Survivability and reactivity of glycine and alanine in early oceans: effects of meteorite impacts

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Abstract Prebiotic oceans might have contained abundant amino acids, and were subjected to meteorite impacts, especially during the late heavy bombardment. It is so far unknown how meteorite impacts affected amino acids in the early oceans. Impact experiments were performed under the conditions where glycine was synthesized from carbon, ammonia, and water, using aqueous solutions containing ¹³C-labeled glycine and alanine. Selected amino acids and amines in samples were analyzed with liquid chromatography-mass spectrometry (LC/MS). In particular, the ¹³C-labeled reaction products were analyzed to distinguish between run products and contaminants. The results revealed that both amino acids survived partially in the early ocean through meteorite impacts, that part of glycine changed into alanine, and that large amounts of methylamine and ethylamine were formed. Fast decarboxylation was confirmed to occur during such impact processes. Furthermore, the formation of *n*-butylamine, detected only in the samples recovered from the solutions with additional nitrogen and carbon sources of ammonia and benzene, suggests that chemical reactions to form new biomolecules can proceed through marine impacts. Methylamine and ethylamine from glycine and alanine increased considerably in the presence of hematite rather than olivine under similar impact conditions. These results also suggest that amino acids present in early oceans can contribute further to impact-induced reactions, implying that impact energy plays a potential role in the prebiotic formation of various biomolecules, although the reactions are complicated and depend upon the chemical environments as well.

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1 Introduction

Amino acids are thought to be the most primary biomolecules related to the origin of life. They have been identified in many extraterrestrial materials [1, 2]. How the prebiotic synthesis and the molecular evolution of amino acids have progressed is an important issue to be solved experimentally. The prebiotic syntheses of amino acids under early Earth conditions were successful in the experiments by Miller (1953) [3], and opened up a new window for prebiotic chemistry, although his modeled conditions do not match the current model for the early Earth [4, 5]. There are several energy sources available for the prebiotic chemistry in nature such as light, heat, electric discharge, and impact energies.

Among them, meteoritic impacts into oceans on the early Earth are considered to have produced a significant amount of ammonia [6], which may help to fix nitrogen required for the formation of amino acids. Sudden prebiotic formation of biomolecules in the ocean, induced by the late heavy bombardment [7, 8], has been modeled as a *big bang*-like situation [9], among other models that have been proposed for the formation of amino acids on the early Earth [10–13]. Since prebiotic formation of glycine has been demonstrated in experiments under conditions similar to marine meteorite impacts [14], locally preferable conditions for the formation of amino acids may have been formed by the shock reactions among ocean, atmosphere, and meteorites. Actually, the formation of reduced gases by post-impact reactions has been suggested by experimental investigation [15].

It will be crucial to know further the way how not only simple biomolecules but also various kinds of biomolecules including amino acids can be formed in the events of marine meteorite impacts that may have occurred during the late heavy bombardment [7, 8]. *Ab initio* molecular dynamics simulations also give support for shock wave synthesis of glycine-containing complexes by cometary ice impacts on the Earth [16]. These results address the importance of impact effects on prebiotic chemistry.

Through studies on glycine at high pressure and temperature under dry conditions, high pressure has been shown to have a significant effect on stability [17] as well as polymerization [18, 19]. High temperature and high pressure induced by meteorite impacts may have fatal changes to amino acids [20, 21]. When amino acids in aqueous solution are subjected to high temperature and high pressure, they transform into other species, depending on the conditions [22, 23]. Most simple amino acids such as glycine, alanine, and valine cannot survive at high temperatures [24]. These studies have clarified the importance of high pressure for stabilizing amino acid under dry and aqueous solution conditions.

In case of marine meteorite impacts, it is necessary to know the survivability and stability of amino acids in aqueous solution under shock conditions. It will be also useful to elucidate the prebiotic chemistry and evolution of amino acids in oceans through impacts. Furthermore, it has been shown that not only temperature and pressure but also coexisting chemical species and minerals influence the stability and chemical reaction of amino acids.

In this report, we investigate the survivability and stability of glycine and alanine in aqueous solutions by impact in order to simulate the chemical reactions of two simple amino acids present in ocean during the late heavy bombardment period. Taking into account two typical species of ammonia and benzene in the early ocean and atmosphere [9] as reactants and

sources for N and C, we checked their effects on the stability of glycine and alanine. Ammonia is thought to be present as a product of impact reactions among meteorite, ocean, and atmosphere [6]. Benzene is thought to be produced by similar processes [25] and to be a simple molecule required to form complex amino acids such as phenylalanine.

In addition, mineral assembly may play an important role for the stabilization and chemical evolution of biomolecules [26, 27]. Coexisting minerals control oxygen fugacity in the system that has an important effect on the stability of amino acids in hydrothermal vents [28]. Therefore, we used two kinds of mineral powders (olivine and hematite) in order to investigate the effects of oxygen fugacity on the stability of amino acids under impact conditions. Hematite has been known to form under oxidative conditions such as banded iron formation (BIF) and on the surface of Mars [29, 30]. The oldest BIF has been found in 3.8-Ga Isua supracrustal belt [29], where graphite as evidence for early life has been reported in the metasedimentary rocks [31]. Also, it has been known that the fossil of carbonate globules formed by biogenic processes existed in Martian meteorite ALH84001 [32]. The presence of hematite or olivine keeps a distinct oxygen fugacity depending on the coexisting phase. The atmosphere on early Earth may have been an entirely oxidative condition [4], while locally reductive conditions in early oceans could be generated by meteorite impacts [6]. Therefore, it is important to investigate the survivability and stability of glycine and alanine as a function of oxygen fugacity.

