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Non-biotic synthesis of organic polymers on H_2S-rich sea-floor: a possible reaction in the origin of life*

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ABSTRACT

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In continuous observations of the anoxic, H_2S-rich floor of the brackish Lake Nakanoumi, ammonia alone was observed to decrease remarkably without a corresponding decrease of total nitrogen or increase of nitrite and nitrate. This newly observed phenomenon cannot be interpreted by conventional physical or biological reactions; it possibly suggests a new chemical synthesis of particulate amino acid on the anoxic lake floor in the presence of hydrogen sulphide. To understand the mechanisms of these results, we carried out some model experiments using hydrogen sulphide as a reagent. In these experiments, we found a new non-biotic synthesis of organic polymers containing amino acids from the reaction of hydrogen sulphide and a mixture of ammonium formate, formaldehyde and magnesium chloride in water at room temperature. This reaction is possibly based on the reduction and dehydration by hydrogen sulphide. This entirely new non-biotic synthesis is an important reaction to consider as the first stage of the origin of life.

INTRODUCTION

The marine environments of coastal regions are characterized by their physical, chemical and biological phenomena. The relative concentrations of nutrients are significantly influenced by location, depth, transportation of water mass, pH, planktonic and bacterial activities, etc.

To survey such natural mechanisms, it is important to measure the chemical compounds continuously both horizontally and vertically.

Recently, we developed a new continuous monitoring system for measuring

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temperature (W.T.), salinity (Sal.), pH, dissolved oxygen (DO), turbidity (Tur.), chemical oxygen demand (COD), phosphate (PO_4-P), total phosphorus (T-P), ammonia (NH_4-N), silicate (Si) and chlorophyll *a* (Chl.) (Fujinaga and Kimoto, 1986).

In October 1986, a continuous observation using this system was made at the centre of the brackish Lake Nakanoumi. The depth of the measuring site was 6.5 m. A strong halocline was found at a depth of 4–4.5 m. Salinity below the halocline was ~30‰ and that above the halocline was ~20‰. In this period, the dissolved oxygen increased at the surface to > 100% saturation by algal photosynthesis, whereas it decreased at the bottom to almost 0% saturation by the biodegradation of organic matter. This anaerobic condition accelerates the entry of phosphate, silicate and ammonia from the sediments. It also generates hydrogen sulphide by bacterial reduction of sulphate.

Hydrogen sulphide is widespread in the hydrosphere in such places as the anoxic sea-floor, hot springs and hydrothermal vents. Also, there is geological evidence of hydrogen sulphide in primitive seawater because pyrite (FeS_2) is found in sediments deposited 3.8 billion years ago.

However, the roles of the hydrogen sulphide in anoxic seawater, especially its contribution to organic reactions, have not been well investigated.

In this paper we describe field observations on an H_2S-rich sea-floor and some laboratory experiments using hydrogen sulphide for organic synthesis.

METHODS

Field observations

The automated measuring apparatus for inorganic phosphate is based on (1) the formation of phosphomolybdate, (2) preconcentration and separation of phosphomolybdate by column, and (3) measurement with a voltammetric detector. Total phosphorus is converted by an acidic persulphate solution to inorganic phosphate in an autoclave at 120°C.

The ammonia monitor is based on the preconcentration and separation of ammonia with a gas-permeable micro-porous membrane, followed by the measurement of the ammonia-enriched acid solution with a conductivity sensor. Chemical oxygen demand is measured by a permanganate oxidation method in an alkaline solution. Silicate is measured through the formation of silicomolybdate and subsequent measurement with a voltammetric detector. Chlorophyll *a* concentrations are determined using a spectrofluorometric method. Temperature, pH, dissolved oxygen, salinity and turbidity are measured by conventional sensors. In this system, two 2-kW diesel electric generators, automatic sampling equipment, a wireless telemetry system and a data logger were installed in a transportable barge of 5.4 m×2.8 m×2.2 m (Fig. 1). A specially designed automatic washing system for the sampling and

