

Prebiotic Synthesis of Glycine from Ethanolamine in Simulated Archean Alkaline Hydrothermal Vents

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Received: 27 July 2016 / Accepted: 5 September 2016 /
Published online: 23 September 2016
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Abstract Submarine hydrothermal vents are generally considered as the likely habitats for the origin and evolution of early life on Earth. In recent years, a novel hydrothermal system in Archean seafloor has been proposed. In this model, highly alkaline and high temperature hydrothermal fluids were generated in basalt-hosted hydrothermal vents, where H₂ and CO₂ could be abundantly provided. These extreme conditions could have played an irreplaceable role in the early evolution of life. Nevertheless, sufficient information has not yet been obtained for the abiotic synthesis of amino acids, which are indispensable components of life, at high temperature and alkaline condition. This study aims to propose a new method for the synthesis of glycine in simulated Archean submarine alkaline vent systems. We investigated the formation of glycine from ethanolamine under conditions of high temperature (80–160 °C) and highly alkaline solutions (pH = 9.70). Experiments were performed in an anaerobic environment under mild pressure (0.1–8.0 MPa) at the same time. The results suggested that the formation of glycine from ethanolamine occurred rapidly and efficiently in the presence of metal powders, and was favored by high temperatures and high pressures. The experiment provides a new pathway for prebiotic glycine formation and points out the phenomenal influence of high-temperature alkaline hydrothermal vents in origin of life in the early ocean.

Keywords Ethanolamine · Glycine · Alkaline hydrothermal vents · Origin of life · Prebiotic chemistry

Introduction

Though the settings for the origin of life are unknown and greatly debated, it is generally believed that life on the Earth was evolved from simple organic compounds (Bada and

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Lazcano 2002; Gollihar et al. 2014; Ruiz-Mirazo et al. 2014). Submarine hydrothermal systems (SHSs) have been regarded as the most likely sites for the origin of life because of their highly reactive chemical environments and possible availability of starting materials (Baross and Hoffman 1985; Martin and Russell 2007; Martin et al. 2008; Martin et al. 2014; Sojo et al. 2016). Since the first discovery of seafloor hydrothermal vents at the Galapagos spreading center, more than 500 hydrothermal vents have been reported throughout the oceans (Takai and Nakamura 2011). There are two typical kinds of hydrothermal vents in the modern oceans, a high-temperature acidic type at mid-ocean ridges, such as “black smocks” (Corliss et al. 1979) and a low-temperature alkaline type at off-ridge ocean floor, such as the Lost City hydrothermal field (Kelley et al. 2001; Früh-Green et al. 2003). “Black smokers” are hot (~350 °C) and acidic (pH 2.0–3.0), the fluids commonly contain high concentrations of transition metals, CO₂, H₂, H₂S and CH₄ (Kelley et al. 2002). The Lost City hydrothermal field, which is driven by the heat of exothermic serpentinization reactions between sea water and mantle rocks, is relatively cool (40–90 °C) and alkaline (pH 9.0–11.0) (Kelley et al. 2005; Foustoukos et al. 2008). The fluids generally contain high concentrations of dissolved H₂, CH₄ and hydrocarbons, but little amount of CO₂ (Ludwig et al. 2006). Hydrothermal synthesis of organics and biomolecules in laboratory simulation experiments had made considerable progress in the past three decades (Imai et al. 1999; Foustoukos and Seyfried 2004; McCollom and Seewald 2007; Feng et al. 2008; Martin et al. 2008; Herschy et al. 2014). However, most of these experiments seem to depend on an important assumption that the chemical property of Archean hydrothermal vents was substantially similar to those of modern hydrothermal vents. It should be presumed that there are significant differences between the modern and Archean hydrothermal vent environments (Sleep 2010). In recent years, Shibuya and co-workers have proposed a new kind of hydrothermal vent system in the Archean ocean by studying the formation processes of Archean chert and banded iron. In this model, both highly alkaline (pH 9.0–11.0) and hot (350 °C) hydrothermal activities were possibly present in the early Archean basalt-hosted hydrothermal vent systems, where H₂ and CO₂ could be abundantly provided (Shibuya et al. 2010; Shibuya et al. 2013). It is excited because such conditions may have provided the favorable environment for prebiotic chemical evolution in Archean ocean (Kitadai 2015; Shibuya et al. 2016). Nevertheless, sufficient information has not yet been obtained for the synthesis of biomolecule at high temperatures and alkaline conditions.

Abiotic synthesis of amino acids, the building blocks of proteins, is of enormous interest in submarine hydrothermal vent systems. Most previous experiments have focused on the hydrothermal synthesis of amino acids from aldehyde, HCN, NH₃ or their salts in a Strecker synthesis route (Hennet et al. 1992; Marshall 1994; Aubrey et al. 2009; Ruiz-Bermejo et al. 2013). Moreover, amino acids also can be synthesized by reductive amination of α -keto acids in the presence of FeS in hydrothermal conditions (Huber and Wächtershäuser 2003). However, a completely deterministic synthetic route of amino acids on the early Earth still seems to be lacking. Future experiments should strive to explore the generation of amino acids in Archean submarine vent systems.

