Nucleobase and amino acid formation through impacts of meteorites on the early ocean

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ABSTRACT

The emergence of life's building blocks on the prebiotic Earth was the first crucial step for the origins of life. Extraterrestrial delivery of intact amino acids and nucleobases is the prevailing hypothesis for their availability on prebiotic Earth because of the difficulties associated with the production of these organics from terrestrial carbon and nitrogen sources under plausible prebiotic conditions. However, the variety and amounts of these intact organics delivered by meteorites would have been limited. Previous shock–recovery experiments have demonstrated that meteorite impact reactions could have generated organics on the prebiotic Earth. Here, we report on the simultaneous formation of nucleobases (cytosine and uracil) found in DNA and/or RNA, various proteinogenic amino acids (glycine, alanine, serine, aspartic acid, glutamic acid, valine, leucine, isoleucine, and proline), non-proteinogenic amino acids, and aliphatic amines in experiments simulating reactions induced by extraterrestrial objects impacting on the early oceans. To the best of our knowledge, this is the first report of the formation of nucleobases from inorganic materials by shock conditions. In these experiments, bicarbonate was used as the carbon source. Bicarbonate, which is a common dissolved carbon species in CO_2-rich atmospheric conditions, was presumably the most abundant carbon species in the early oceans and in post-impact plumes. Thus, the present results expand the possibility that impact-induced reactions generated various building blocks for life on prebiotic Earth in large quantities through the use of terrestrial carbon reservoirs.

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1. Introduction

Extraterrestrial objects impacted the early Earth intensively, as suggested by the lunar impact history (Culler et al., 2000; Hartmann et al., 2000; Valley et al., 2002), and such events delivered large amounts of metals as well as biologically important elements to the early Earth (Anders, 1989; Chyba and Sagan, 1992; Pasek and Lauretta, 2008). Carbonaceous chondrites and interplanetary dust particles (IDPs) may have supplied fragile organic molecules such as amino acids and nucleobases (Anders, 1989; Chyba and Sagan, 1992). Such extraterrestrial delivery of intact amino acids and nucleobases is currently the dominant model, as opposed to the Miller–Urey model for the emergence of amino acids and HCN polymerization for nucleobases on the prebiotic Earth (Miller, 1953; Oró, 1961; Oró and Kimball, 1961; Harada and Suzuki, 1977; Ferris et al., 1978; Shapiro, 1999; Miyakawa et al., 2002a), and this has been supported by evidence involving the identification of amino acids and nucleobases in carbonaceous chondrites (Kvenvolden et al., 1970; Cronin and Moore, 1971; Stoks and Schwartz, 1979, 1981; Martins et al., 2008; Callahan et al., 2011).

While carbonaceous chondrites contain various biologically relevant organics, such chondrites could have only delivered a limited amount of intact organics to the surface of the Earth (Anders, 1989). By comparing the mass fluxes of extraterrestrial objects including meteorites, IDPs, and crater forming objects at present, it was found that the mass flux of meteorites is several hundred times smaller than those of IDPs and crater forming objects (Anders, 1989). These comparative trends were likely similar for the ancient Earth. Thus, the IDPs likely provided a far higher mass flux of carbon to the ancient Earth than chondrites (Anders, 1989), but the specific components and concentrations of amino

acids and nucleobases in IDPs remains unclear (Glavin et al., 2004; Maurette, 2006).

Larger projectiles have higher energies and generate stronger shock waves and post-impact heating when they impact the Earth. Such projectiles, which include crater-forming objects, have been estimated to have high mass fluxes similar to those of IDPs (Anders, 1989). During such hypervelocity impacts, significant amounts of fragile organic compounds in the extraterrestrial objects decompose (Peterson et al., 1997; Ross, 2006). However, these impacts cause chemical reactions between meteoritic materials, the ocean, and the atmosphere. Formation of reduced volatiles from inorganic materials has been reported in simulations of post-impact reactions on the early Earth (Fegley et al., 1986; Mukhin et al., 1989; Gerasimov et al., 2002; Schaefer and Fegley, 2010; Kurosawa et al., 2013; Furukawa et al., 2014). Furthermore, our research group has investigated such post-impact reactions with experimental simulations and demonstrated the formation of glycine and aliphatic carboxylic acids from inorganic carbon in the meteorites (Nakazawa, 2008; Furukawa et al., 2009). Amino acid formation has also been proposed for impacts involving simulated cometary ice composed of ammonia, methanol, and carbon dioxide (Goldman et al., 2010; Martins et al., 2013). These studies support the importance of impact-induced reactions as a mechanism for the provisioning of life's building blocks to the early Earth.