2 Methods

2.1 Shock recovery experiments

Shock recovery experiments were carried out with a 30-mm-bore-diameter propellant gun [33] at the National Institute for Materials Science, Tsukuba, Japan. A projectile (30 mm in diameter and 45 mm long) with a metal flyer (29 mm in diameter and 2 mm thick) was accelerated to a required velocity. The actual impact velocity of the projectile was measured with the magnetoflyer method [33], recording the time interval between electromagnetic induction signals at two fixed coils (100 mm separated). We used a stainless-steel (304) flyer and container. Measured impact velocities were 0.8–0.9 km/s. Shock pressure was calculated with the measured impact velocity using the impedance match method [33].

According to the impedance match method, shock pressure P is calculated using two equations:

$$U = C + S u_p \quad (1)$$

and

$$P = \rho U u_p \quad (2)$$

where U , u_p , ρ , C , and S are shock velocity, particle velocity, density, and two constants. Hugoniot data were taken from Marsh (1980) [34]. We used U (km/s) = $4.58 + 1.49 u_p$ (km/s) for stainless steel 304, U (km/s) = $3.09 + 1.51 u_p$ (km/s) for mixtures of olivine and water, and U (km/s) = $2.67 + 1.45 u_p$ (km/s) for mixtures of hematite and water. The equation for the mixture was given using a mixing model. The components of amino acids, ammonia, and benzene were neglected in calculating pressure due to their relatively small amounts. The pressure range was 4.4–6.6 GPa in the present study.

2.2 Starting materials

We used glycine labeled by two ^{13}C (Isotec, Glycine- $^{13}\text{C}_2$, >99 atomic% ^{13}C) and alanine labeled by one ^{13}C (Isotec, DL-Alanine-3- ^{13}C , 99 atomic% ^{13}C) due to commercial availability. Aqueous solutions of glycine and alanine were prepared from the corresponding ^{13}C labeled starting materials. We used ^{13}C labeled amino acids as starting materials in order to distinguish between experimental products and contaminants such as ^{12}C molecules.

The analytical results of the starting materials are listed in Table 1. As described later, our starting ^{13}C labeled glycine (Isotec, Glycine- $^{13}\text{C}_2$, >99 atomic% ^{13}C) and alanine (Isotec, DL-Alanine-3- ^{13}C , 99 atomic% ^{13}C) contained about 0.0013 mol% $^{13}\text{C}_3$ -alanine and 0.31 mol% $^{13}\text{C}_2$ -glycine, respectively. Powders of olivine and hematite were prepared from natural olivine $[(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4]$ from San Carlos and $\alpha\text{-Fe}_2\text{O}_3$ (Wako, purity 99.9%). The average grain sizes of olivine and hematite were in the range of 20–30 μm and several microns, respectively.

2.3 Target assembly and sample recovery

Aqueous solutions of $^{13}\text{C}_2$ -glycine (sample G) and $^{13}\text{C}_3$ -alanine (sample A) and powder (olivine or hematite) were simulated as early ocean and meteorite, respectively. The concentrations used in the present study were 100 mM (samples G1–G7) and 1 mM (samples G8–G10) for $^{13}\text{C}_2$ -glycine, and 1 mM (samples A1–A12) for $^{13}\text{C}_3$ -alanine. Each solution (110–130 μl) was set with the powders (~200 mg) and air gap (~1 mm thick) in the sample room (18 mm in diameter and ~2 mm high) in a sealed steel container (30 mm in diameter and 30 mm long), as illustrated in Fig. 1.

We used a lead ring as sealant for the edge corner between two screws, as shown in Fig. 1. The seal condition of each container was checked by the weight loss after keeping it under vacuum for 1 h. Some containers showed quick weight loss of more than ~40 mg and these were not used in the experiments. After shots, the skin portions of the whole surface of the steel containers were first cut off, washed out with ethanol and purified water three times each repeatedly, and then immersed into liquid nitrogen. Subsequently, three holes (~2 mm diameter) were drilled on the impact surface at the liquid nitrogen temperature to reach the sample room. Then each container was kept overnight in a limited amount of pure water (30–50 ml) at room temperature to collect the water-soluble run products. Recovered grains of olivine and

Table 1 Abundance (mol%) of glycine (Gly) and alanine (Ala) in sample G and sample A used in the present study

Components	Sample G	Sample A
$^{13}\text{C}_0$ -Gly	0.0093	0.089
$^{13}\text{C}_1$ -Gly	0.88	0.018
$^{13}\text{C}_2$ -Gly	99.1	0.31
$^{13}\text{C}_0$ -Ala	0.0017	0.75
$^{13}\text{C}_1$ -Ala	<0.0003	86
$^{13}\text{C}_2$ -Ala	0.007	12
$^{13}\text{C}_3$ -Ala	0.0013	1.4
Total	100.00	100.57

Fig. 1 Schematic diagram of the shock recovery container used in the present study. The container consists of a body (stainless steel 304) and two screws (oxygen-free copper). The lower screw has a 60-degree conical edge to contact the 45-degree inner wall of the container, and the space between inner wall, lower, and upper screws was sealed with lead. The impact plane is subjected to a shock wave due to hypervelocity impact of a 2-mm-thick flyer plate on a polyethylene sabot

hematite were also collected, after drying, through the holes or by cutting open the sample room.

2.4 Analytical method

Amino acids and amines in the starting and recovered solutions from sample G and sample A were analyzed after vacuum concentration and derivatization by the same method as described by Furukawa et al. (2009) [14]. Each solution of 5 ml was concentrated ten times by using a centrifugal separator for 4 h. Samples for amine analysis were added hydrochloric acid before the vacuum concentration in order to prevent volatilization.