Ammonia (NH₃) is likely a prerequisite for the formation of amino acids and other organic nitrogen compounds on the early Earth leading up to the origin of life (Rushdi and Simoneit 2004). However, inorganic nitrogen exists primarily in the forms of N₂ and NO₂⁻/NO₃⁻ in the ocean. Several possible pathways for the reduction of N₂ and NO₂⁻/NO₃⁻ to their chemically more reactive form NH₃/NH₄⁺ have been proposed: hydrothermal reduction of N₂ in the presence of minerals (Schoonen and Xu 2001; Dörr et al. 2003) or Ni-Fe metals (Smirnov et al. 2008); the

reduction of $\text{NO}_2^-/\text{NO}_3^-$ by Fe^{2+} (Summers and Chang 1993) or on the surface of FeS in hydrothermal vents (Summers 2005; Gordon et al. 2013). Ethanolamine could have originally formed from $\text{NH}_3/\text{NH}_4^+$ in hydrothermal environments on early Earth (Miller and Schlesinger 1993; Austin and Waddell 1999), and its important role in the evolution of lipid membranes have been widely investigated (Rao et al. 1987; Maheen et al. 2010). It may also contribute to the emergence of glycine in the Archean ocean due to its similar structure to glycine. Until now, there has been no demonstration of prebiotic synthesis of glycine from ethanolamine. The experiments reported here were designed to simulate the environment of Archean alkaline hydrothermal vents to test ethanolamine as a possible candidate precursor of glycine. Our observation provides an alternative route for the synthesis of amino acids and points out the possibility of life began at hot-alkaline hydrothermal vents.

Materials and Methods

Materials

All chemicals used were analytical grade. Ethanolamine (purity >99 %) and acetylchloride (purity >98.5 %) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Glycine (purity >99.5 %) was purchased from Alfa Aesar (Tianjing, China). NaHCO_3 (purity >99 %), methanol (purity >99.7 %), ethanol (purity >99.8 %), metal powders (cobalt powder, iron powder, copper powder, nickel powder, 200 mesh), CoCO_3 , Co_2O_3 and Co_3O_4 were all obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Dichloromethane (purity >99.9 %) was purchased from Tjshield (Tianjin, China). Trifluoroacetic anhydride (purity >8 %) was purchased from TCI (Shanghai, China). High-purity water (Pall Purelab Plus) with a resistivity of $18.2 \text{ M}\Omega\cdot\text{cm}$ was used in all the experiments.

Experimental method

Experiments were carried out in a stainless steel autoclave which contains a 50 mL Teflon lining. The experiment was started with conversion of ethanolamine in the presence of different metal powders, including Fe, Co, Ni and Cu. We selected metal powders as catalysts for two reasons. First, primitive Earth's atmosphere and ocean have a negligible oxygen concentration (Kasting 1993; Lyons et al. 2014), so the oxidation of ethanolamine to glycine (from $-\text{CH}_2\text{OH}$ to $-\text{COOH}$) may undergo a dehydrogenation oxidation process. And in our previous study, we found metal powders are efficient catalysts for dehydrogenation of alcohols in hydrothermal conditions (Zhang et al. 2013). Second, native metals are commonly formed during serpentinization and other hydrothermal reactions, and the conditions are sufficiently reducing for stabilization of native metals (Dekov 2006; Pinti et al. 2009; Dekov et al. 2013; Schwarzenbach et al. 2014; Foustoukos et al. 2015). In a typical reaction, 10 mL of a mixed solution containing 1 mmol ethanolamine and 5 mmol catalyst were put into the autoclave. Since the Archean basalt-hosted hydrothermal vent was highly alkaline and CO_2 -rich, the pH of solution was adjusted to 9.70 by adding 1 mmol NaHCO_3 . After being purged third times with high purity nitrogen to remove dissolved oxygen, the pressure of the reactor was raised to a selected value under ambient temperature. Then the reactor was put into the oil bath between 60 °C and 160 °C for 3 to 24 h. The reactor was taken out and cooled to room temperature when the reaction finished. The

pH did not change significantly since it was buffered by HCO_3^- - CO_3^{2-} equilibrium. The products were detected by gas chromatography-mass spectrometry (GC-MS).

Analysis of reaction products

All samples were derivatized and analysis with GC-MS. The derivatization method was based on H. Brückner's work but with some modification (Pätzold et al. 2006). 1 mL of sample was acidized by adding 0.1 mL HCl, then evaporated to dryness in a stream of nitrogen in a water bath at 50 °C and derivatized as described in Scheme 1.