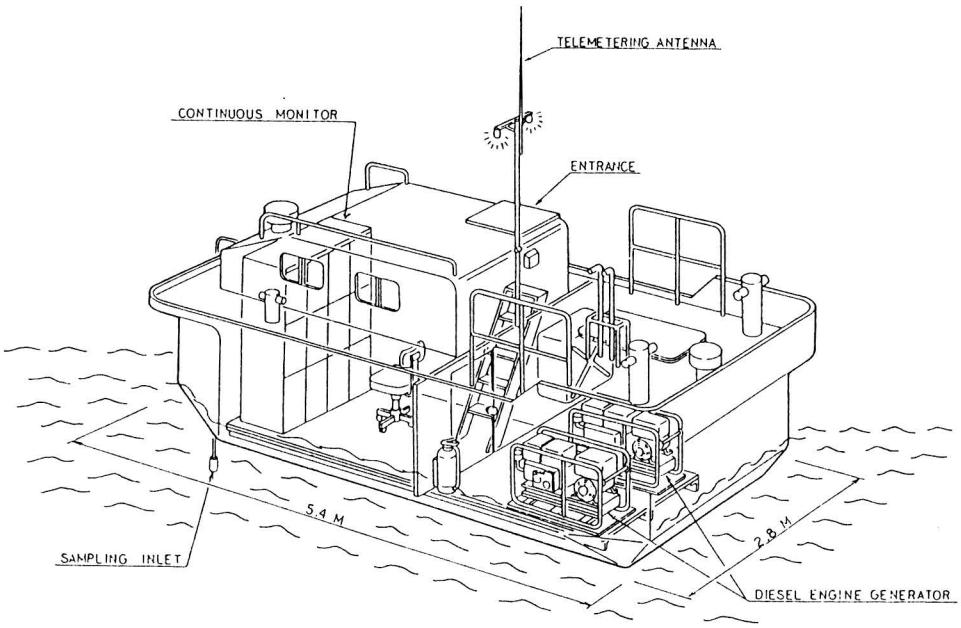


Fig. 1. Continuous water quality monitoring system

measuring equipment overcame the problems caused by the growth of algae in the equipment. The sampling intake was automatically controlled and was set to definite sampling depths for each 1-h sampling period.

Sampling was conducted at two depths; 1 m below the surface (Upper; U) and 1 m up from the floor (Bottom; B). The depth of the measuring site (Stn. 4) was 6.5 m. Simultaneous manual observations were performed on water temperature, salinity, dissolved oxygen (Winkler method), phosphate (Molybdate Blue method), nitrite (NO_2-N; Griess method), nitrate (NO_3-N; cadmium reduction – Griess method) and total nitrogen (T-N; Kjeldahl method). A weather station for measuring wind direction (W.D.), wind speed (W.S.), current flow rate at 1 m up from the floor (C.F.), water level (W.L.), ambient temperature and atomospheric pressure was also installed.

Lake Nakanoumi (35°30′N, 133°10′E, Shimane Pref., Japan) is connected with the Japan Sea only via the Sakai Channel, which is ~0.3 km wide and 7.5 km long (Fig. 2). The lake has a surface area of 97.5 km^2 and total storage volume of 5.2×10^8 m^3 at a mean water-level of 0.2 m. The mean depth of the lake is 5.4 m and ~70% of this area is shallower than 7 m.

Salinity decreases toward the interior of Lake Nakanoumi from 30–35‰ at Sakai Channel to 5–10‰ at Ohashi Channel (Ohtake et al., 1984).

