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Hydrogen enhances the stability of glutamic acid in hydrothermal environments

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ABSTRACT

The potential for chemical evolution of complex organic molecules such as peptides in hydrothermal environments requires the persistence of the component amino acids under such conditions. Here, we show experimentally that the redox state (activity of H_2) of the aqueous fluids plays a key role in the stability of glutamic acid during hydrothermal processes. The results demonstrate that highly reducing redox conditions imposed by elevated concentrations of dissolved H_2 suppresses the oxidative decomposition of glutamic acid at elevated temperatures. Our experimental data support proposals that amino acids may persist, albeit metastably, under geochemically relevant hydrothermal conditions. The reduced nature of deep-sea vent fluids might have been a critical parameter in sustaining the needed ingredients for the origin of life on the early Earth, and may currently play a role in facilitating the persistence of biomolecules supporting heterotrophic microbial communities in modern near-seafloor hydrothermal environments.

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1. Introduction

Origin of life scenarios that focus on deep-sea hydrothermal vent environments highlight the exceptional physicochemical conditions where small organic molecules such as amino acids may form abiotically and condense into primitive macromolecules (Shock, 1992; Amend and Shock, 1998; Huber and Wächtershäuser, 1998; Cody, 2004; Russell et al., 2005; Shock and Canovas, 2010; Milner-White and Russell, 2011). Sub-seafloor hydrothermal circulation within the oceanic crust generally results in hydrothermal vent fluids characterized by elevated temperatures, a wide range of pH, and highly reducing conditions indicated by the presence of dissolved H_2. The stability of amino acids in these environments is essential if such simple molecules are to form peptides. Some studies have shown very promising routes to oligopeptide synthesis occurring at room temperature and under hydrothermal conditions (Huber et al., 2003; Leman et al., 2004). However, numerous experimental studies have reported that amino acids are intrinsically unstable under hydrothermal conditions (Miller and Bada, 1988; Bada et al., 1995; Andersson and Holm, 2000; Cox and Seward, 2007; Lemke et al., 2009). In contrast, theoretical calculations point to the possibility of metastable equilibria between amino acids and CO_2–NH_3 in H_2-enriched hydrothermal vent fluids (Shock, 1990; Shock and Canovas, 2010). This possibility has been investigated experimentally by only one study (Andersson and Holm, 2000) where it was shown that the decomposition rates of amino acids at 200 °C were suppressed in the presence of mineral assemblages intended to buffer the H_2 concentration in the fluids. However, kinetic barriers can prevent equilibrium with mineral buffer assemblages at 200 °C; thus, the actual H_2 content in the fluid, which was not measured, may have been well below the intended equilibrium values. No experimental hydrothermal study of amino acid stability has been reported in which a known H_2 concentration was imposed at levels relevant to modern deep-sea hydrothermal vent systems.

Here we report experimental results that show the effect of $H_{2(aq)}$ on the hydrothermal stability of glutamic acid. Two sets of homogeneous experiments were conducted at 200 °C and 250 °C at 140 bars. First, we followed the decomposition of glutamate in water without added $H_{2(aq)}$ and initial $pH_{25\ °C} \sim 10$. A second experiment was conducted involving aqueous solutions enriched with 13.1 ± 1.8 mM dissolved $H_{2(aq)}$ at the same initial pH. Measurements were made on the decomposition products of glutamic acid. Overall, these conditions of T, P, pH or $H_{2(aq)}$ are similar to those in some natural ultramafic-hosted hydrothermal systems such as the Lost City hydrothermal vents at 30°N on the Mid-Atlantic Ridge (Seyfried et al., 2004; Kelley et al., 2005; Foustoukos et al., 2008).

2. Materials and methods

2.1. Materials

All solutions were made from milli-Q water (Millipore resistance 17.9 MΩ). L-Glutamic acid (Acros Organics, 99%) and L-pyroglutamic

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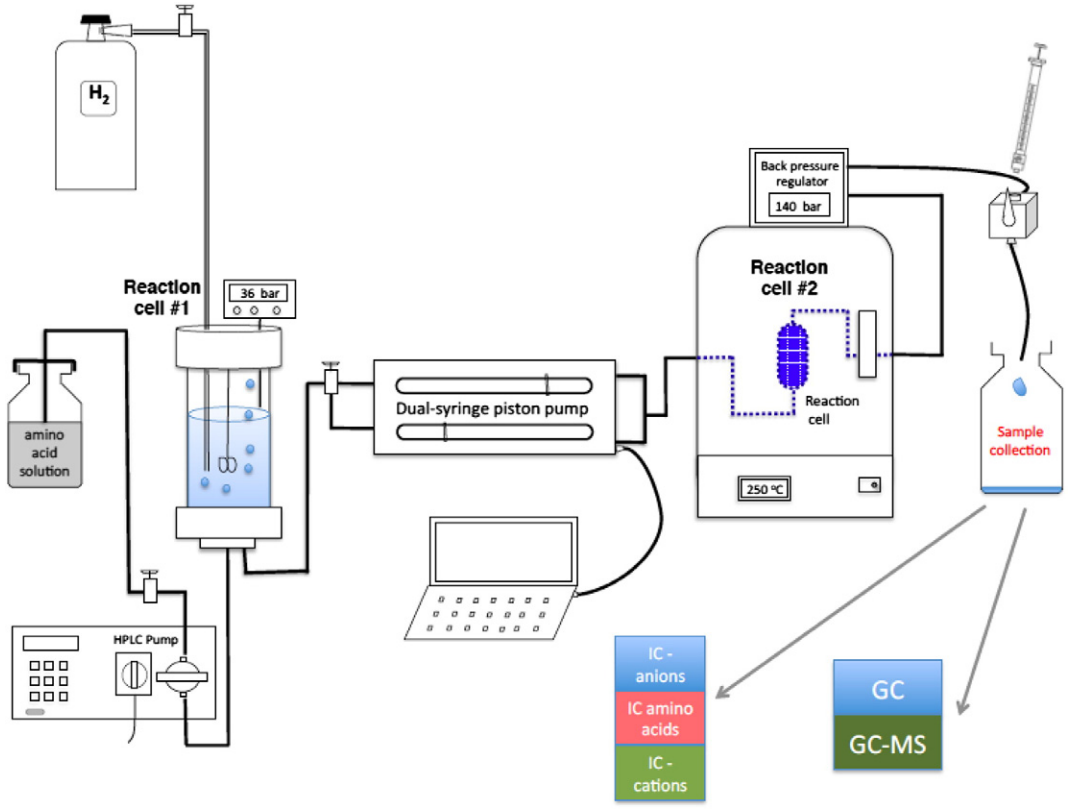

