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Amino acids in the 308 °C deep-sea hydrothermal system of the Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean

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Abstract

Deep-sea hydrothermal systems are of significant interest as a new scientific frontier in a number of fields. This report analyzes data obtained in ocean-drilling surveys at submarine hydrothermal vents on the Suiyo Seamount in the Izu-Bonin Arc, Pacific Ocean. These surveys obtained direct data regarding subjacent extreme environments under extreme conditions of 308 °C and greater than 14 MPa. Evaluation of the vertical distribution and stereo-chemistry of amino acids in such vigorous hydrothermal system leads to a model of deep-sea subterranean chemistry and biology that describes a lack of evidence of abiotically synthesized amino acids. Large enantiomeric excesses of L-form amino acids supported the existence of a vigorous subjacent microbial oasis in a hydrothermal system.

Key words

Deep-sea hydrothermal system, Benthic multi-coring system (BMS), Amino acids, Enantiomeric Excesses, Biological activity

1. Introduction

The discovery of the Galapagos submarine hot springs [1] has lead many researchers to consider that deep-sea hydrothermal systems are suitable environments for chemical evolution and may be implicated in the origins of life on Earth [2]. Anomalous
5 concentrations of glycine in the Red Sea may also support the notion of deep-sea chemical evolution [3]. In fact, a number of submarine ecological colonies have been recognized near black or clear smokers and the associated organic-rich seafloor mats [4]. Now, ocean-drilling experiments at submarine hydrothermal vents have made it possible to directly analyze subjacent extreme environments [5]. The biological
10 environment of extreme ocean-floor vents can be well characterized by bioorganic compounds, particularly amino acids, which are common components of all organisms and constitute a major fraction of organics [6]. The present report describes the vertical distribution and stereo-chemistry of L- and D- form amino acids under extreme conditions of 308 °C and greater than 14 MPa in the hydrothermal system [5]. This
15 approach allows a model of deep-sea subterranean chemistry and biology to be put forth. The chemical aspects of abiotically synthesized amino acids [7,8] and the associated stereo-chemistry is of notable interest in the process of chemical evolution. Biologically, it is considered that hyperthermophiles [9] or barophiles with affinity for high pressure [10] are likely to be widespread in regions immediately below
20 hydrothermal vents, which extends the known terrestrial habitable zone significantly.

Submarine hydrothermal systems are of significant interest as a new scientific frontier [5], and while the existence of a deep bacterial biosphere in oceanic sediment has been reported [11] and is a remarkable discovery, sub-surface of the hydrothermal system has yet to be described.

2. Geological significance and core sampling

The present report builds a model of this environment based on deep-sea hydrothermal system core samples collected as part of the Archaean Park Project in a
5 cruise over the Suiyo Seamount (28°33 N, 140°39 E)[Ref.12] in the Pacific Ocean in July, 2001. The seamount has a large-scale submarine volcanic caldera with area of approximately 1,500 m × 500 m, and the deep-sea subterranean biosphere and geochemical interaction were examined by taking core samples using a fixed seafloor benthic multi-coring system (BMS) for pinpoint drilling in the caldera [5]. Boring site
10 APSK 05, the objective site in this study, is located in the northern part of the central hydrothermal venting area in the caldera floor. Surface sediment at the site consists primarily of approximately 30 cm of sandy volcanic clastics. Below the clastics zone, partially recovered core samples suggest that unaltered volcanic rocks, mainly pumice deposits, dominate down to a depth of about 2.1 m below seafloor (mbsf). The
15 unaltered zone was penetrated easily, but the drilling speed decreased significantly at greater depth due to the prevalence of clay-dominated material, presumed to be altered dacite. Mixed-layer clay minerals chlorite and montmorillonite are the dominant hydrothermal minerals, and anhydrite cements the rocks and fills pores [13]. The anhydrite is considered to have precipitated from hot seawater, as evidenced by the
20 sulfur isotopic signature and calcium/strontium ratio [13,14] . Sulfide grains, mostly pyrite (up to 1 mm diameter), were observed at several zones, representing possible vestiges of hydrothermal veining. Below 3.7 mbsf, the recovered rocks are less altered, and core samples of 4.3 to 4.7 mbsf are more porous and contain a mixture of mica and chlorite. Oxygen isotopic signatures of these clay minerals indicate that the temperature