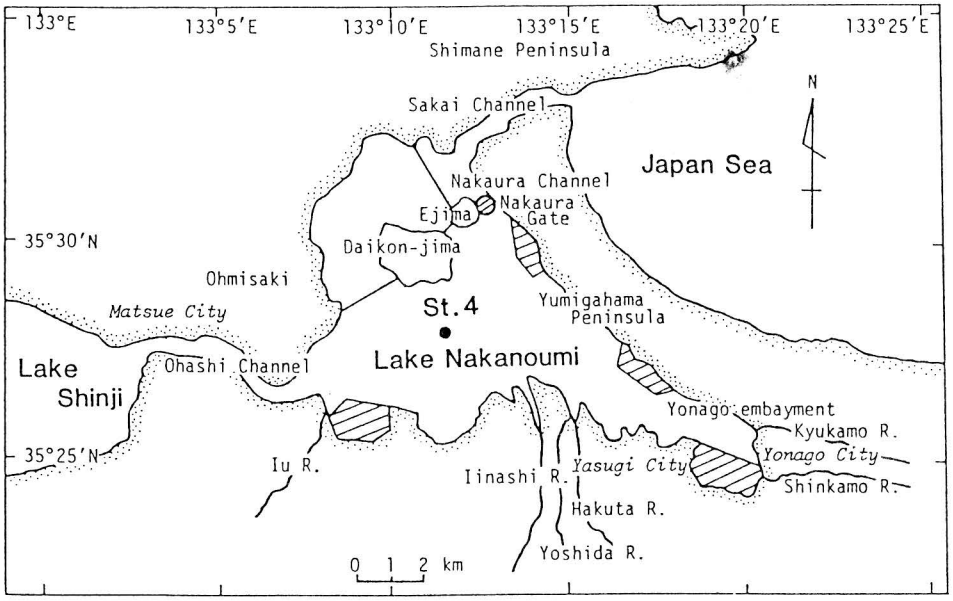


Fig. 2. Map of brackish Lake Nakanoumi.

Laboratory experiments

Elemental composition was obtained with a conventional CHN analyser for organic elemental analysis. Appropriate molecular weight (a.m.w.) was measured by gel permeation chromatography (GPC) on a Toyo Soda TSK gel G2500H with tetrahydrofuran (THF) as the carrier reagent, at a flow rate of 1 ml min^{-1}. Standard polystyrene was used for the calibration. Acid hydrolysis used a vacuum hydrolysis tube (Pierce Co., IL, U.S.A. 5-ml volume) heated by a temperature-controlled aluminium heating block. To minimize the possibility of contamination, only highly purified reagents were used. Twice-distilled hydrochloric acid was used. Amino acid analysis were carried out by two different methods. One was the conventional Moore–Stein method automatic amino acid analyser, with the ninhydrin reaction as the detection step. The other method was *o*-phthaldialdehyde–N-acetyl-L-cysteine (OPA–NAC) pre-column derivatization and high-performance liquid chromatography (HPLC; Buck and Krummen, 1984; Nimura and Kinoshita, 1986). A Toyo Soda model CCPE HPLC analyser and 250×4.6 mm Develosil ODS-5 (C_{18}) column were used. The mobile phases were: A, 100% methanol; B, 50 mM sodium acetate. The column was equilibrated with 100% B. A gradient was set up as follows: 0–15 min: 0–10% A; 15–20 min: 10% A; 20–45 min: 10–30% A; 45–75 min: 30–60% A; 75–90 min: 60–100% A. The column effluent was monitored with a Jasco model FP-110 Fluorescence HPLC detector at an excitation wavelength of 340 nm and an emission wavelength of 450

nm. With the OPA–NAC technique, the enantiomers of amino acids were separated.

RESULTS AND DISCUSSION

Field observations

Tables 1 and 2 show the daily average concentrations and the correlation coefficients for data obtained at the upper and the bottom sampling points from October 16 to 29, 1986. A total of 168 hourly samples were taken.

The production of organic compounds by photosynthesis was very active in the surface water, and biodegradation in the bottom water produced remarkably anoxic conditions (Table 1). pH and dissolved oxygen decreased and phosphate, ammonia and silicate were eluted simultaneously.

The concentrations of phosphate, silicate and ammonia at the bottom were correlated inversely with the concentration of dissolved oxygen (Table 2). These results also confirm that anoxic conditions accelerate the elution of those substances from the sediment.

Phosphate and silicate have a high correlation (0.90), whereas the correlation coefficients between the ammonia concentration and that of phosphate and silicate respectively were low, at 0.78 (vs. PO_4-P) and 0.66 (vs. Si) (Table 2). This is a result of a faster decrease in the ammonia concentration at the bottom than for the phosphate and silicate concentrations.

During the first half of this observation, we found some peaks in the concentrations of phosphate, silicate and ammonia at the bottom, caused by diffusion from the sediment. However, all of the data indicated that the ammonia peaks decreased more quickly than those of phosphate and silicate (Kimoto et al., 1988).

To investigate the reason for the ammonia decrease, we measured the concentrations of nitrite, nitrate and total nitrogen vertically by manual methods when the ammonia concentration increased at the bottom during the second half of the observation period. The results of these observations for nitrogen balance are shown in Fig. 3. The concentrations of nitrogen-containing compounds in Fig. 3 are normalized by the total phosphorus concentration to cancel any variations caused by the diffusion; it should be noted that the ammonia decreased vertically only between 6 m water depth (within 50 cm of the bottom) and 5 m water depth (Fig. 3).