Analyses with liquid chromatography/mass spectrometry (LC/MS) were carried out with a Waters LC/MS system (2695 separation module and Quattro-micro API) at Tohoku University. We selected glycine, alanine, valine, and phenylalanine for amino acids, and methylamine, ethylamine, propylamine, and *n*-butylamine for amines. In all cases, the molecules with all carbons of ^{13}C were analyzed. The species were identified using the peaks with the same retention time as the corresponding standard solution. The contents were determined as the peak area against their standard solutions with all carbons of ^{12}C in a LC/MS single ion chromatogram. The concentrations of products in recovered samples were calculated by using the calibration curve based on three concentrations of each standard solution. Analytical errors were estimated to be within 50% relative error for low concentrations and much better for high concentrations, based on the previous studies whose equipment and method are the same as ours [17, 19].

We have investigated the recovered grains of olivine and hematite by using X-ray diffraction (XRD) using copper radiation at 40 kV and 40 mA. Recovered olivine grains were also checked using scanning electron microscopy (SEM, S-5200; Hitachi High-Technologies) and transmission electron microscopy (TEM, JEM-2010; JEOL).

2.5 Oxygen fugacity

Recovered solids were also investigated to confirm the change of olivine and hematite powders by X-ray diffraction (XRD). Typical XRD patterns of recovery samples are shown in Figs. 2 and 3. There was no change in peak positions of olivine, but significant peak broadening and

additional peaks for container stainless steel (SUS in Fig. 2) were observed by a comparison with the initial olivine patterns. These data are consistent with the previous results that the crystallite sizes of olivine became smaller as a result of the shock wave [35, 36].

SEM observations of the recovered olivine grains indicated that some olivine grains were covered with metal films of which compositions are close to that of the container (SUS 304). Thus, oxygen fugacity (f_{O_2}) in the sample set with olivine was thought to be close to that of a buffer of metal (SUS304, 0.7Fe-0.2Cr-0.1Ni) and olivine ($(Mg_{0.9}, Fe_{0.1})_2 SiO_4$). Then, we estimated oxygen fugacity in shots with olivine, using XRD results and thermodynamic data [37].

We calculated f_{O_2} at 1300 °C, which corresponds to the maximum temperature in our experiments according to the previous estimate [36]. Using ΔG (Gibbs free energy of formation) data and α (activity) assumed to be equal to composition, the following reaction gives f_{O_2} under equilibrium.

The activities of α_{Fe} and $\alpha_{Fe_2SiO_4}$ are based on the ideal solution model from the chemical compositions. We ignore the volume change of reaction (3) because of its negligible amount under the present shock condition of ~ 5 GPa. Thus, the obtained f_{O_2} in samples set with olivine is estimated about 3×10^{-9} Pa at 1300 °C.

Next, the XRD pattern of the recovered sample set with hematite is compared with that of the starting hematite in Fig. 3. Although no magnetite peaks were detected in the starting hematite, both hematite and magnetite (labeled as asterisks) were identified in all the recovered hematite samples. Thus, f_{O_2} in samples set with hematite was kept close to that of the Fe_2O_3 - Fe_3O_4 buffer. According to the following reaction

the oxygen fugacity was estimated to be ~ 9 Pa at 1300 °C. These calculations indicate that hematite keeps higher f_{O_2} than olivine so that we can investigate the effect of oxygen fugacity on the chemical reaction of amino acids by using two powders of hematite and olivine. When temperature changes from 1300 °C, hematite keeps higher f_{O_2} than olivine. The oxygen present in the air gap initially can be equilibrated by reactions (3) and (4), and it is negligible.

Fig. 2 X-ray powder diffraction patterns for shocked olivine in sample A5 (a), compared with that of the starting olivine (b). Copper radiation ($K\alpha$) was used to measure. Vertical units are arbitrary

Fig. 3 X-ray powder diffraction patterns for shocked hematite in sample A12 (**a**), compared with that of the starting hematite (**b**). Magnetite and stainless-steel peaks are labeled as *asterisk* and *SUS*, respectively. Both peaks of hematite and magnetite were detected in all the recovered hematite samples A6–A12

3 Results

3.1 Starting amino acids

The initial amino acids in samples G and A were determined and are listed in Table 1, and analyzed with the same analytical method as the recovered samples. Sample G consists of 99.1 mol% $^{13}\text{C}_2$ -glycine and 0.0013 mol% of $^{13}\text{C}_3$ -alanine. Sample A contains 1.4 mol% of $^{13}\text{C}_3$ -alanine, 0.31 mol% of $^{13}\text{C}_2$ -glycine, and 86 mol% of $^{13}\text{C}_1$ -alanine. Most of the alanine used in the present study (sample A) consists of $^{13}\text{C}_1$ -alanine, although the position of ^{13}C was not determined. Other amino acids than glycine and alanine were not detected from the two starting materials in the present study.

3.2 Amounts of ^{12}C molecules as contaminations

The ^{12}C molecules and ^{13}C molecules in the recovered solutions were measured separately in the present study. The ^{12}C molecules of amino acids and amines were detected in all samples, although we paid attention to processes during recovery and analysis. For example, ^{12}C -methylamine/ ^{13}C -methylamine and $^{12}\text{C}_2$ -ethylamine/ $^{13}\text{C}_2$ -ethylamine were 0.29 and 0.58 in sample G10, respectively. It was found that large amounts of ^{12}C molecules in the selected amino acids and amines existed together with ^{13}C molecules in recovery samples. Therefore, it was necessary to use ^{13}C labeled starting amino acids and to measure ^{13}C molecules as experimental products in this study. LC/MS used in this study could separate and analyze molecules such as amino acids and amines with different mass numbers.