Glycine was converted into glycine esters at ambient temperature using treatment with a mixture of 1 mL acetylchloride (AcCl) in the methanol (1:9, v/v) for 3 h (esterification with methanol). After evaporation of reagents with a stream of nitrogen, trifluoroacetic anhydride (0.2 mL) in dichloromethane (1 mL) was added for the N-perfluoroacyl glycine esters. After 30 min reaction time at room temperature, reagents were removed with a stream of nitrogen, the remaining derivatives were dissolved in ethanol (1 mL), and then analyzed with a TRACE DSQ GC-MS (Thermo Fisher Scientific Int.), with ionization achieved by electron impact at 70 eV, equipped with a capillary column: DB-FFAP (30 m long \times 0.25 mm i.d. \times 0.25 μm film thickness).

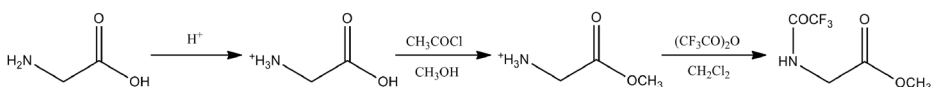
The operating conditions of the GC-MS analysis were as follows: 0.4 μL injection volume; injection port temperature, 200 °C; interface temperature, 250 °C; column oven temperature program: 80 °C for 1 min, ramped at 15 °C min^{-1} to 200 °C with 4 min hold, the total running time was 13 min. The mass spectrometer was operated in the electron ionization mode with quadrupole temperature of 250 °C. Data acquisition was performed in the full-scan mode (29–300). Helium (99.999 % purity) was used as carrier gas at a constant flow rate of 1.0 mL min^{-1} . The injector was operated in the split mode with a split ratio of 100. The GC-MS assay was done at least three times for each sample. Identification of compounds was identified by comparing the mass spectra (Fig. 1) and retention times of the chromatographic peaks with the authentic sample.

Method for calculating the yield of glycine

Standard solutions of different concentrations were prepared by diluting appropriate amounts of glycine in the water. They were detected by GC-MS after being treated with derivatization method. A five-point standard curve was drawn between the concentration and the peak area (Fig. 2). Correlation coefficient of the standard curve was 0.995. The yield of glycine was calculated by comparing the peak area of the products with the standard curve.

Results and discussion

All the four kinds of metal powders were effective for the synthesis of glycine, as shown in Table 1 (Entry 1–4). Furthermore, the catalytic performance of cobalt powder (glycine yield was up to 6.84 %) was superior to that of Fe, Ni and Cu. While these metals also gave good yield of



Scheme 1 The reaction pathways of glycine derivatization

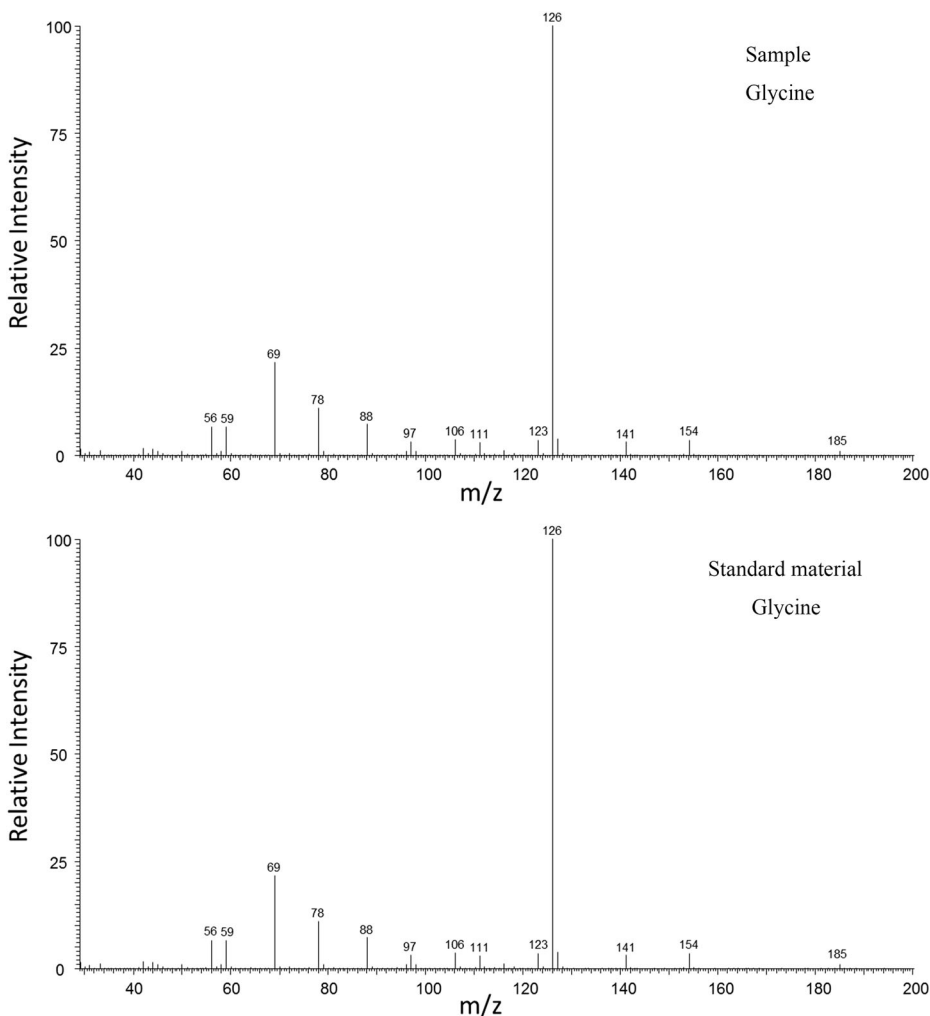
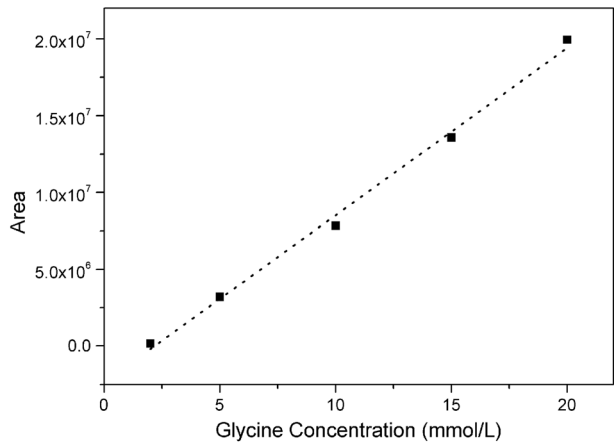


