove these shock recovery experiments synthesized various ^{13}C-carboxylic acids and ^{13}C-amines as well as ^{13}C-glycine. Table 1 presents the quantities of these organic molecules along with experimental conditions.

Our results demonstrate the production of various biomolecules and their precursors in laboratory impact reactions involving metals, carbon, water and gaseous nitrogen (SA007). Carboxylic acids and amines with different saturated hydrocarbon substituents

were identified from these reactions. The carboxylic acids included fatty acids with hydrocarbon chains longer than the propyl group. Glycine, an amino acid, is also produced when the starting material contains aqueous ammonia (SA004). It is noteworthy that the present glycine was synthesized using a more natural mechanism than Miller-type synthesis. In that synthesis, amino-acid precursors are heated with strong acid for hydrolysis[9]. For detection of amino acids in meteorites, a similar treatment by strong acid is used[23]. Such treatment does not occur in natural synthesis of amino acids.

Among the products obtained in this study, there must be other, as yet undetermined, products. In fact, the saturated hydrocarbon chains of the carboxylic acids and amines that were formed suggest the presence of unsubstituted hydrocarbons as long as hexane (Table 1, Supplementary Information, Fig. S6). Alcohols, aldehydes, nitriles and sugars might also be available as products.

These results demonstrate that the starting materials all reacted strongly under the condition of the in-shock high pressures, 6 GPa, and in post-shock high temperatures, 2,900–5,000 K. Such high temperatures would probably ionize or atomize all vaporized materials. Organic molecules were therefore most likely to have been synthesized following the temperature decrease during the post-impact process.

Natural impacts on the early oceans occurred on far larger scales in terms of projectile size and velocity than in the present experiments[6,7]. Such impacts must have been followed by large post-impact plumes containing large amounts of source materials and variable conditions of temperature, pressure and gas composition. Therefore, natural impacts to the Hadean oceans probably synthesized a greater abundance, variety and complexity of organic molecules than those of the present experiments. The resultant hydrophilic molecules could have been dissolved, accumulated in the early oceans and subjected to successive impacts of similar objects containing metals. Such a sequence of events might have synthesized increasingly elaborate molecules. The glycine synthesized in the present experiment using aqueous ammonia as a nitrogen source verifies this explanation (SA004) because ammonia might have been formed in a previous impact[19]. The present results therefore suggest that
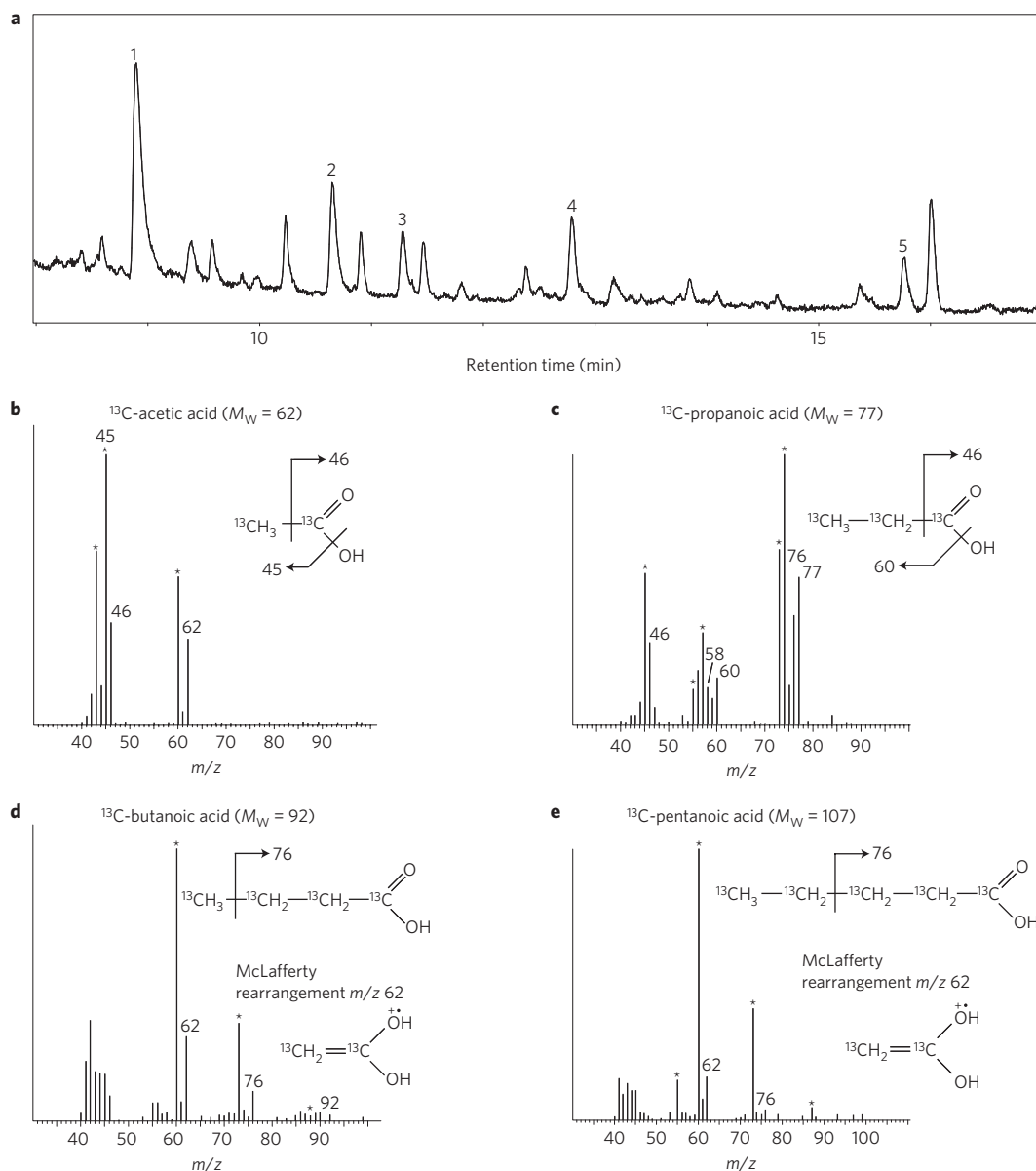
Figure 1 | TIC and respective mass spectra of carboxylic acids for SA007. a, TIC. Numbered peaks: 1, acetic acid; 2, propanoic acid; 3,2-methylpropanoic acid; 4, butanoic acid; 5, pentanoic acid. **b**, Mass spectrum for peak 1 in **a**. **c**, Mass spectrum for peak 2 in **a**. **d**, Mass spectrum for peak 4 in **a**. **e**, Mass spectrum for peak 5 in **a**. The numbers indicate the molecular weights of fragmented ions shown in the inset molecular diagram. Asterisks indicate fragmented ions originated from contaminated ^{12}C-carboxylic acids.