3.3 Pressure and temperature estimations during impact process

Table 2 summarizes the shock conditions and analytical results on $^{13}\text{C}_2$ -glycine and $^{13}\text{C}_3$ -alanine. Peak shock pressure under the present experimental conditions (Table 2) was estimated using the measured impact velocity and Hugoniot data for the sample, container, and flyer. For the post-shock conditions [19], the strength of the container was taken into account, and temperature was estimated based on thermodynamic considerations.

The present experimental conditions are very similar to those by Furukawa et al. [19]. According to their estimation, the sample temperature reaches $\sim 300^\circ\text{C}$ at peak shock pressure of 5 GPa quickly after impact, $\sim 1300^\circ\text{C}$ at 0.34 GPa (as post-shock condition) after about 0.8

μs , and $\sim 50^\circ\text{C}$ in 10 min. Therefore, amino acids in the solutions can be decomposed at the highest temperature. The present results suggest that considerable amounts of glycine and alanine survived at such high temperatures or recombined during the quenching process. This may be explained due to too short a time available at high temperature or quick recombination of broken bonds in the presence of fluid water. We will discuss the stability of glycine and alanine in early oceans based on the present results.

3.4 Products from samples G and A

We have carried out five shots (samples G1–G3 and samples A1–A2) as the first series of experiments, and seven shots (samples G4–G7 and samples A3–A5) as the second series of experiments. In these series, we tried to detect small amounts of products, if any. The results are listed in Tables 2 and 3 for amino acids and amines, respectively.

Figure 4 illustrates LC/MS single-ion chromatograms for amino acids of standards and run products from sample G. The yield of $^{13}\text{C}_2$ -glycine ranges between 5 and 29% (Table 2) on samples G1–G3. Figure 5 illustrates LC/MS single-ion chromatograms for amino acids of standards and run products from sample A. $^{13}\text{C}_2$ -glycine and $^{13}\text{C}_3$ -alanine were detected in all recovered samples, but neither valine nor phenylalanine was detected (Table 2).

Figures 6a and b illustrate the yields of $^{13}\text{C}_2$ -glycine and $^{13}\text{C}_3$ -alanine as a function of pressure from five samples (G1–G3, A1, and A2). Although the yields of $^{13}\text{C}_2$ -glycine were below 30% (Fig. 6a), those of $^{13}\text{C}_3$ -alanine (Fig. 6b) were more than 100% from three samples G1–G3 and below 20% from samples A1 and A2. The molar ratios of $^{13}\text{C}_3$ -

Table 2 Shock conditions on sample G and sample A with olivine as the first series (samples G1–G3 and samples A1–A2) and the second series (samples G4–G7 and samples A3–A5 with ammonia and/or benzene), and their analytical results of selected amino acids glycine (Gly) and alanine (Ala) with all carbons of ^{13}C

Sample no.	Starting materials					Impact pressure (GPa)	¹³ C ₂ -Gly		¹³ C ₃ -Ala	
	¹³ C ₂ -Gly (nmol)	¹³ C ₃ -Ala (nmol)	NH ₃ (nmol)	¹³ C ₆ H ₆ (nmol)	Olivine (mg)		Amount (nmol)	Yield (mol%)	Amount (nmol)	Yield (mol%)
First series										
G1	12,800	0.17	-	-	200	5.0	3670	29	7	4000
G2	12,800	0.17	-	-	200	5.5	780	6	0.4	220
G3	12,800	0.17	-	-	200	6.6	690	5	0.4	220
A1	35	160	-	-	200	5.1	3	9	22	14
A2	39	175	-	-	200	5.0	1	3	33	19
Second series										
G4	10,900	0.14	2 × 10 ⁵	-	200	4.9	1320	12	3	2100
G5	11,300	0.15	-	1 × 10 ⁵	200	5.5	220	2	3	2200
G6	11,300	0.15	-	1 × 10 ⁵	200	5.8	270	2	1	930
G7	10,400	0.14	2 × 10 ⁵	1 × 10 ⁵	200	5.5	1740	17	1	700
A3	32	144	2 × 10 ⁵	-	200	5.2	0.5	2	2	1
A4	35	157	-	1 × 10 ⁵	200	5.1	0.5	1	16	10
A5	33	150	2 × 10 ⁵	1 × 10 ⁵	200	5.5	0.5	2	3	2

Table 3 Analytical results of selected amines with all carbons of ^{13}C in the recovered samples with olivine as the first series (samples G2–G3 and A1–A2) and the second series (samples G5–G6 and A3–A5 with ammonia and/or benzene)

Sample no.	Impact pressure (GPa)	^{13}C -methylamine (nmol)	$^{13}\text{C}_2$ -ethylamine (nmol)	$^{13}\text{C}_3$ -propylamine (nmol)	$^{13}\text{C}_4$ -butylamine (nmol)
First series					
G2	5.5	13	1	ND	ND
G3	6.6	102	4	0.04	ND
A1	5.1	1	5	ND	ND
A2	5.0	1	6	ND	ND
Second series					
G5	5.5	193	0	0.04	ND
G6	5.8	365	3	0.1	ND
A3	5.2	1	3	ND	ND
A4	5.1	1	12	ND	ND
A5	5.5	8	7	0.6	0.1

alanine/ $^{13}\text{C}_2$ -glycine in samples G1–G3, however, were about 10^{-3} (sample G1) to 10^{-4} (samples G2 and G3), and significantly greater than the initial ratio of sample G ($\sim 10^{-5}$). This indicates that $^{13}\text{C}_3$ -alanine has been formed from sample G. On the other hand, the yields of $^{13}\text{C}_2$ -glycine in samples A1 and A2 (triangles in Fig. 6a and b) are less than 30%. The present results indicate that only alanine can be formed from glycine, but that glycine is not formed from alanine.