Fig. 1 Mass fragmental patterns of derivative of glycine in the sample, compared with standard glycine material

glycine (3.12 % for Ni, 4.97 % for Fe and 5.04 % for Cu). The comparative experiments were conducted at the same conditions in the absence of catalyst (Entry 5), but no glycine was detected.

After the reaction, the color of solutions changed slightly towards the color of metal ions. The concentration of metal ions in solution were analyzed using inductively coupled plasma spectroscopy (ICP), only a little amount of catalyst was dissolved, the concentration of Fe, Co, Ni and Cu were 1.86, 78.43, 38.40 and 12.78 ppm, respectively. To compare the surface and structure changes of the catalysts before and after the reaction, the catalysts were collected and checked by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Before the reaction, the catalysts were well dispersion and the surface of metals were smooth, while after the reaction, Fe, Co, Ni and Cu were all fretted and lost their luster in hot-alkaline condition (Fig.3 and Fig. 4). The XRD patterns were shown in Fig.5, it can be seen that FeCO_3 and CoCO_3 were formed on the surface of Fe and Co, which was consistent with the SEM analysis. However, structure changes on Ni and Cu failed to be observed, which indicated that the

Fig. 2 The calibration curve of glycine



corrosion on Ni and Cu were smaller than that on Fe and Co, this may due to the higher activity of Fe and Co than Ni and Cu. To demonstrate that the reaction was catalyzed by native metal powders rather than carbonate or metal oxide formed in their surface, we test the catalytic performance of CoCO_3 and metal oxides (Co_2O_3 and Co_3O_4). The results were shown in Table 1 (Entry 6–8). No glycine was detected when catalyzing by CoCO_3 or Co_2O_3 , and only a trace amount of glycine was detected using Co_3O_4 as catalyst.

Table 1 Comparison of different types of catalysts used in the synthesis of glycine and the influence of different concentration and pH for the reaction. The reaction time was 6 h

Entry	Catalyst	Temperature (°C)	Pressure (MPa)	Ethanolamine Concentration (mol/L)	Glycine Yield(%)
1	Ni	160	4	0.1	3.12
2	Fe	160	4	0.1	4.97
3	Cu	160	4	0.1	5.04
4	Co	160	4	0.1	6.84
5	None	160	4	0.1	ND ^b
6 ^a	Co_3O_4	160	4	0.1	Trace ^c
7 ^a	Co_2O_3	160	4	0.1	ND ^b
8 ^a	CoCO_3	160	4	0.1	ND ^b
9 ^d	Co	80	4	0.1	8.07
10 ^d	Co	160	4	0.1	23.54
11	Co	160	6	0.1	7.19
12	Co	160	6	0.01	Trace ^c
13	Co	160	6	0.005	Trace ^c
14	Co	160	6	0.001	ND ^b