organic molecules were accumulated during oceanic impacts of extraterrestrial objects and were subsequently evolved to larger molecules by successive impacts.

The total mass of accreted materials on the Earth during 4.4 to 3.8 Gyr ago has been estimated as 4×10^{24} g (ref. 20). Considering this estimation and the fact that ordinary chondrites have average carbon concentrations of 0.1 wt%, the accumulated mass of organics that could be made available during successive oceanic impacts can be estimated as at least 1.04×10^{17} g using the 'conversion' rate from solid carbon to organic compounds in the present experiment: 2.6×10^{-5} (see Supplementary Information). The value of the accumulated organic mass, 1.04×10^{17} g, must be an underestimate because the amount of unanalysed organic compounds is not included in the 'conversion' rate that is used here.

Amino acids and various organic compounds have been identified in some carbonaceous chondrites and were formed in some experiments simulating cometary environments. These engender the hypothesis that prebiotic amino acids were delivered by extraterrestrial objects to the early Earth[23,24]. However, decomposition of organic molecules by heat generated by the impact is inevitable[25]. Furthermore, the lack of metallic iron in the carbonaceous chondrites promotes the oxidation of these organic compounds during impact events. These factors suggest that the organic compounds in carbonaceous chondrite, although they can be delivered, might have difficulty surviving ocean impacts in a large mass. A numerical simulation shows that amino acids and other organics in a comet of typical size are unlikely to survive impacts on the Earth[26]. Moreover, comet impacts were likely to have been too infrequent to explain the accumulation of organic molecules on the Earth, as suggested by the discrepancy in hydrogen isotope ratios between the Earth's ocean and comets[27].