increases with depth, with mica forming at about 280 °C [Ref.13]. Although, drilling below 4.7 mbsf was very speedy, no core could be recovered. This easily penetrated zone may be very porous rock or even a void. Thus, this porous zone and overlying cemented, impermeable sulfate rocks are considered to form a hydrothermal fluid reservoir and cap. This shallow reservoir less than 10 m below the seafloor, and is the most noticeable feature of the Suiyo hydrothermal field. Removal of the drilling pipe was followed immediately by vigorous emission of hot fluid (> 308 °C) from the drill hole.

As to terrestrial origin of organics onto Suiyo seamount, it was reported that total fatty acid compositions in surface sediments obtained from Suiyo hydrothermal system, Izu-Bonin Arc were not significant sedimentary organic matter [14]. Analytical result of the surface sediments indicated very low contribution of terrestrial origin of sediments [14]. Besides age determination of unaltered dacite by Ar-Ar method showed $9,000 \pm 8,000$ yrBP, suggesting zero age [15]. Consequently Suiyo seamount is a young dacitic volcanism and had almost no chance to be covered by biogenic sediments.

3. Experimental

3.1. Pre-treatment of core samples

Rock core samples were carefully obtained and quickly sealed with dehydrating and deoxygenation agent package (AGELESS, Mitsubishi Gas Chemicals Co.). The interior portion of five hundred mg each of the freeze-dried rock samples were ground and digested with 5 ml of 5 M HF- 0.1 M HCl mixture in a sealed Teflon vessel at 110 °C for 16 h. Then the mixtures were evaporated to dryness on a hot plate placed in a draft

chamber. The organic residues were dissolved in pure water while applying ultrasonic waves. The aqueous solutions were filtered through GF/A glass filters, and then freeze-dried in test tubes. They were hydrolyzed in sealed test tubes with 6 M HCl at 110 °C for 2 hours. After evaporation to dryness, the hydrolysates were dissolved in water, adjusted to pH 1, and injected into a Bio-Rad AG-50W-X8 cation-exchange resin column (200-400 mesh) for desalting. Before injection of the sample, the resin was washed by passing 1 M HCl, H₂O, 1 M NaOH and H₂O, successively. The resin was reactivated with 1 M HCl and rinsed with H₂O immediately prior to analysis. The amino acid fraction was eluted from the column with 10 % NH₃ aqueous solution. The eluted fraction was evaporated to dryness and re-dissolved in 0.1 M HCl before amino acid analysis.

3.2. Amino acid analysis

The concentration of amino acids were determined by ion-exchanged HPLC, which was composed of two high performance liquid chromatography pumps (Shimadzu LC-6A), a cation-exchange column (Shimpak ISC-07/S1504, 4 mm i.d. × 150 mm), a post column derivatization system, and a Shimadzu RF-535 fluorometric detector [17]. The derivatized reagents used were N-acetyl-L-cystein (N-AceCys) and *o*-phthalaldehyde (OPA) in borate buffer. Separation of D- and L-amino acid enantiomers was achieved by high-performance liquid chromatography (RP-HPLC) using HPLC pumps (CCPM II, TOSOH), a reversed-phase column (YMC-pack Pro C18, 4.6 mm i.d. × 250 mm), and a TOSOH FS fluorometric 8020 detector (excitation wavelength 355 nm, emission wavelength 435 nm). An aliquot of the pre-treated sample was mixed well with N-AceCys and OPA in a glass vial and injected into the HPLC column. A gradient

elution was applied using the following eluents: A, 40 mM sodium acetic acid buffer (pH 6.5); B, 100% methanol (ultra-pure HPLC grade). The gradient program was performed as follows: 10 min (Eluent B: 0 %) – 25 min (Eluent B: 10 %) – 65 min (Eluent B: 20 %) – 80 min (Eluent B: 20 %) – 85 min (Eluent B: 40 %) – 115 min (Eluent B: 60 %) – 120 min (Eluent B: 80 %) – 135 min (Eluent B: 0 %). Total organic carbon (TOC) and total nitrogen (TN) were also analyzed by CE Instruments NA1500 as preliminary experimental procedures [18].