^a The amount of catalyst was 0.295 g

^b Not detected

^c Only a trace amount of glycine was detected

^d pH value was adjusted to 12 with NaOH

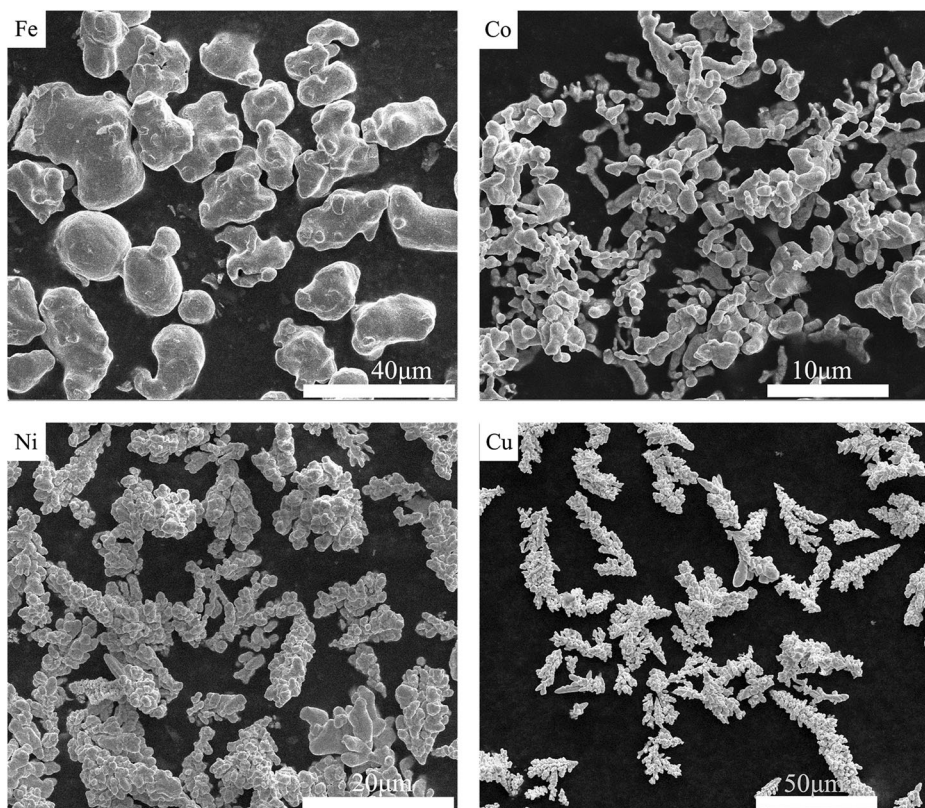


Fig. 3 SEM images of Fe, Co, Ni and Cu before the reaction

All above results suggest that the metal powders exhibit good performances on the synthesis of glycine from ethanolamine in alkaline hydrothermal conditions and cobalt powder exhibits the best performances on the reaction. These results also confirm our speculation that metal powders which are efficient in dehydrogenation of alcohols also show high activity in the dehydrogenation of ethanolamine. Thus the first step of the oxidation of ethanolamine to glycine (from $\text{H}_2\text{NCH}_2\text{-CH}_2\text{OH}$ to $\text{H}_2\text{NCH}_2\text{-COOH}$) may undergo a dehydrogenation oxidation process from $\text{H}_2\text{NCH}_2\text{-CH}_2\text{OH}$ to $\text{H}_2\text{NCH}_2\text{-CHO}$.

The conversion from $\text{H}_2\text{NCH}_2\text{-CHO}$ to $\text{H}_2\text{NCH}_2\text{-COOH}$ in alkaline conditions may through a Cannizzaro Reaction which is very sensitive to pH. Then we studied the effect of pH on the reaction. Experiments were conducted at 80 °C and 160 °C for 6 h with initial pressure of 4 MPa and the pH value was adjusted to 12 with NaOH (Entries 9–10). It can be clearly seen that this catalytic reaction is very sensitive to pH. The yield of glycine could be reach to 8.07 % even at 80 °C when the pH was 12, and the yield increased to 23.54 % when the temperature increased to 160 °C. The experiment results show that pH plays an important role in the reaction and high pH favors the formation of glycine.

Based on the above experiments, we propose a reaction mechanism from ethanolamine to glycine on the metal powders in alkaline hydrothermal environments. The reaction may start from the dehydrogenation oxidation of ethanolamine to form 2-aminoacetaldehyde and hydrogen over metal catalysts. This was followed by a Cannizzaro Reaction to give glycine and ethanolamine in the presence of OH^- derived from the hydrolysis of HCO_3^- (Scheme 2).

