

B-5. 3. Study on the diagenetic process from marine particulate matter to sedimentary particles and the related carbon cycle

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Abstract Amino acids are common components of all organisms and constitute a major fraction of nitrogenous compounds in sediments and interstitial waters. They are liable to alteration during early diagenesis. So it is important to analyze the mean concentration and characteristics of amino acids in interstitial waters in order to evaluate the size of organic matter in interstitial water reservoir of the marine sediments. We analysed interstitial water from Antarctic Ocean, equatorial upwelling area in Pacific and Indian Ocean, and hemipelagic regions. The results suggest that the DCAA (dissolved combined amino acids) is strongly affected by sedimentary particles (e.g., siliceous plankton, carbonaceous plankton), that higher ratio of neutral to acidic amino acid fractions in the DFAA (dissolved free amino acids) than in the DCAA was attributed mainly to the reaction or adsorption with carbonates, and that biological and/or chemical reaction rates between the DCAA and the DFAA were much higher than the digestion and/or transformation rates of the THAAS (total hydrolyzable amino acids in the sediments). The mean values of the total DFAA and total DCAA in the interstitial water from four areas of Pacific, Indian and Atlantic Oceans are 4.95 $\mu\text{mol/L}$ and 6.16 $\mu\text{mol/L}$, respectively.

Key words Interstitial water, sediments, early diagenesis, amino acids

1. INTRODUCTION

Amino acids are common components of all organisms and constitute a major fraction of nitrogenous compounds in sediments and interstitial waters^{2, 3)} They undergo decomposition and transformation during early diagenesis. Amino acid compounds dissolved in interstitial waters should be very sensitive indicators of these processes. The analyses of total dissolved amino acids show much higher concentrations in interstitial waters than in the overlying seawater, indicating that some processes in sediments must be supplying soluble compounds. Several studies of amino acids in interstitial waters have been carried out but they concerned only dissolved free amino acids^{1, 3, 11, 12)}. However, in studies by Ishizuka *et al.* (1988)⁵⁾, Kawahata and Ishizuka (1989)⁷⁾, and Kawahata *et al.* (1990)⁸⁾ both dissolved combined and free amino acids in interstitial waters were analyzed.

The purposes of this study are to present the characteristics of amino acids compositions of several kinds of marine sediments and interstitial waters and to evaluate their relations during early diagenesis.

2. METHODS

2.(1) Sampling and storage

Interstitial waters were collected on R/V ODP JOIDES RESOLUTION by hydraulic squeezing. All interstitial water samples were filtered through 0.22-mm Millipore cellulose acetate filters in the shipboard laboratory. For amino acid analysis in

interstitial waters, a 5 ml aliquot of the water sample was taken in a precombusted glass ampoule. The ampoule was sealed after flushing with helium, stored in a refrigerator for one month and returned to the land-based laboratory. After sampling interstitial waters, squeezed sediments were stored at -20°C before the analysis.

2.(2) Analytical procedures of amino acids

Dissolved free amino acids (DFAA) in interstitial water were analysed after the addition of 7 ml of distilled 2M HCl with 0.7 ml of an interstitial water sample. Each amino acid concentration was determined by direct injection into an automated liquid chromatograph (Hitachi Model 835). Reagent blank was suitably corrected.

For analyses of total hydrolyzable amino acids (THAA), samples of 1ml of the interstitial water were added to distilled concentrated HCl to a final concentration of 6M solution and were hydrolyzed at 110°C for 22 hrs in precombusted glass ampoules under an argon atmosphere. The hydrolyzed samples were gently evaporated using a rotary evaporator at a temperature below 42°C and the residue redissolved in 1ml of 0.01 M HCl. The aliquots were then injected into the amino acid analyzer. The standard deviation for amino acid analysis based on replicated measurements of a standard solution (about 1mmol/l for amino acids) was less than 10% and the detection limit of our method was about 0.03 mmol/l. Low values in free and hydrolyzable amino acids near the detection limit may not be dependable. Nevertheless, we retain these values because they confirm that the amino acid concentration is low 5).