It has been reported (Seike et al., 1986) that the decrease in ammonia might be caused by bacterial nitrification and dinitrification. If these biological reactions are the major reason for the decrease, then the nitrite and nitrate concentrations should increase or the total nitrogen concentration should decrease. In fact, these concentrations changed very little (Fig. 3).

Some anaerobic chemosynthetic bacteria could also be responsible for the

TABLE 1

Daily average concentrations from the field observation

Date	W.S. ($m\ s^{-1}$)	W.D.	C.F. ($cm\ s^{-1}$)	W.L. (cm)		Tur. (ppm)	W.T. (°C)	Sal. (‰)	pH	DO (ppm)	PO_4-P (ppb)	T-P (ppb)	NH_4-N (ppb)	Si (ppm)	CHL (ppb)	COD (ppm)
Oct. 16	6.0	WSW		28	U	4.5	19.2	20.0	8.04	8.3	29	66	9	0.76	15	3.9
			6.53		B	4.3	21.8	29.2	7.71	2.0	88	98	104	1.11	6	1.6
17	7.2	ENE		26	U	4.8	18.7	20.4	7.95	7.8	28	65	2	0.61	17	4.2
			9.03		B	4.8	20.9	27.3	7.66	3.1	74	94	48	0.95	11	2.6
18	4.6	WSW		17	U	5.1	17.6	20.2	7.83	8.1	27	66	1	0.62	16	4.1
			5.66		B	5.8	21.4	28.4	7.48	2.0	95	113	85	1.16	8	2.1
19	5.5	ENE		17	U	5.2	16.9	19.6	7.85	8.4	19	59	0	0.55	17	4.2
			7.04		B	5.0	20.4	27.0	7.61	3.8	61	83	15	0.84	13	2.6
20	3.7	WSW		11	U	4.7	16.8	19.7	7.89	8.0	16	57	0	0.65	17	3.8
			5.99		B	5.7	20.7	27.8	7.58	2.2	78	98	57	1.05	11	2.1
21	4.2	ESE		27	U	4.6	17.2	19.8	8.00	8.1	13	50	0	0.58	15	3.9
			5.53		B	3.7	20.0	28.1	7.74	3.8	48	64	20	0.71	9	2.1
22	7.0	ENE		34	U	4.7	16.9	20.4	7.96	8.0	11	52	0	0.52	16	4.3
			4.54		B	4.4	20.2	28.7	7.68	3.4	50	68	23	0.79	8	2.3
23	3.3	WSW		13	U	5.2	16.4	19.1	7.94	8.2	14	54	0	0.65	16	4.1
			4.27		B	4.2	20.2	28.8	7.70	3.4	48	68	16	0.77	10	2.3
24	3.1	WSW		24	U	5.3	15.5	18.7	7.97	9.1	10	52	0	0.63	16	4.2
			5.61		B	3.6	19.2	28.3	7.75	4.5	39	54	4	0.55	7	1.9
25	2.4	ENE		24	U	4.9	15.6	19.3	8.02	9.0	6	47	0	0.57	13	3.7
			2.26		B	3.3	19.4	29.1	7.75	3.9	36	48	24	0.52	5	1.5
26	3.0	WSW		30	U	5.0	16.1	18.8	8.02	9.7	4	46	1	0.48	13	4.4
			3.34		B	4.6	19.7	29.7	7.65	2.9	62	73	35	0.64	5	1.8
27	4.4	WSW		26	U	4.8	16.2	19.1	8.00	9.5	4	45	3	0.40	14	1.0
			2.65		B	6.2	19.9	29.7	7.65	2.9	68	81	55	0.70	5	1.4
28	2.8	WSW		28	U	5.2	16.1	18.9	8.03	10.0	6	48	2	0.41	15	4.7
			2.61		B	3.7	19.5	29.4	7.69	3.2	47	59	9	0.58	5	2.2
29	4.5	W		23	U	4.9	15.7	19.5	8.13	10.6	7	49	4	0.41	16	4.9
			3.29		B	3.1	19.5	29.6	7.86	3.5	45	57	26	0.62	4	2.7