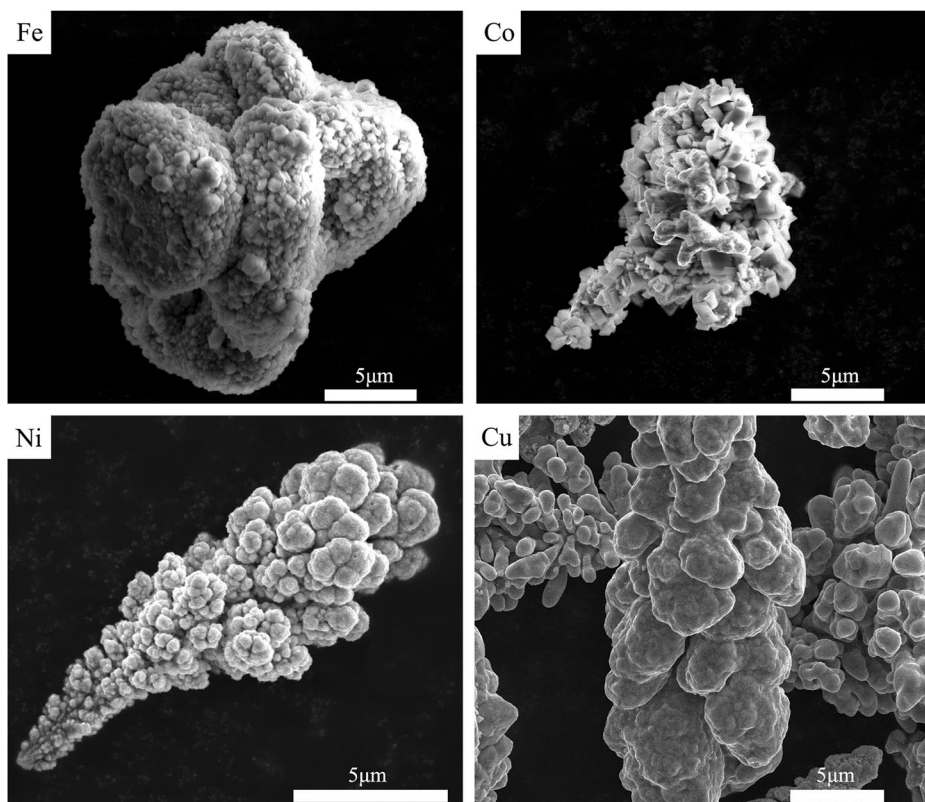


Fig. 4 SEM images of catalysts surface after the reaction

We briefly examined the plausibility of the proposed mechanism by using 2-amino-1-propanol as reactant under the similar conditions, alanine was detected as expected after the reaction. There is reason to speculate that amino alcohols maybe the precursors of amino acids in early Archean ocean.

Reactions were also conducted at various initial concentrations of ethanolamine, from 0.1 to 0.001 mol/L, under the conditions of 6 MPa and 160 °C for 6 h (Table 1, Entries 11–14). The glycine yield was 7.19 % when the concentration of ethanolamine was 0.1 mol/L. Even the concentration of substrate was 0.01 mol/L or 0.005 mol/L, glycine was still detected. Because of limitations in analytical techniques and derivatization method, the reaction produces no detectable quantities of glycine when the concentration of ethanolamine declined to 0.001 mol/L. It is not possible to make a realistic estimate of the ethanolamine produced in Archean ocean, but ethanolamine can be easily transformed to glycine under hot-alkaline hydrothermal conditions. Ethanolamine maybe the best candidate for the synthesis of glycine in the Archean alkaline hydrothermal vents.

As is well known, pressure increases with the depth of the ocean. Discoveries of life in deep-ocean and microbial communities in hydrothermal vents point to the possibility that pressure plays a significant role in the prebiotic synthesis of key biomolecules (Hazen et al. 2002; Daniel et al. 2006). Thus, the effect of pressure on the yield of glycine was investigated by pressuring the reactor with high purity nitrogen to initial pressure of 0.1, 1.0, 2.0, 4.0, 6.0 MPa under ambient temperature. When the reaction temperature reached to 160 °C, the total pressure was