Table 3 summarizes analytical results on amines in samples G2–G3 and A1–A2 as the first series. ^{13}C -methylamine and $^{13}\text{C}_2$ -ethylamine were detected in all of them. In addition, a small amount of propylamine was formed from only sample G3, but butylamine was not detected in the first series. The amount of ^{13}C -methylamine was larger than that of $^{13}\text{C}_2$ -ethylamine in

Fig. 4 LC/MS single-ion chromatograms of standards and run products from sample G for amino acids after derivatization. The peaks at $m/z=248$ and 263 correspond to the m/z values of derivatized $^{13}\text{C}_2$ -glycine and $^{13}\text{C}_3$ -alanine, respectively. **a** $m/z=248$ of sample G1, **b** $m/z=263$ of sample G1, **c** $m/z=246$ of the standard $^{12}\text{C}_2$ -glycine and, **d** $m/z=260$ of the standard $^{12}\text{C}_3$ -alanine. In addition to glycine and alanine, we analyzed valine and phenylalanine but the amounts were below detection limits. R is $\text{C}_{10}\text{H}_7\text{N}_2\text{O}$

Fig. 5 LC/MS single-ion chromatograms of standards and run products from sample A for amino acids after derivatization. The peaks at $m/z=248$ and 263 correspond to the m/z values of derivatized $^{13}\text{C}_2$ -glycine and $^{13}\text{C}_3$ -alanine, respectively. **a** $m/z=248$ of sample A2, **b** $m/z=263$ of sample A2, **c** $m/z=246$ of the standard $^{12}\text{C}_2$ -glycine, and **d** $m/z=260$ of the standard $^{12}\text{C}_3$ -alanine. In addition to glycine and alanine, we analyzed valine and phenylalanine but the amounts were below detection limits. R is $\text{C}_{10}\text{H}_7\text{N}_2\text{O}$

samples G2–G3, while the amount of $^{13}\text{C}_2$ -ethylamine was larger than that of ^{13}C -methylamine in samples A1–A2. Figure 7 illustrates the amounts of ^{13}C -methylamine and $^{13}\text{C}_2$ -ethylamine as a function of shock pressure. With increasing shock pressure, the amounts of ^{13}C -methylamine and $^{13}\text{C}_2$ -ethylamine increased simply in sample G (open symbols), as connected by dotted lines in Fig. 7. The amine formation (decarboxylation) from glycine is dependent on shock pressure from a comparison between the results on samples G2–G3, suggesting that the decarboxylation rate of glycine is faster with increasing pressure or the stability of amine such as methylamine and ethylamine increases under high pressure. On the other hand, in sample A (solid symbols), $^{13}\text{C}_2$ -ethylamine was formed in larger amounts than ^{13}C -methylamine. The results are in contrast to those from sample

Fig. 6 **a** yields of $^{13}\text{C}_2$ -glycine from samples G1–G3, A1, and A2 and **b** yields of $^{13}\text{C}_3$ -alanine from samples G1–G3, A1, and A2 as a function of shock pressure. Circles and triangles are samples G1–G3 and A1–A2, respectively

Fig. 7 Amounts of ^{13}C -methylamine and $^{13}\text{C}_2$ -ethylamine from samples G2–G3 (*open symbols*) and samples A1–A2 (*filled symbols*) as a function of shock pressure. *Squares* and *diamonds* indicate methylamine and ethylamine, respectively

G under similar conditions, and suggest that formation of amine (decarboxylation) depends on the initial amino acid as well.

3.5 Products from amino acid solutions with ammonia and benzene

The results in the previous section 3.4 indicated that complicated amino acids such as valine and phenylalanine were not produced from sample G and sample A. We conducted the second series of experiments with ammonia and benzene in order to check the formation of complicated amino acids. It has been known that these chemical species can be formed easily during marine impacts [6, 25]. The purpose of the added ammonia was to serve as a nitrogen source for amino acids. Benzene was added as a carbon source for complicated amino acids having a benzene ring such as phenylalanine.

Table 2 summarizes the analytical results of $^{13}\text{C}_2$ -glycine and $^{13}\text{C}_3$ -alanine in the recovered samples G4–G7 and A3–A5 as the second series of experiments with ammonia and/or benzene. $^{13}\text{C}_2$ -glycine and $^{13}\text{C}_3$ -alanine were detected from all of the samples but valine and phenylalanine were not detected, even in the presence of ammonia and benzene. The amount of alanine (2200 mol%) in sample G5 with benzene was higher than that in sample G2 (220 mol%) without benzene at a similar pressure. The yields of amino acids in samples A3 with ammonia were smaller than in sample A1 without ammonia at a similar pressure. The addition of ammonia made the decomposition rate of amino acids faster or the reaction of amines became faster. Table 3 summarizes the analytical results of amines on samples G5–G6 and samples A3–A5. In samples G5–G6, the amounts of methylamine were higher than those of samples G2–G3 without any addition. On the other hand, from sample A4 with benzene, the amount of methylamine was higher than those of samples A1–A2. Figure 8 illustrates LC/MS single ion chromatograms of standard amines and run products in sample A5. From only sample A5 (with both added ammonia and benzene), $^{13}\text{C}_4$ -*n*-butylamine was detected.