4. Result and discussion

4.1. Subterranean biological origin of amino acid specimens

The abundance of amino acids in the core samples ranged from 26.0 to 107.4 nmol/g-rock as shown in Table 1. Fresh internal samples of core rock contained predominantly glycine, with lesser concentrations of proteinous amino acids such as alanine, serine and aspartic acid, as shown in Figure 1. Although non-proteinous amino acids such as β -alanine, α -aminobutyric acid, and γ -aminobutyric acid have been found as major products in laboratory experiments simulating hydrothermal systems [7,8], they were present as only minor constituents in the present core samples. The vertical distribution of amino acids in these samples differs from typical ocean seafloor sediment in that the concentration of amino acids in normal, simple sedimentation decreases rapidly with depth due to diagenesis [19]. Diagenesis in sediment may cause decomposition of amino acid *via* decarboxylation [20], by which aspartic acid will alter to β -alanine by specific decarboxylation of the α -carboxyl group [21]. However, as seen in Figure 2, the correlation in the relative abundance of β -alanine and aspartic acid with depth was not observed.

Haberstroh and Karl (1989) reported the vertical concentration of dissolved free amino acids (DFAA) and ATP in the Guaymas sediment-covered hydrothermal system [22]. Concentration of DFAA and ATP in the Guaymas sediment drastically decreased with the depth in the early stage of diagenesis [22]. Hence, the amino acid distribution is essentially independent from the surface circumstances, with energy derived from chemical sources in the form of fluids migrating upward from deeper levels in the present study.

It was demonstrated in the room experiment that monomer amino acids were not stable in hydrothermal condition [23]. In the actual hydrothermal systems, however, large amount of organic matter derived from microbial activities might be more than that of thermal degradation in the sediment. Then, apparent concentration of hydrolyzed amino acids would be determined on the base of biogenic organic matter.

4.2. Stereo-chemical implication of biosphere below the hydrothermal system

The D/L ratio of amino acids converges to around 1.0, as typical for amino acids formed abiotically [7], however, the large enantiomeric excess of L-form amino acids may indicate that the amino acids were derived by biotic processes (Table 2). The low D/L ratio for aspartic acid and glutamic acid in the vertical profile is evidence of microbial activity as shown in Figure 2. The lower sediment column exhibited a low D/L ratio of 0.04 to 0.16 for aspartic acid. Preliminary investigation of the caldera revealed a high-temperature hydrothermal pool covered with several meters of volcanic sediment with sulfate and boundary cap rock [5]. Therefore, this low D/L ratio in the lower column sediment may indicate that the prevailing thermal gradient in that area gives rise to a living temperature that is optimal for subterranean microbes.

4.3. Organic carbon and total nitrogen

Concentrations of total organic carbon (TOC) and total nitrogen (TN) in the core samples were in the ranges 74 to 301 $\mu\text{g C/g-rock}$ and 60 to 3,100 $\mu\text{g N/g-rock}$,
5 respectively. These values are significantly lower than those for common ocean-floor sediments except for one sample that contained significantly higher TN (3,100 $\mu\text{g N/g-rock}$). The atomic ratios of TOC to TN (C/N) range from 0.1 to 2.7 (average 0.8), and the ratios are significantly lower than those for normal marine bacteria or phytoplankton [24] and the suspended particulate organic materials from hydrothermal
10 vent water [25,26]. Although the C/N ratio for bacteria-inhabited hydrothermal vent environments is not known, the present values are noticeably rich in nitrogen. Fourier transform infrared (FT-IR) analysis of clay minerals in the core samples suggests that ammonium ions are present at interlayer sites [13]. Ammonia is present in hydrothermal fluid [27] at concentrations from 10 to 20 μM and is an important source
15 of nitrogen nutrition for the sub-vent ecosystem. The high TN layer may therefore represent a region of ammonia concentration in the clay minerals. The TOC remains high in the first 2.2 mbsf, decreases with depth down to 3.2 mbsf, then increases again below 4 mbsf. This trend is similar to the distribution of total amino acids, suggesting that the organic carbon and amino acids are derived from in situ organisms, viable
20 and/or nonviable.