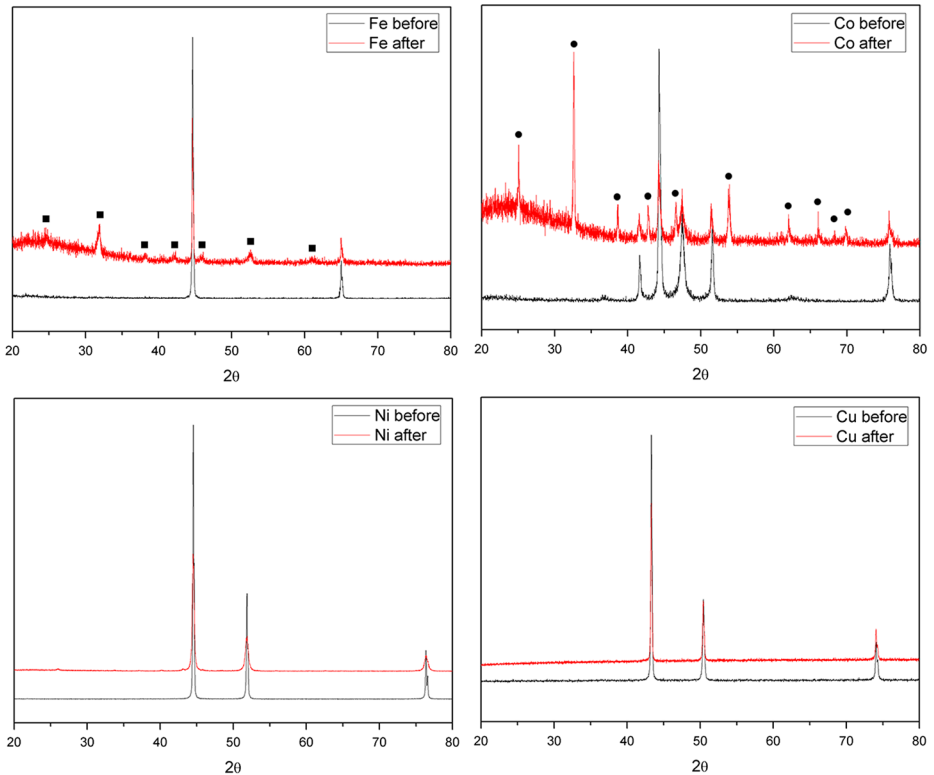


Fig. 5 Comparison of XRD spectra of catalysts before (black) and after (red) the reaction, Solid square and circle represent FeCO_3 and CoCO_3

0.3, 1.5, 3.0, 5.5, 8.0 MPa, respectively. As shown in Fig. 6, the yield of glycine increased rapidly from 1.27 % to 7.19 % when the pressure increased from 0.3 MPa to 8.0 MPa, which showed that pressure facilitated the conversion of ethanolamine to glycine in alkaline hydrothermal environment. We could confirm that high pressure (at least in the range of 0.1–8.0 MPa) favors the formation of glycine from ethanolamine in high-alkaline condition.

Scheme 2 Reaction pathways for metal powder catalyzed ethanolamine conversion

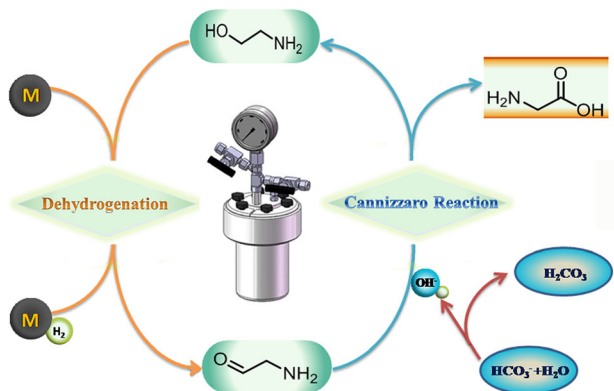
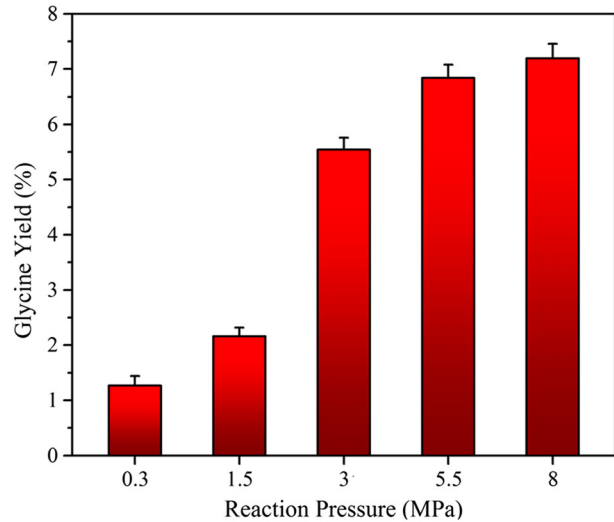


Fig. 6 Effect of the reaction pressure on the yield of glycine. (Experimental conditions: 5 mmol of Co powder, 0.1 mol/L of ethanolamine, pH = 9.70, 160 °C and for 6 h)



At last, we studied the influence of temperature and reaction time on the reaction. Prebiotic chemistry points to a low-temperature origin because most of biomolecules decompose rapidly at high temperature (Miller and Lazcano 1995; Sato et al. 2004). Hence, we discussed the effect of temperatures on the conversion. We decreased reaction temperature from 160 °C to 60 °C at the interval of every 20 °C with initial pressure of 6 MPa for 6 h. As shown in Fig. 7, the yield of glycine decreased from 7.19 % to 2.10 % when the temperatures vary from 160 °C to 80 °C. When the temperature was 60 °C, no glycine was detected. The reaction can be occurred over large ranges of temperature, it also gives good yield of glycine even at 80 °C, which makes the transformation from ethanolamine to glycine easy to achieve in the early ocean.