Fig. 8 LC/MS chromatograms for selected amines in run products from sample A5. **a** $m/z=203$ (^{13}C -methylamine), **b** $m/z=218$ ($^{13}\text{C}_2$ -ethylamine), **c** $m/z=233$ ($^{13}\text{C}_3$ -propylamine), **d** $m/z=248$ ($^{13}\text{C}_4$ -*n*-butylamine), and **e** standard solution of methylamine, ethylamine, propylamine, and *n*-butylamine. Peaks without marks could not be identified in the present study

3.6 Amine formation from low concentration solutions with ammonia and benzene

The results in the previous section 3.5 indicated that complicated amines such as butylamine could be formed from sample A with added ammonia and benzene. Therefore, we investigated the products from a diluted sample G under similar conditions. Table 4 lists the experimental conditions and analytical results on amine in the recovered samples G8–G10, in which the concentrations of $^{13}\text{C}_2$ -glycine were set at the same order as those of $^{13}\text{C}_3$ -alanine in sample A. The concentration of samples G8–G10 was ~ 1 mM for $^{13}\text{C}_2$ -glycine. Samples G9–G10 contained ammonia and/or benzene. Methylamine was formed in all the samples G8–G10. In addition, ethylamine was detected in sample G9 with ammonia, and both propylamine and

butylamine were detected in sample G10 with ammonia and benzene. These results indicate that coexisting chemicals such as ammonia and benzene have an important effect in facilitating the formation of complicated amines that are not formed only from amino acids.

3.7 The effects of high oxygen fugacity

Table 5 summarizes the experimental conditions for sample A with hematite and the analytical results of selected amino acids and amines in samples A6–A12. Shock pressures were 4.4–5.7 GPa. The concentration of $^{13}\text{C}_3$ -alanine was ~ 1 mM, and samples A9–A12 contained ammonia and/or benzene. Oxygen fugacity in the sample with hematite was estimated to be 10^9 times higher than that with olivine at 1300 °C, as described in section 2.5. Analytical results on amino acids indicate that glycine and alanine were detected but not valine and phenylalanine. These results are similar to those of samples A1–A5 with olivine. On the other hand, analytical results on amines indicate that methylamine and ethylamine were detected but not propylamine and butylamine even in the cases with ammonia and benzene. This contrasts with the results in samples A1–A5 with olivine.

Figure 9 illustrates the amounts of ^{13}C -methylamine (Fig. 9a) and $^{13}\text{C}_2$ -ethylamine (Fig. 9b) as a function of shock pressure in shocked sample A with olivine (low f_{O_2}) and hematite (high f_{O_2}). The amounts of amines formed in samples with hematite (A6–A12) are more than ten times larger than those with olivine (samples A1–A5). In samples A6–A8 with hematite and no addition, the total amounts of amines (methylamine + ethylamine) were about 170–190 nmol after shock experiments. This indicates that most of the starting amino acid changed to amines during impact because the amounts of starting amino acids (glycine + alanine) were about 200 nmol. This result indicates that the high oxygen fugacity condition causes almost complete decomposition of amino acids to amines by impact.

4 Discussion

4.1 Stability and reactions of glycine and alanine in early oceans following meteorite impacts

We have conducted impact simulation experiments on glycine and alanine dissolved in water. The present experimental results on the aqueous solutions for glycine and alanine indicate that glycine and alanine show various chemical reactions to decrease their initial amounts in the impact processes. It has been confirmed that alanine was formed significantly from the glycine solutions under the present experimental conditions. Alanine can be formed from glycine via the following reaction:

Benzene easily transforms to hydrocarbons such as methane and ethane at high temperatures [38, 39]. The methyl group can be produced by the decomposition of benzene and amino acid. In fact, the amount of alanine in the recovered sample G5 with benzene increased compared with that in sample G2 without benzene at a pressure of 5.5 GPa (Table 2). Also, it has been

Table 4 Shock conditions on ~1 mM sample G with olivine, and analytical results of selected amines with all carbons of ^{13}C in the recovered samples G8–G10

Sample no.	Starting materials			Impact pressure (GPa)	Amine products					
	¹³ C ₂ -Gly (nmol)	¹³ C ₃ -Ala (nmol)	NH ₃ (nmol)		¹³ C ₆ H ₆ (nmol)	Olivine (mg)	¹³ C-methylamine (nmol)	¹³ C ₂ -ethylamine (nmol)	¹³ C ₃ -propylamine (nmol)	¹³ C ₄ -butylamine (nmol)
G8	166	0.002	-	-	200	5.1	0.7	ND	ND	ND
G9	166	0.002	2 × 10 ⁵	-	200	5.4	3	0.4	ND	ND
G10	166	0.002	2 × 10 ⁵	1 × 10 ⁵	200	5.4	6	1.1	0.3	0.03

Table 5 Shock recovery experimental conditions on sample A with hematite, and analytical results of selected amino acids and amines with all carbons of ^{13}C in the recovered samples A6–A12

Sample no.	Starting materials				Impact pressure		¹³ C ₂ -Gly		¹³ C ₃ -Ala		Amine products			
	¹³ C ₂ -Gly (nmol)	¹³ C ₃ -Ala (nmol)	NH ₃ (nmol)	¹³ C ₆ H ₆ (nmol)	Hematite (mg)	Impact pressure (GPa)	Amount (nmol)	Yield (mol%)	Amount (nmol)	Yield (mol%)	¹³ C-methylamine (nmol)	¹³ C ₂ -ethylamine (nmol)	¹³ C ₃ -propylamine (nmol)	¹³ C ₄ -butylamine (nmol)
A6	37	168	-	-	200	4.9	ND	-	12.8	7.6	43	124	ND	ND
A7	37	168	-	-	200	5.4	ND	-	0.7	0.4	52	143	ND	ND
A8	37	168	-	-	200	4.4	0.7	1.8	23.3	13.9	47	119	ND	ND
A9	34	154	2 × 10 ⁵	-	200	5.1	0.2	0.5	5.9	3.8	56	156	ND	ND
A10	34	154	-	1 × 10 ⁵	200	4.8	0.1	0.4	5.4	3.5	61	185	ND	ND
A11	31	140	2 × 10 ⁵	1 × 10 ⁵	200	5.1	0.1	0.5	4.4	3.1	34	103	ND	ND
A12	31	140	2 × 10 ⁵	1 × 10 ⁵	200	5.7	0.1	0.2	1.5	1.1	12	55	ND	ND