5. Conclusions

The currently accepted thermal limit of life is 121 $^{\circ}\text{C}$ [28], and although some proteins from hyperthermophiles are more active at high pressure, high pressure does

not increase the thermal stability of micromolecules [29]. It is therefore interesting to note that approximately 10^4 cell/ml of microbes were found in hydrothermal fluid from the drill hole at APSK 05 when the drill hole was cased with metal to block infiltration of interstitial water [30]. It still appears difficult for life to exist at over 308 °C, however, the thermal gradient at this site may be such that optimum temperatures for microbial life may be prevalent in hydrothermal systems. The amino acids detected in the Suiyo Seamount indicate a biogenic origin rather than abiotic chemical synthesis. The large enantiomeric excess of L-form amino acids and sensitive geothermal indicators of aspartic acid and β -alanine are also likely to be consistent with a large microbial population. The present findings are therefore strong evidence that hydrothermal systems are a previously unknown extreme environment biosphere and may represent a subterranean habitable zone.

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Figure 1

Fig. 1. Ion-exchanged chromatograms of hydrolyzed amino acids in deep-sea hydrothermal system core samples of APSK 05 at Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean. Abbreviations: Asp, aspartic acid; Thr, Threonine; Ser, serine; Glu, glutamic acid; α-AAA, α-aminoadipic acid; Gly, glycine; Ala, alanine; α-ABA, α-aminobutyric acid; Val, valine; Met, Methionine; Ile, isoleucine; Leu, leucine; Tyr, tyrosine; Phe, phenylalanine; β-Ala, β-alanine; γ-ABA, γ-aminobutyric acid; δ-AVA, δ-aminovaleric acid.

Figure 2

Figure 2 (continued)

Fig. 2. Vertical distribution of total hydrolyzed amino acids (a), D/L ratio of aspartic acid (b), mole ratio of aspartic acid and β -alanine (c), total organic carbon (d), total nitrogen (e) and C/N ratio (f) in submarine hydrothermal system core samples of APSK 05.

Table 1

*core No.	Asp	Thr	Ser	Glu	α -AAA	Gly	Ala	α -ABA	Val	Cyt	Met	Ile	Leu	Tyr	Phe	β -Ala	β -AlBA	γ -ABA	Total
1-01	2.4	6.8	10.2	13.0	3.7	29.1	15.7	0.2	4.9	n.d.	1.6	3.4	5.6	n.d.	2.0	1.1	n.d.	0.6	99.5
1-02	11.2	3.8	6.8	6.5	0.9	26.0	10.6	tr.	3.7	n.d.	tr.	0.9	2.7	0.5	2.3	1.4	n.d.	1.3	78.6
2-02	13.3	5.4	11.2	11.8	n.d.	25.7	13.1	n.d.	3.8	n.d.	tr.	5.1	10.1	1.9	4.6	0.5	n.d.	1.0	107.4
2-03	8.9	3.2	8.9	7.2	n.d.	24.7	9.0	n.d.	4.3	n.d.	tr.	2.9	6.8	n.d.	0.7	0.3	n.d.	0.3	77.3
3-01	4.5	2.6	6.6	4.0	n.d.	13.8	5.4	n.d.	3.4	n.d.	tr.	1.5	4.2	n.d.	0.9	0.3	n.d.	0.5	47.7
3-03	2.9	1.8	5.9	3.0	n.d.	16.5	3.6	n.d.	2.6	n.d.	n.d.	1.0	3.4	n.d.	0.8	0.4	n.d.	0.2	42.2
4-02	4.7	2.3	9.8	4.5	n.d.	21.5	4.9	n.d.	3.9	n.d.	n.d.	1.6	4.4	0.4	1.6	0.4	n.d.	0.5	60.5
5-02	2.8	1.2	5.4	2.2	n.d.	15.3	3.0	n.d.	2.2	n.d.	n.d.	0.9	2.6	tr.	1.0	0.2	n.d.	0.2	37.1
5-03	2.1	1.2	4.0	1.8	n.d.	11.6	2.9	n.d.	1.9	n.d.	n.d.	0.5	2.6	tr.	1.1	0.4	n.d.	0.3	30.4
5-04	1.4	0.7	2.7	1.3	7.2	7.1	1.8	n.d.	1.1	n.d.	n.d.	0.4	0.9	n.d.	0.5	0.4	n.d.	0.3	26.0
5-06	1.9	1.3	5.6	2.1	n.d.	14.4	3.1	n.d.	1.2	n.d.	n.d.	0.9	2.8	tr.	0.5	0.4	n.d.	0.8	35.0
5-09	3.6	2.1	9.9	3.4	n.d.	19.0	4.7	n.d.	1.2	n.d.	n.d.	1.2	3.5	0.2	1.4	0.3	n.d.	1.0	51.5