TABLE 2

Correlation coefficients of each measuring item

	Upper layer (1-m depth from the surface)										
	W.T.	Sal.	pH	DO	PO_4-P	T-P	NH_4-N	Si	Chl.	COD	Tur.
W.T.		0.42	−0.08	−0.52	0.85	0.71	−0.01	0.51	0.17	−0.19	−0.31
Sal.	−0.02		0.01	−0.41	0.32	0.29	0.02	−0.06	0.36	−0.04	−0.28
pH	−0.53	0.04		0.53	−0.42	−0.33	0.09	−0.19	−0.19	0.13	−0.39
DO	−0.73	−0.34	0.64		−0.60	−0.52	0.22	−0.50	−0.15	0.46	0.14
PO_4-P	0.77	0.09	−0.72	−0.85		0.80	−0.05	0.64	0.22	−0.20	−0.13
T-P	0.75	−0.09	−0.73	−0.76	0.96		−0.04	0.51	0.31	−0.15	−0.09
NH_4-N	0.56	0.30	−0.46	−0.70	0.77	0.69		−0.17	0.07	0.25	0.08
Si	0.82	−0.08	−0.65	−0.82	0.90	0.91	0.65		−0.12	0.38	−0.15
Chl.	−0.10	−0.74	0.00	0.36	−0.11	0.11	−0.36	0.04		0.29	0.20
COD	−0.20	−0.44	0.14	0.42	−0.25	−0.08	−0.34	−0.17	0.56		0.24
Tur.	0.31	−0.05	−0.61	−0.45	0.66	0.71	0.60	0.49	0.10	−0.05	

Bottom layer (1 m up from the floor)

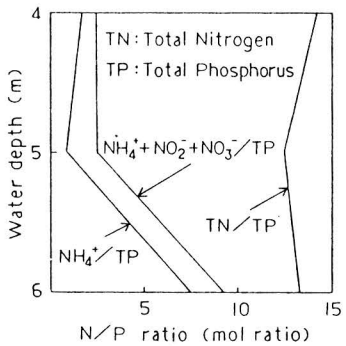


Fig. 3. Vertical nitrogen balance.

phenomenon. If the ammonia decrease was caused by such biologic reactions, the discrepancy between the total phosphorus and the phosphate concentration should increase vertically. However, the discrepancy was too small to establish this point; therefore, we thought that this observation might suggest a new route for non-biotic synthesis of nitrogen-containing organic matter, and we carried out some model experiments using hydrogen sulphide as the reagent.

Laboratory experiments

The first experiment (Kimoto and Fujinaga, 1988) involved the reaction of 5 M ammonium formate, 0.1 M formaldehyde and 0.1 M magnesium chlo-

ride in water, and 1% hydrogen sulphide gas which was bubbled through the reaction mixture, at ~20°C and pH 4.8.

During the reaction, a white precipitate was suddenly formed after a definite transition period in the vessel. After 24 h, the precipitate weighed 720 mg. The precipitate contained 25 wt.% carbon, 5 wt.% hydrogen and 8 wt.% nitrogen (C:H:N=25:5:8 wt.%).

In the absence of hydrogen sulphide or formaldehyde, the reaction did not produce the precipitate; therefore, the formation of the precipitate is supposed to be the result of reduction of formaldehyde by hydrogen sulphide. After hydrolysis by 5.7 *N* hydrogen chloride at 105°C and 24 h, 0.2 μg mg^{-1} glycine was found by the Moore–Stein method automatic amino acid analyser.

A similar precipitate could be obtained by adding sodium sulphide instead of bubbling hydrogen sulphide gas through the reaction mixture. Although a precipitate was formed by the reaction mixture of ammonium chloride, formaldehyde and sodium sulphide, glycine could not be detected.

The precipitate was slightly soluble in water (~1 mg l^{-1}) and in tetrahydrofuran (~10 mg l^{-1}). By use of GPC with the UV detector at a wavelength of 254 nm, three peaks were found, as shown in Fig. 4. The appropriate molecular weight of the largest peak was 260 a.m.w.

Figure 5 shows the OPA–NAC HPLC analysis for the reaction mixture of 0.1 M ammonium bicarbonate, 0.1 M acetaldehyde, 0.1 M magnesium chloride, 1 mM potassium ferrocyanide and 0.1 M sodium sulphide at pH 7.0.