For the total hydrolyzable amino acids (THAAS) of a sediment, 0.1g of the sediments, together with distilled concentrated HCl, to make 6N solution, were placed into a precombusted glass ampoules and hydrolyzed at 110°C for 22 hrs under argon atmosphere. After hydrolyzation, the samples were filtered through a 0.2µm filter. Other procedures were the same as those of the analysis of THAA in interstitial waters.

3. RESULTS AND DISCUSSIONS

3.(1) Antarctic Ocean

Site 695 lies on the southeast margin of the South Orkney microcontinent on the northern margin of the Weddell Sea, at 62°23.48'S, 43°27.10'W in 1305m water depth. The inorganic properties of interstitial waters at this site, including sulfate reduction, biogenic methane production, and high concentrations of ammonia and phosphate, imply of microbial activity (e.g., sulfate reduction or methane production) can be identified.

The THAA (total hydrolyzable amino acids) values range between 2.45 and 17.31 µmol/L, averaging 7.14 µmol/L. The mean concentrations and relative abundance values of acidic, basic, neutral, aromatic and sulfur containing amino acids are 1.34 (18mol%), 1.09 (15%), 3.93 (54%), 0.50 (8%), and 0.02 (0%) µmol/L, respectively. Glycine is the most abundant amino acid residue, with serine, glutamic acid, and ornithine next. The DFAA (dissolved free amino acids) values range from 0.10 to 12.73 µmol/L, averaging 4.07 µmol/L. The acidic, basic, neutral, aromatic, and sulfur-containing amino acids are on average 0.21, 0.79, 2.56, 0.41, and 0.01 µmol/L, respectively. The relative abundances of acidic, basic, neutral, and aromatic amino acids average 4mol%, 18%, 58%, and 15%, respectively.

Predominance of DFAA over DCAA (dissolved combined amino acids = THAA - DFAA) in interstitial waters of Lithologic Units I and II is contrary to the predominance of DCAA over DFAA in other interstitial waters and seawater. The comparison of amino acid compositions between DCAA and siliceous plankton suggests that the DCAA in interstitial waters originally comes from amino acids derived from siliceous plankton. However, other sources which are much enriched in glutamic acid contribute to the DCAA composition 8).

3.(2) Panama Basin

Biogenic siliceous and calcareous sediments were drilled at Sites 677 and 678 on the flank of Costa Rica Rift in the Panama Basin. We analysed DCAA (dissolved combined amino acids) and DFAA (dissolved free amino acids) in the interstitial waters as well as THAA (total hydrolyzable amino acids) in the sediments in order to evaluate the relationship between THAA, DCAA, and DFAA.

Comparison of the THAA in the sediments and in marine settling particulate matter ⁴⁾ showed that the concentration of non-protein amino acids (e.g., β -alanine, γ -aminobutyric acid, and ornithine) was much higher in the sediments and that the neutral amino acid fraction were depleted in the sediments. These results as well as organic carbon profile indicated that the production of non-protein amino acids occurred mainly in shallow depth but still continued through the sedimentary column at slow rate and that the neutral amino acid fraction was more liable to decomposition than acidic and basic amino acid fractions.

Positive correlation between the total DCAA and the total DFAA and weak correlation of the total amino acid concentrations between the interstitial waters and sediments suggested that biological and/or chemical reaction rates between the DCAA and the DFAA were much higher than the digestion and/or transformation rates of the THAA in the sediments. Higher ratio of neutral to acidic amino acid fractions in the DFAA than in the DCAA was attributed mainly to the reaction or adsorption with carbonates and partly to the contribution of decomposed products of the neutral fraction in the THAA of the sediments ^{7, 10}).

3.(3) Indian Ocean

Sites 717, 718, and 718 were located around 1°S, 81°24'E in the lower fan of the Bay of Bengal, the central Indian Ocean. Sedimentation at the three sites has been dominated by fan sedimentation processes since the early Miocene and consists mainly of different types of turbidites. These are mostly of silt and mud grade, but also include wood fragments and sand-sized grains. Siliceous microfossils are almost absent in spite of the location of the sites within the supposed equatorial high-productivity zone. Also calcareous microfossils are also scarce except within bioclastic turbidites.