Fig. 9 Amounts of **a** ^{13}C -methylamine and **b** $^{13}\text{C}_2$ -ethylamine as a function of shock pressure. We labeled as squares with NH_3 , diamonds with C_6H_6 , triangles with NH_3 and C_6H_6 , and circles without NH_3 and C_6H_6 . Open and filled marks indicate samples set with olivine and hematite, respectively

known that alcohol can be supplied from hydrocarbon under water-rich conditions [40, 41]. Then, the following reaction among ethanol, amino group formed by the deamination of amino acids, and carboxylic group formed by the decarboxylation of amino acids could occur under present conditions [42, 43] as follows:

The present results also indicate the difficulty of producing amino acids other than glycine and alanine under the present impact conditions. There are many factors to be considered for further reactions of amino acids in early oceans, such as the degree of shock strength, the limited reaction time of shock duration, the availability of carbon and nitrogen sources, and coexisting chemical species in early oceans and atmosphere.

As high pressure helps to stabilize amino acids to higher temperatures [17, 23], shock conditions also may help to stabilize amino acids even in a limited duration. We have analyzed the surviving glycine and alanine and the shock-recovered amines in the post-shock samples. A significant decrease of the amino acids has been confirmed to be mostly about 10%. This implies that the amino acids present in early oceans must be decreased by meteorite impacts. The reactions include decarboxylation to amines and deamination to carboxylic acids [13, 42, 43]. Under the present shock conditions, the decarboxylation has been confirmed experimentally to occur within a few microseconds. The decarboxylation of glycine and alanine has been shown also under supercritical and subcritical conditions of water [43], and it needs sufficient reaction times. The decarboxylation in the shock process is found to be very fast.

We have observed that glycine converts to alanine in the present study. Although not all of the products were analyzed in the present study, deamination might have occurred

simultaneously. If this is the case, then glycine quickly produces formaldehyde via glycolic acid reaction. The reactions for a mixture of formaldehyde, ammonia, and water were well investigated by heating [44], photosynthesis [45], and hydrothermal treatments [46] to form several amino acids including predominantly glycine and alanine. We may have two reactions to form amines in the present system. The first scheme is a direct decarboxylation of amino acids:

This reaction suggests the formation of the amine corresponding to an amino acid. Our experimental results indicate the formation of methylamine and ethylamine from glycine and alanine respectively via this reaction.

Our results that product amounts of simple amines, such as methylamine and ethylamine, increase when either ammonia or benzene is added in the system, suggests that ammonia and benzene are source materials to form amines. It is considered that these amines were formed via reaction (6) between alcohol and ammonia [39] because it has been known that alcohol is one of the decomposition products of amino acids [42]:

Another reaction between hydrocarbon and ammonia also forms amines in the presence of benzene. Hydrocarbons such as methane and ethane were easily formed from benzene at high temperatures [40]. Ammonia was formed via deamination reaction (8) of amino acids, and hydrocarbon may easily change to alcohol in H_2O under high temperature. Then reaction (9) can occur and the present results suggest there were several formation processes of amines under the present conditions:

Propylamine and butylamine, however, can not be formed via this reaction. As a second scheme, reactions (10) and (11) are needed between ammonia from deaminated amino acid and alcohol produced by hydrolyses of hydrocarbons at high temperatures [39, 41]. Propylamine and butylamine can be formed via the following reactions:

Benzene in this study could be the source of hydrocarbon [38, 40].

4.2 Oxygen fugacity effect on stability and reaction of amino acid

It has been known that the decomposition rate of *n*-alkyl- α -amino acid is much faster in the presence of the mineral assemblage hematite–magnetite–pyrite (HMP) than with the assemblage pyrite–pyrrhotite–magnetite (PPM) [47]. Thus, it is considered that a coexisting mineral plays an important role in reactions of amino acids. The present study indicates that the product amounts of amine with hematite were much larger than those with olivine (Fig. 9), and in the

previous section it was described that olivine kept lower oxygen than hematite. These results suggest the following reactions occurred in glycine and alanine set with hematite:

Hematite may have played a role as an oxidizer to form amine from amino acids via reactions (12) and (13). According to our experimental results that complicated amines such as propylamine and butylamine were able to form only under low fO_2 conditions, it is suggestive that reductive conditions were preferred for chemical evolution.

In order to see the effect of fO_2 , the conversion rate C of glycine and alanine to amines on sample A is calculated as the nitrogen mass balance: $C = [\text{Total amount of analyzed amines in recovered sample}] \times 100 / [\text{Total amounts of glycine and alanine in starting solution}]$. C values for samples A1 and A2 with olivine (without ammonia and benzene) and samples A6–A8 with hematite (without ammonia and benzene) are 3.1–3.3 mol% and 81.0–95.1 mol%, respectively. The results indicate that amine formation from amino acid by decarboxylation increases considerably at high oxygen fugacity. As nitrogen atoms in samples A1 and A2 left as amino acids (~14–19% in Table 2) and amines (~3%), more than 78% of the starting amino acids reacted out as reactants other than amines in the shock recovered samples with olivine powders. The possible products are ammonia, carbon dioxide, carboxylic acids, and diketopiperazine (DKP). DKP is a dimerization product of amino acids at high temperatures [22, 48].