Chromatogram D was the analytical result of the standard solution containing 25 μM each of DL-serine (DL-Ser), glycine (Gly) and DL-alanine (DL-Ala). These amino acids were determined at retention times of 27 min (L-Ser), 28 min (D-Ser), 40 min (Gly), 49 min (D-Ala) and 50 min (L-Ala). The solutions for analysis were pipetted from the reaction vessel at reaction

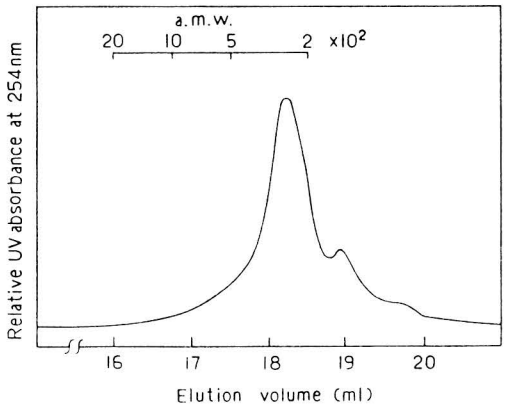
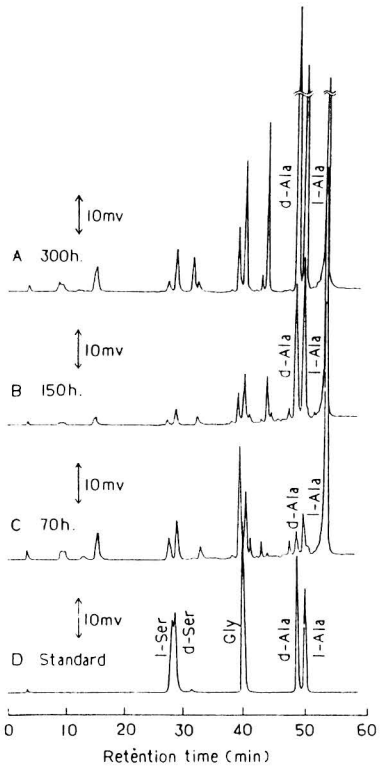


Fig. 4. Gel permeation chromatography of the precipitate.



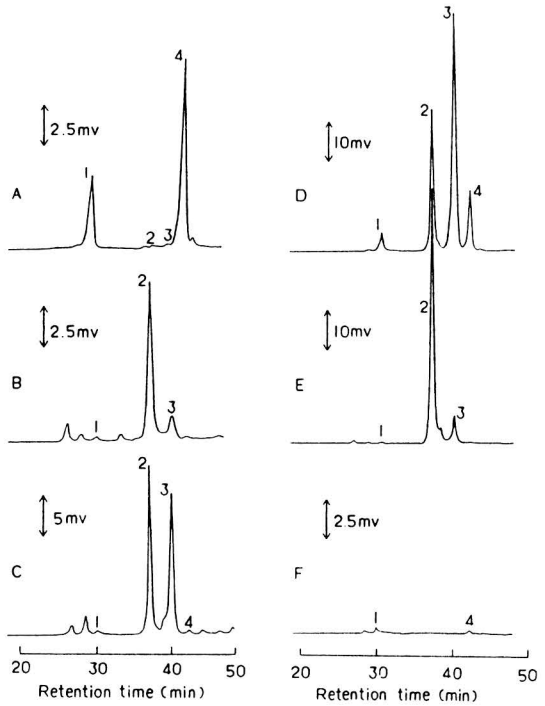
	Peak height (mv)	
Chromatogram	d-Ala	l-Ala
A	198.8	172.5
B	34.1	39.4
C	6.0	10.5
D	33.5	25.8

Fig. 5. OPA–NAC HPLC analysis of the products containing DL-Ala.

times of 70 h (C), 150 h (B) and 300 h (A). After the hydrolysis, the samples were reacted with the OPA–NAC reagent and were measured by HPLC.

In this experiment, a slight amount of the adhesive precipitate was formed, and DL-alanine was gradually formed in water (Fig. 5). From the reaction mixture in the absence of ferrocyanide, DL-alanine was also formed but the amounts were $\sim 1/10$ of those in the presence of ferrocyanide. The concentrations of alanine agreed with the analytical results obtained from the Moore–Stein method automatic amino acid analyser.

Figure 6 shows additional experimental results for aliquots (400 ml) of the reaction mixture of 0.1 M ammonium bicarbonate, 10 mM formaldehyde, 50 mM magnesium sulphate, 10 mM calcium chloride and 20 mM sodium sul-



Chromatogram	Peak height (mv)			
	1 (30min)	2 (38min)	3 (40min)	4 (42min)
A	4.5	0.1	0.1	11.7
B	0.4	9.7	1.5	0.2
C	0.6	20.7	17.2	0.6
D	4.6	35.3	59.1	15.0
E	0.4	62.0	6.9	N.D.
F	0.5	N.D.	N.D.	0.1

Fig. 6. OPA–NAC HPLC analysis of the solution and the precipitate.