Fig. 1. Materials, experimental setup and methods.

acid (Aldrich, ≥99.0%) were used without any further purification. The solutions were sonicated for more than 15 min and visually checked prior to the use to ensure complete dissolution. The pH was adjusted to alkaline values (i.e. 10) by adding precise volumes of standardized NaOH. Measurement of pH was carried out using a combination electrode (Thermo-Electron, Orion 8103 BNUWP) that was previously calibrated with standardized pH buffers. Argon gas was constantly purged through the solution to avoid contamination by atmospheric CO_2 prior to the experiments. The solution was kept under argon headspace.

The high initial pH of the glutamate solution was also chosen to provide minimal interaction with the TiO_2 reactor surface layers (see below) (Maielle and Brill, 1998). It is known that TiO_2 has a point of zero charge (pH_{pzc}) near 5.4 at 25 °C (Jonsson et al., 2009; Foustoukos et al., 2011) and that it decreases with increasing temperature (Machesky et al., 1998). The in-situ pHs were estimated using an aqueous speciation model (Shock et al., 1989; Shock and Helgeson, 1990; Wolery, 1992). The calculations show that at 250 °C, the pH range of the glutamate solution is around 7 ± 0.5 for all solutions (neutral pH at 250 °C is 5.58). Additionally, pHs of the quenched fluid were measured to be around ~9.7. Preliminary calculations show that its quenched pH is consistent with the model high-temperature pH. Consequently, we can expect that glutamate has negligible interactions with TiO_2 at the pH values of our experiments due to electrostatic repulsion (Jonsson et al., 2009).

2.2. Experimental setup

The hydrothermal flow-through experiments were performed by using two titanium flow-through cells configured in-series and by following procedures similar to those described in Foustoukos et al., (2011) and Lee et al., (2014) (Fig. 1). The titanium reactors/pressure tubing was combusted in air to generate inert TiO_2 layers clearly evident by the blue color prior to the experiments. The initial L-glutamic acid solution (9.6 mM, pH = 10) was first introduced into a 50 ml titanium pressure vessel (reaction cell #1) (autoclave engineers). Once headspace was created in the pressure vessel and highly pressurized $H_{2(g)}$ was introduced, it was allowed to dissolve at elevated concentrations by a magnetic agitator operating at high pressure at 600 revolutions/min at room temperature. Time series sampling indicated that 36 bar of $H_{2(g)}$ at the headspace resulted in nearly 13 mM of dissolved H_2 within 30 min of agitation. It should be noted that due to the limited volume of reaction cell #1, fluid was depleted and replenished separately for each flow rate. Consequently, the dissolved H_2 concentrations may have differed slightly between flow rates, yielding an average of 13.1 ± 1.8 mM (Tables 1, 2). The H_2-enriched solution was delivered to the reactor cell #2 (fixed volume of 3.55 ml) located inside a gravity-convection Lindberg/Blue oven (with temperature uniformity of 4 °C at 200 °C). Fluid delivery was facilitated by a high-precision dual-cylinder gas-tight titanium pump (Quizix SP5000) at constant flow rate of between 0.1 and 1.4 ml/min, while maintaining constant pressure conditions (140 bar) by an inline titanium backpressure regulator (Coretest DBPR-5). Flow rates determined the residence time of the fluid in the high temperature Ti-reactor cell #2. Accordingly, samples were taken at different reaction times with gas tight syringes.

Three different types of ionic chromatography (IC) were adopted for aqueous species analyses. For the detection and measurement of amino acids and other anionic organic molecules a Dionex ICS-5000 AAA-Direct IC was used. The chromatograph was equipped with a 2-250 AminoPac PA 10 analytical column and an integrated pulsed amperometry electrochemical detector (IPAD). Aliphatic decomposition products such as formate and pyroglutamate were analyzed with a Metrohm MIC-3 Advanced ionic chromatograph equipped with a Metrosep A sup 7-250 column and conductivity detector. Cationic decomposition products such as ammonium ion were monitored and analyzed with the Dionex ion chromatograph ICS-5000 using a 250 IonPac CS12A analytical column and conductivity detector. For ammonium analyses, the sample aliquots were acidified immediately upon the collection and kept in the refrigerator for later analyses. The