The THAA values range between 3.7 and 38.6 $\mu\text{mol/L}$. They average 16.1 $\mu\text{mol/L}$ at Site 717; between 3.18 and 29.72 $\mu\text{mol/L}$, averaging 13.66 $\mu\text{mol/L}$ at Site 718; and between 2.57 and 46.44 $\mu\text{mol/L}$, averaging 14.60 $\mu\text{mol/L}$ at Site 719. The DFAA values show between 2.24 and 37.7 $\mu\text{mol/L}$, averaging 9.45 $\mu\text{mol/L}$ at Site 717; between 0.43 and 21.64 $\mu\text{mol/L}$, averaging 10.1 $\mu\text{mol/L}$ at Site 718; and between 0.91 and 12.92 $\mu\text{mol/L}$, averaging 6.6 $\mu\text{mol/L}$. DFAA in the Bay of Bengal constitute, in most cases, less than 50% of the THAA in the pore water at the sediment surface, and this ratio increases downsection. Concentrations approach 100% in the deepest interstitial water samples. Sulfate reduction and methane fermentation are the only bacterial processes acting in the deeper sediment samples of the Bay of Bengal, Leg 116. Bacteria first act to easily decomposed proteins and carbohydrates within the sedimentary organic matter. However, it may be more difficult for bacteria to further decompose organic matter after the decomposition of protein and carbohydrate, and to make a large colony change free amino acid to its inorganic constituents ⁴⁾.

3.(4) Izu-Bonin Island arc

Sites 790 and 791 lie in the eastern half graben of the Sumisu Rift, a backarc graben west of the active Izu-Bonin arc volcanoes Sumisu Jima and Tori Shima, at 30°54.96'N, 139°50.66'E, in 2,223m water depth and 30°54.97'N, 139°52.20'E, in 2,268m water depth, respectively. A small decrease in the sulfate concentration in the interstitial waters from these sites suggests fairly low microbial activity by sulfate-reducing bacteria.

The values of the DFAA in the interstitial waters from both sites range from 1.26 and 6.82 $\mu\text{mol/L}$, with an average of 3.81 $\mu\text{mol/L}$. The average concentrations

and relative abundance of the acidic, basic, neutral, aromatic, and sulfur-containing amino acids average 0.32 (8 mol%), 0.50 (13 mol%), 2.71 (72 mol%), 0.15 (4 mol%) and 0.09 $\mu\text{mol/L}$ (1 mol%), respectively. Glycine, serine, alanine, ornithine, and aspartic acid are major constituent amino acids. The DCAA values range between 1.25 and 44.35 $\mu\text{mol/L}$, with an average of 10.36 $\mu\text{mol/L}$. The mean concentrations and relative abundances of the acidic, basic neutral, aromatic, and sulfur-containing amino acids are 2.29 (22 mol%), 0.60 (6 mol%), 6.70 (65 mol%), 0.09 (1 mol%), and 0.00 $\mu\text{mol/L}$ (0 mol%), respectively. Glycine is the most abundant amino acid residue, followed by glutamic acid, serine and alanine. The predominance of DCAA over DFAA present in the interstitial waters from Sites 790 and 791 is consistent with previous results from interstitial-water and seawater analyses.

The most plausible source for the DCAA is biogenic calcareous debris. A much greater depletion of aspartic acid and the basic fraction, except for ornithine, is found in the DCAA. The decomposition of the basic amino acid fraction or its incorporation to clay minerals would result in a decrease in its relative abundance, whereas ornithine is produced during early diagenesis. The characteristics of the amino acids in the interstitial waters are (1) a greater depletion of the acidic amino acid fraction in the DFAA than in the DCAA and (2) the enrichment of glycine and serine in both. The adsorption or reaction of the amino acids in interstitial waters with biogenic carbonates would be responsible for the lower relative abundance of the acidic fraction of the DFAA. The production of glycine during early diagenesis and its stability in solution would raise its relative abundance in the interstitial waters⁹).

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