A previous report has proposed formation of carboxylic, hydroxy and amino acids on the basis of experiments assuming Hadean submarine hydrothermal environments[28]. However,
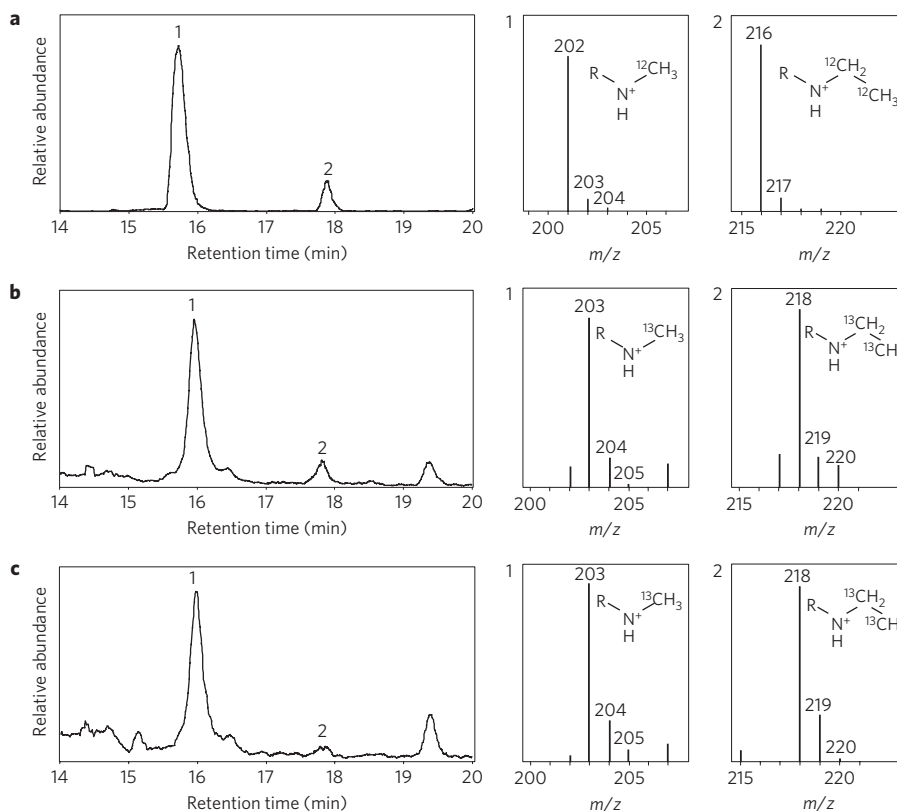
Figure 2 | TICs, $m/z = 201$–221 and respective mass spectra of amines for a standard test solution, SA004 and SA007. Numbered peaks: 1, derivatized methylamine; 2, derivatized ethylamine. The subsistent group, R, in the inset molecular diagrams is $C_{10}H_7N_2O$. **a**, Standard test solution containing derivatized methylamine and ethylamine. **b**, Derivatized SA004. **c**, Derivatized SA007. The mass spectra reflect syntheses of these amines, which are composed of ^{13}C-carbons.
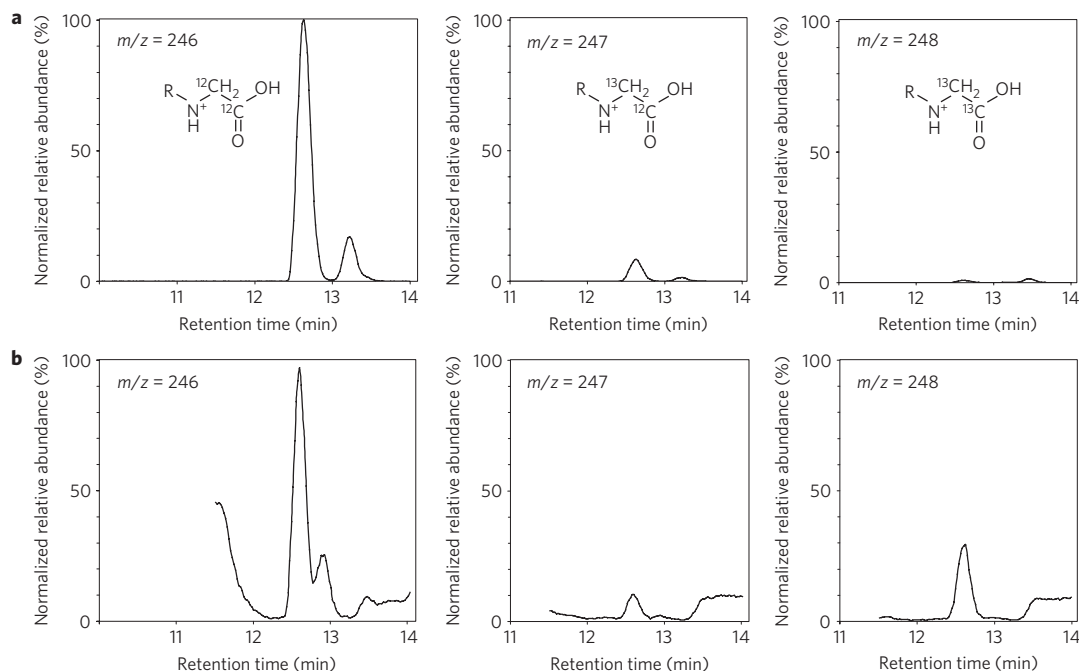
Figure 3 | Comparison of respective selected-ion chromatographs of derivatized standard glycine and SA004 for $m/z = 246$, 247 and 248. R: $C_{10}H_7N_2O$. **a**, Derivatized glycine standard solution. Their relative abundances, normalized by that for $m/z = 246$, reflect the natural carbon isotope ratio. **b**, Derivatized SA004 for $m/z = 246$, 247 and 248. Peaks for $m/z = 246$ and 247 are attributable to contamination represented by the similarity of their relative abundance with those of standard glycine. The peak for $m/z = 248$, higher than that for $m/z = 247$, reflects the experimental origin of glycine: it is composed entirely of ^{13}C-carbons.