4.3 Comparison of amino acid reactions between hydrothermal conditions and marine meteorite impacts

It is widely believed that the prebiotic chemical reactions were required to produce simple biomolecules as the origin of life on Earth. The related environments and processes remain open to debate, but plausible environments include marine hydrothermal conditions. There are some experimental studies on amino acids under hydrothermal conditions at high temperatures up to a few hundred Kelvin and pressures up to a few tens of MPa. A comparison between impact reactions and hydrothermal reactions is instructive to understand the characteristics of prebiotic reactions. Under hydrothermal conditions at temperatures of 250–400 °C and pressures of 22.2 and 40 MPa [46], the effects of temperature and pressure on the dimerization and decomposition of glycine were investigated and the decomposition was coincided with the dimer formation. During the decomposition process, a large amount of diketopiperazine was detected in the products from glycine. The amount of diketopiperazine produced from dry glycine at 150 °C and 5–100 MPa increased gradually in ~10 days with increasing reaction time [18]. We did not analyze diglycine and diketopiperazine, but according to the previous studies [43, 46], they might have been formed in our products. By continuous-flow reactor experiments at 200–450 °C and 20–34 MPa [42, 43, 49], amino acid decomposed to produce ammonia and organic acid by deamination and carbonic acid and amines by decarboxylation, and the predominant nitrogen compounds were ammonia and ethylamine [50]. Ethylamine is more stable than

alanine at high temperatures [51]. Therefore, ethylamine will play an important role in driving prebiotic reactions at high temperatures corresponding to the hydrothermal and marine impact conditions. Actually, the molar fractions of the amine produced by the present impact experiments are 0.1–3.3 and 2.1–7.6% as ^{13}C -methylamine/initial $^{13}\text{C}_2$ -glycine in sample G and $^{13}\text{C}_2$ -ethylamine/initial $^{13}\text{C}_3$ -alanine in sample A with olivine, respectively. On the other hand, the fractions reached ~40% in glycine and ~20–30% in alanine under hydrothermal conditions at 400–450 °C and 34 MPa, respectively [43]. The decomposition of glycine and alanine was very fast to react out almost within 5 seconds at such high temperatures, but significant amounts of glycine and alanine survived in the present impact conditions. The different results between hydrothermal and impact conditions suggest that impact reactions give a chance for simple biomolecules to react under non-equilibrium, heterogeneous conditions, although we need to investigate further the difference in more detail.

Although it is difficult to compare the hydrothermal experimental results with the impact results directly, there is no detectable amount of amino acid in hot hydrothermal vents of the Guayman Basin [52], suggesting a time scale difference. Shock duration and shock strength are two key factors for survival of amino acids. Blank and Miller [53], simulating the kinetic conditions of pyrolysis at high shock pressure, suggested that the rate of pyrolysis at 7000 K and 100 GPa would be comparable to that at 900 K and 1 atm. Therefore there seems to be a chance for amino acids to survive even relatively violent impacts. Some molecules, including amino acids, may react out, decompose, polymerize, and survive depending on the impact condition and duration time, although we have not investigated polymerization in this study.

4.4 Implications for formation and reactions of simple biomolecules by impact energies

The present experimental pressure (4.9–6.6 GPa) will be low, compared with natural impact conditions. When flying objects of ordinary chondrite, carbonaceous chondrite, and comets impact early oceans, the corresponding impact velocities are estimated to be 1.6–2.0, 2.0–2.5, and 2.5–3.0 km/s, respectively, based on their known Hugoniot [54].

Compared to the Earth's escape velocity (11.2 km/s), they are one-quarter to one-sixth for vertical impacts and half to one-third for 30°-angle impacts. Taking into account the atmospheric deceleration and impact angle of flying objects, the impact pressures in the present study were substantially low due to the technical problems of sample recovery. However, actual pressures induced by meteorite impacts will decay as a function of distance from the impact center, depending on the size of the meteorite. The present conditions correspond to low-velocity impact sites, the surrounding areas outside the impact site, or the deep ocean below the site where the shock pressures are at most 5–7 GPa, being below ~4 km/s for ordinary chondrite, ~5 km/s for carbonaceous chondrite, and ~6 km/s for a comet, respectively. These impacts might have occurred frequently as small-scale impacts and strongly affected prebiotic chemistry.

Shock wave syntheses of organic molecules including amino acids have been reported by several studies. Gilvary and Hochstim [55] suggested a process in which a meteorite passes through the terrestrial atmosphere on early Earth. Bar-Nun et al. [56] succeeded in shock heating syntheses of amino acids in high yields, but later results suggested a much smaller yield by ~1/30 in a gas mixture of methane, ethane, ammonia, and water [57]. Furukawa et al. [14] demonstrated shock-synthesis of glycine and other biomolecules under the conditions similar to

meteorite impacts into early oceans. The experiments simulated reactions among meteoritic carbon, water, and ammonia that nitrogen was fixed in oceans by the impact reactions until then among meteoritic iron, ocean water, and atmospheric nitrogen [6]. The present study extends the experimental simulation to know how the glycine joins further chemical reactions to produce new, complicated biomolecules. The present results indicate that it may not be a simple process and that locally complicated non-equilibrium reactions at late heavy bombardment may contribute to promote the prebiotic chemistry that we do not know yet. We need to investigate further in order to understand the shock reactions related to the origin of life.

5 Conclusions

The present experimental results on the aqueous solutions for glycine and alanine indicate that glycine and alanine show various chemical reactions during impact processes. Glycine produces the second simplest amino acid, alanine, when a meteorite impacts the ocean under conditions similar to the present experiments. However, the present results also suggest that it will be difficult to produce complicated amino acids under the present impact conditions. Coexisting chemical species such as ammonia and benzene help to form butylamine from simple amino acids such as glycine and alanine. Hematite may play a role as an oxidizer of amino acids to form amines. The stabilities of glycine and alanine in aqueous solutions in the process of impact depend not only on pressure and temperature but also on the coexisting chemical species such as ammonia and benzene and minerals such as olivine and hematite.

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