Table 1. Vertical concentration of amino acids in deep-sea hydrothermal system core samples of APSK 05 at Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean. Core samples were collected by a seafloor fixed type Benthic Multi-coring System (BMS). Maximum depth was 6,650 mm below sea floor. The recovery of core samples were 53.9 %. Each value stands for the unit of nmol/g-rock. tr. is trace amount (detected but not quantified), and n.d. is not detected.

Table 2

core No.	Asp	Glu	Ala
1-01	0.21	0.03	0.08
1-02	0.25	0.16	0.08
2-02	0.08	0.02	0.00
2-03	0.23	0.12	0.14
3-01	0.07	0.04	0.05
3-03	0.17	0.12	0.15
4-02	0.07	0.08	0.03
5-02	0.16	0.09	0.23
5-03	0.07	0.02	0.05
5-04	0.04	0.04	0.07
5-06	0.09	0.04	0.07
5-09	0.06	0.05	0.01
σ^*	0.008	0.007	0.004

Table 2. D/L ratios of amino acid enantiomers in submarine hydrothermal system core samples of APSK 05 at Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean. Standard deviations (σ) of aspartic acid (Asp), glutamic acid (Glu) and alanine (Ala) in this analytical condition were noted.

Table 3

core No.	TOC (wt%)	TN (wt%)	C/N atomic ratio
1-01	0.011	0.027	0.48
1-02	0.015	0.078	0.23
2-02	0.030	0.310	0.11
2-03	0.026	0.026	1.15
3-01	0.014	0.011	1.54
3-03	0.010	0.006	1.88
4-02	0.019	0.008	2.70
5-02	0.010	0.056	0.20
5-04	0.007	0.068	0.13
5-06	0.008	0.073	0.13
5-09	0.025	0.042	0.70

Table 3. Vertical distribution of total organic carbon (TOC) and total nitrogen (TN) in deep-sea hydrothermal system core samples of APSK05 at Suiyo Seamount, Izu-Bonin Arc, Pacific Ocean.

(a)

(a) Geological location of the Izu-Bonin Arc on the eastern edge of the Philippine Sea plate, western Pacific ocean.

(b) Topographic map of the Suiyo seamount in the Shichiyo seamount chain. Abbreviations. Si = Suiyo Seamount; OR = Ogasawara Ridge; OT = Ogasawara Trough; S = Sofugan Island; N = Nichiyo Seamount; G = Getsuyo Smt.; K = Kayo Smt.; M = Mokuyo Smt.; Kn = Kinyo Smt.; D = Doyo Smt.; Ns = Nishinoshima Island.

(c) Distribution of chimneys, mounds, and BMS drilling sites in the bottom of the caldera at Suiyo Seamount