The effects of different reaction time on the yield of glycine at 160 °C and 6 MPa initial pressure were reported in Fig. 8, the yield of glycine reached to 5.6 % at the first 3 h. The yield of glycine increased with longer reaction time, reached to 11.5 % after 24 h. The results show

Fig. 7 Influence of temperature on the yield of glycine. (Experimental conditions: 5 mmol of Co powder, 0.1 mol/L of ethanolamine, pH = 9.70, 6 MPa initial pressure and for 6 h)

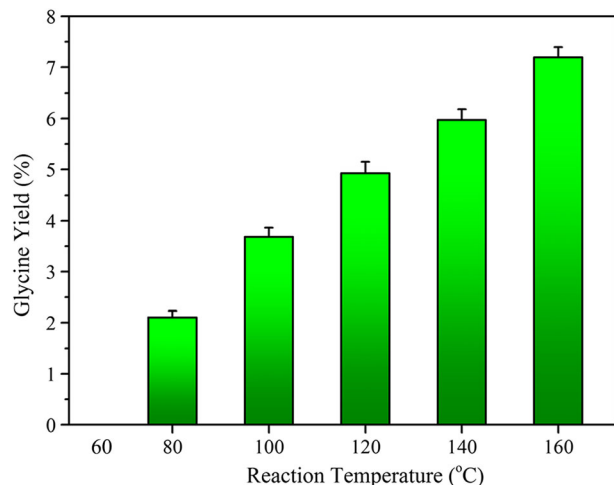
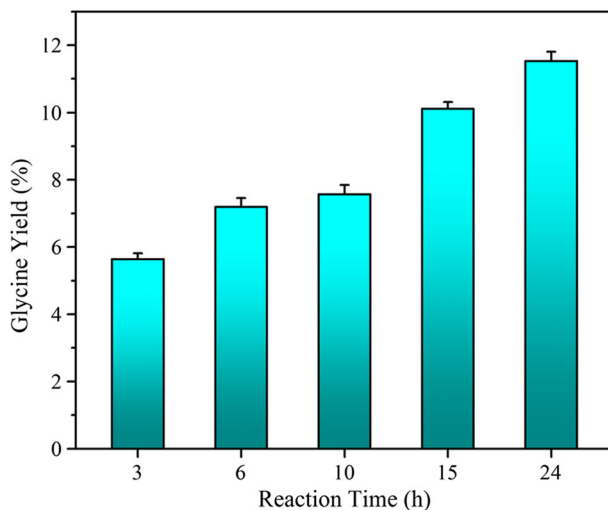


Fig. 8 Influence of reaction time on the yield of glycine. (Experimental conditions: 5 mmol of Co powder, 0.1 mol/L of ethanolamine, pH = 9.70, 160 °C and 6 MPa initial pressure)



that the formation of glycine from ethanolamine occurred rapidly and efficiently at such conditions, this was crucial to prebiotic synthesis of biomolecules due to their ease of destruction. Furthermore, polymerization reactions of glycine are favored by high temperature and alkaline pH (Sakata et al. 2010; Kitadai 2014), this reaction would be conducive for subsequent reactions toward more complicated biomolecules.

Conclusion

In summary, glycine was synthesized from ethanolamine using metal powders as catalyst under simulated Archean alkaline hydrothermal vents conditions. Metal powders including Fe, Co, Cu and Ni are all effective for the reaction, and high yield of glycine was obtained at 80–160 °C in 3–24 h. Furthermore, the reaction is very sensitive to pH and favors high pH, which indicates that the reaction starts from dehydrogenation of ethanolamine to 2-aminoacetaldehyde and followed by Cannizzaro Reaction to give glycine. The reaction occurs rapidly and efficiently in the presence of metal powder in alkaline hydrothermal condition, and high temperatures and high pressures favor the formation of glycine. In addition, the facts that glycine can be synthesized even at low concentration (0.005 mol/L) and mild temperature (80 °C), make the reaction easy to achieve in the early ocean. Our observation provides a new pathway for prebiotic glycine formation and points out the phenomenal influence of high-temperature alkaline hydrothermal vents in origin of life in the early ocean. Amino alcohols, with the similar structure to amino acids, may be the precursors of amino acid. Further experiment with amino alcohols in simulated Archean submarine alkaline vent systems may confirm a coherent narrative of amino acids evolution.

Acknowledgments This work was supported by grants from the National Natural Science Foundation of China (No.21427802, 21131002, 21201075 and 20901026) and Specialized Research Fund for the Doctoral Program of Higher Education of China (SRFDP, No.20110061130005).

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