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previous syntheses of biomolecules in submarine hydrothermal conditions have been questioned because of the assumptions of geologically unusual conditions: high concentrations of CO, KCN and CH_3SH (ref. 29). In contrast, the experiments described herein are based on more plausible sources of carbon and nitrogen on the early Earth, and also on a plausible mechanism to form a locally reduced atmosphere that is chemically adequate for synthesis of organic compounds.

An experimental simulation presuming a terrestrial impact of ordinary chondrite showed synthesis of hydrogen cyanide, acetaldehyde and some hydrocarbons[3]. Those are, however, simple molecules that differ greatly from biomolecules. The present results suggest that an impact to water (ocean) is necessary for sufficient hydrogenation of carbon to synthesize biomolecules and their precursors necessary for life's origin.

In a previous study involving experimental simulation of an oceanic impact by ordinary chondrite, we formed ultrafine particles of olivine and serpentine[22]. Those fine particles can be dispersed in the ocean and altered easily to clay minerals. They could have absorbed substantial amounts of the concurrently synthesized organic molecules[18]. They might then have been deposited as marine sediments in which further pre-biotic evolution is expected to have proceeded[17,18,30]. A fraction of the molecules might have undergone further evolution as a precurser to life, with the remainder subducting to the deep crust and mantle, where conversion to graphite or diamond occurred.

Methods

Materials. All experimental tools used for manipulation of samples and solvents were fabricated from glass and heated at 450 °C for at least 6 h before every use to eliminate organic contaminants from the experiments.

Starting materials were mixtures of iron (99.9 wt%, powder, <45 μm in diameter; Wako Pure Chemical Industries), nickel (99.95 wt%, sponge; Wako) and carbon powder (97 wt%, 99% ^{13}C, amorphous; Cambridge Isotope Laboratories). Both iron and nickel were washed with acetone (HPLC grade; Wako) and hexane (RP·PCB analytical grade; Wako), followed by rinsing with a large amount of distilled water (HPLC grade; Wako). The cleaning process was applied three times before experimental runs. The sample container was washed using a process similar to that for the metal powders. Powder of ^{13}C-enriched carbon was pre-heated at 1,500 °C in vacuum for 2 h and at 2,000 °C in N_2 gas for 2 h. These powders were mixed with either water (HPLC grade; Wako) or ammonia hydroxide (28 wt%, double distilled, PPB/TEFLON grade; Aldrich). The N_2 gas used as a starting material was of >99.99995% volume purity. The mixtures of powders and N_2 were enclosed in stainless-steel sample containers, as shown in Supplementary Information, Fig. S1.

Extraction procedures. Extraction procedures for the organic molecules produced in the shock experiments are shown schematically in Supplementary Information, Fig. S3. Both amines and carboxylic acids are volatile, therefore, hydrochloric acid (constant boiling; Sigma-Aldrich) and potassium hydroxide (<85 wt%; Wako) were used respectively to convert them to non-volatile salts. Carboxylic acids were extracted into dichloromethane (RP·PCB analytical grade; Wako) before GC–MS analyses.

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Author contributions
H.N. proposed the impact synthesis hypothesis and conducted this study. Y.F. and T.S. carried out the shock recovery experiments. Y.F. extracted organic compounds and analysed amines and amino acids using LC–MS. M.O. and Y.F. analysed carboxylic acids using GC–MS. Y.F. and H.N. prepared an earlier manuscript. All authors discussed and prepared the final manuscript.

最も一般的な種類の隕石が初期の海洋に衝突することで、生命に必要なある種の複雑な有機物分子が生成された、とNature Geoscience（電子版）の研究が報告している。

初期の生命に使われる元素の多くは初期地球に存在したが、それが生命の構成材料としてどのように組織されたかはよくわかっていない。東北大学の古川善博らは推進銃を用いて、鉄と炭素を含む隕石と地球の初期海洋の化学組成を模した水とアンモニアとの衝突をシミュレーションした。高速の衝突の後で研究チームは簡単なアミノ酸を含む有機物分子の混合物を得ることが出来た。

研究チームは、初期地球で頻繁に起きていた隕石衝突事件は、生命の基礎を形成した複雑な有機物分子を生成することに寄与したと結論づけている。