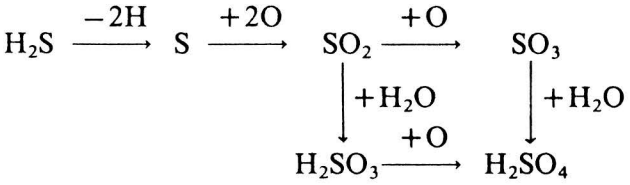
phide at pH 5.2 (carbon dioxide made small bubbles on the wall in the reaction vessel). The adhesive precipitate began to form within 1 h. After 24 h, the amino acids contents were analysed both in the precipitate (the yield of the precipitate was 67 mg, C:H:N=33:10:9 wt.%) and in the solution by the OPA–NAC HPLC method (Fig. 6).

Chromatograms A and B were the analytical results for the solution without hydrolysis (A) and with hydrolysis (B). Chromatogram C was for the precipitate with hydrolysis. Chromatograms D and E were for the sample solutions which were spiked with 100 μM glycine before the analysis or hydrolysis (D was for the solution without hydrolysis, and E for the solution with hydrolysis). Chromatograph F was for the blank solution without hydrogen sulphide.

From chromatogram A, two unknown peaks (perhaps organic amines) were

found at retention times of 30 min (peak 1) and 42 min (peak 4). It is clearly seen by comparison with chromatogram F that the reaction with sulphide is responsible for these two compounds. After hydrolysis (chromatogram B), although these two compounds were decomposed, new peaks occurred at retention times of 38 min (peak 2) and 40 min (peak 3: glycine).

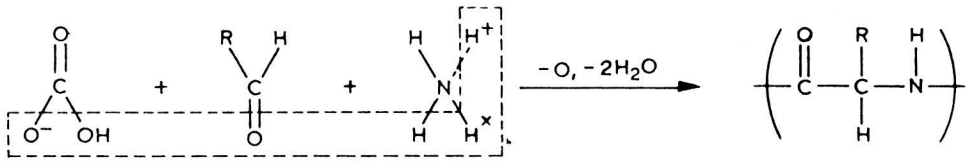
Peak 2 in chromatogram D (spiked with glycine) is ~4 times larger than that in chromatogram A. After hydrolysis (chromatogram E), peak 2 doubled in height and peak 3 was diminished (glycine). Peak 2 may be a derivative of glycine and the hydrolysis may stimulate the formation of the peak 2 compounds from glycine



It is clearly seen that these reactions depend on the reactivity of hydrogen sulphide. It is supposed that this reactivity is based on reduction and dehydration by hydrogen sulphide as follows.

After the reactions above, aldehydes in the reaction mixture are reduced to form the precipitate. The main reaction to form the precipitate may be similar to the well-known Formose reaction. However, this reaction has unique features because the effects of hydrogen sulphide differ from those of the conventional Formose reaction: the reaction is very fast at room temperature in comparison with the Formose reaction and can form a precipitate below 1 mM, whereas the Formose reaction needs a high concentration of formaldehyde (usually > 1 M).

To consider the net reaction for synthesis of amino acids from the reaction mixture of carbonate (or formate), aldehydes and ammonia, reduction and dehydration are required, as shown in the following equation:



It can be assumed from these equations that hydrogen sulphide may play an important role not only in the formation of the precipitate but also in the synthesis of amino acids with support from some catalytic ions such as magnesium ion or ferrocyanide.

Recent geochemical assessments of primitive Earth conditions (reviewed by Kerr, 1980) suggest that a primordial atmosphere consisted largely of carbon dioxide and nitrogen, in contrast to the hydrogen-rich highly reducing atmosphere in which numerous experiments have demonstrated successfully the production of pre-biotic organic compounds such as amino acids. In a carbon dioxide and nitrogen atmosphere, such pre-biotic organic compounds were not formed.

In the course of our new studies of reactions using hydrogen sulphide, we propose that the chemical evolution began in an H_2S-rich primitive seawater in mild climatic conditions.

In the early stages of formation of the Earth (Matsui and Abe, 1986), the surface temperature was > 1500 K, so that the high-pressure atmosphere consisted of water vapour ($\sim 8\times10^{22}$ mol), carbon dioxide ($\sim 5\times10^{21}$ mol), nitrogen ($\sim 3\times10^{20}$ mol), hydrogen chloride ($\sim 9\times10^{20}$ mol), sulphur dioxide ($\sim 7\times10^{19}$ mol), etc. (These values are rough estimates from abundances in the geosphere.)