In our previous study, in which we showed the formation of glycine, solid amorphous carbon was used as the carbon source (Furukawa et al., 2009). Here, high partial pressure of CO_2 in the early Hadean atmosphere has been presumed (Holland, 1984; Walker, 1985; Kasting, 1993), and therefore, dissolution of large quantities of bicarbonate in the early oceans would have occurred (Morse and Mackenzie, 1998). Hence, such carbon would have been readily available in the post-impact plumes. Utilization of this huge carbon reservoir on the early Earth in impact-induced reactions might have provided various kinds of organic compounds important for life. Notably, ammonia can be formed through the reduction of terrestrial nitrogen species in the ocean, crust, and impact plumes (Summers and Chang, 1993; Brandes et al., 1998; Nakazawa et al., 2005; Smirnov et al., 2008; Schaefer and Fegley, 2010; Furukawa et al., 2014). Thus, both bicarbonate and ammonia were likely reasonably available in the impacted environments and may have become carbon and nitrogen sources for prebiotic organic synthesis reactions on the early Earth. The purpose of the present study was to examine if various nucleobases and amino acids could have been generated from bicarbonate and ammonia through the interactions with meteoritic minerals during shock conditions.

2. Experimental

2.1. Materials

Commercially available metallic iron (99.9 wt%, powder, <45 µm in diameter; Wako), magnetite (powder; Wako), and metallic nickel (99.95 wt%, sponge; Wako) were used as starting materials. Natural forsterite from Myanmar was also used as a starting material; this material was ground and heat-treated at 450 °C for 6 h prior to use. These powders were first mixed with an agate mortar and pestle. Then, the mixture was placed in a reaction container with a ^{13}C-labeled NH_4HCO_3 solution. The $NH_4H^{13}CO_3$ (~90 wt%) solution was prepared with commercial ^{13}C-labeled CO_2 (Cambridge Isotope Lab) and an ammonia solution (Sigma–Aldrich). The stoichiometry of $NH_4H^{13}CO_3$ was verified using an elemental analyzer (Carlo Erba), and the absence of ^{13}C-labeled amino acids and nucleobases in non-shocked $NH_4H^{13}CO_3$ was confirmed with ultra-high performance liquid

chromatography–tandem mass spectrometry (UHPLC–MS/MS) analyses that employed identical methods to those used for product analyses. The sample container was constructed of low carbon content stainless steel (SUS304L). Additional details about the sample container, flyer, and the alignment of samples in the container are described elsewhere (Furukawa et al., 2009). Gaseous nitrogen (>99.995%) was introduced into the head space of the sample container.

Commercially available cytosine (Wako), uracil (Wako), an amino acid mixture (AN-2; Wako), methylamine (Wako), ethylamine (Wako), propylamine (Wako), and butylamine (Wako) were used as standards for the UHPLC–MS/MS analyses. All of the glassware used for the experiments was heated at 450 °C for 6 h to avoid contamination.

2.2. Shock–recovery experiments

We conducted shock–recovery experiments using forsterite (Mg_2SiO_4), metallic iron, magnetite (Fe_3O_4), and metallic nickel as the components of simplified meteorite materials as well as ^{13}C-labeled ammonium bicarbonate solution and gaseous nitrogen as oceanic and atmospheric components, respectively. Based on those compositions, the starting materials were termed IM1 and IM2 (representative of iron meteorites), OC1 and OC2 (representative of ordinary chondrites), and CC1 and CC2 (representative of carbonaceous chondrites) (Table 1).

The shock–recovery experiments were conducted using a single-stage propellant gun (Sekine, 1997). These starting materials were enclosed in a tightly sealed metallic container and subjected to the impact of a metallic flyer at ~0.855 ± 0.035 km/s. The pressures of the samples reached 4–7 GPa for ~1 µsec and then rapidly dissipated. Detailed temperature and pressure profiles were similar to those reported in a previous study (Furukawa et al., 2011).

2.3. Sample analysis

Aqueous products were extracted using 20 mL deionized water at room temperature. The extraction solution was divided into three portions. The first portion was used for the analysis of amines after addition of a 6 M HCl solution (0.5 mL) followed by dehydration in vacuum conditions at room temperature. The second and third portions were used for amino acid and nucleobase analyses, respectively, after dehydration in vacuum conditions at room temperature. Then, the first and second portions were treated with AccQ-Tag reagent (Waters) to derivatize the amino groups of amino acids and amines. For all analyses, samples were not treated with heated acids or bases to avoid hydrolysis and additional reactions.

Ultra-high performance liquid chromatography (UHPLC) coupled with tandem mass spectrometry (MS/MS) was conducted using a Shimadzu LCMS-8040 while targeting ^{13}C-labeled nucleobases. ^{13}C-labeling ensured accurate identification of the products and helped us to distinguish contaminants. The combination of high resolution UHPLC and MS/MS also facilitated the identification of specific products by constraining molecular polarity, mass of the target ion, and mass of the fragment ion generated from the target. An amide column (BEH Amide, 2.1 mm I.D., 50 mm length, 1.7 µm; Waters) was used for analyses at temperatures of 30 °C or 35 °C. A linear gradient of 10 mM ammonium formate buffer (pH 3.0) and acetonitrile was used as the eluent at a flow rate of 0.3 or 0.5 mL/min. The concentration of ammonium formate buffer in the gradient was 5% for 0–1 min at a 0.5 mL/min flow rate, 25% for 10 min at a 0.3 mL/min flow rate, 5% for 0–1 min at a 0.5 mL/min flow rate, and finally 25% for 6 min at a 0.5 mL/min flow rate. Positive- and negative-mode electrospray ionization (ESI) was used to ionize the cytosine and uracil, respectively. The flow rates of