It is assumed that when the surface temperature decreased below 650 K, the water vapour in the atmosphere suddenly condensed on the surface to make the primitive ocean. At that time, the primitive ocean was highly acidic because of the water-soluble gases such as hydrogen chloride and sulphur dioxide dissolved in it. It is easy to estimate that minerals in the lithosphere

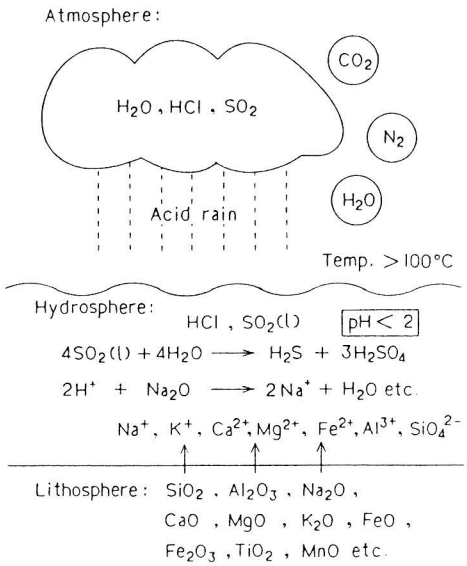


Fig. 7. A hypothesis for the formation of the primitive ocean.

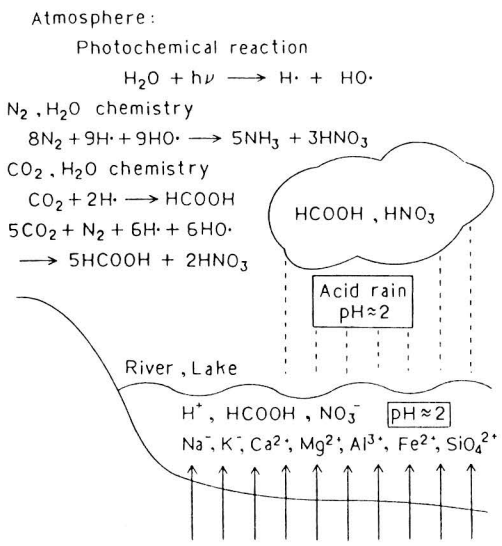


Fig. 8. A hypothesis for the chemical reactions in the primitive atmosphere.

quickly neutralized the acids and the dissolved sulphur dioxide disproportionated to form sulphate and sulphide as shown in Fig. 7.

After these drastic reactions were complete, the atmosphere was mainly carbon dioxide, nitrogen and water vapour. The water vapour was photochemically decomposed to hydrogen and hydroxide radicals. Owing to these radical reactions with carbon dioxide and nitrogen, formic acid and nitric acid would be formed and accumulate on the ground (Fig. 8).

The composition of the primitive ocean would be similar to the present ocean, but the pH is estimated to be ~3–5, from the equilibrium of dissolved carbon dioxide. Thus, excess metal ions such as calcium ion and ferrous ion would be dissolved.

In the primitive ocean, the following reactions would occur, with sulphur compounds as a reducing and dehydrating energy source (some catalysts might accelerate these reactions):

$$HNO_3 + H_2SO_3 \rightarrow HNO_2 + H_2SO_4$$
$$HNO_2 + 3H_2S \rightarrow NH_3 + 3S + 2H_2O$$
$$H_2CO_3 + H_2S \rightarrow HCOOH + S + H_2O$$
$$HCOOH + H_2S \rightarrow H_2CO + S + H_2O$$
$$HCOONH_4 + SO_2 \rightarrow HCONH_2 + H_2SO_3$$
$$HCONH_2 + SO_2 \rightarrow HCN + H_2SO_3$$
$$HCONH_2 + SO_2 + S \rightarrow HSCN + H_2SO_3$$

CONCLUSION

In the course of an environmental study on an anoxic lake floor using a newly developed continuous monitoring system, we have found an entirely new non-biotic organic synthesis by hydrogen sulphide.

Although the mechanism of this reaction is not well investigated, further study of the chemistry of the H_2S-rich anoxic regions would give a new stepping-stone for the evolution of organic substances at the Earth's surface.

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