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## Diagenetic Significance of $\gamma$ -Aminobutyric Acid in Marine Sediment<sup>†</sup>

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### Abstract

The diagenetic significance of the non-protein amino acid [ $\gamma$ -aminobutyric acid, ( $\gamma$ -ABA)] in marine sediment from the Okhotsk Sea has been investigated. In a core sample collected from a station of the Okhotsk Sea (53°53'N, 149°00'E), it was found that the abundance of  $\gamma$ -ABA relative to other amino acids increased with depth. The ratio of glutamic acid to  $\gamma$ -ABA was ca. 8 at the surface and 1 at a depth of 3 m. It is presumed that the relative increase of  $\gamma$ -ABA was due to the decarboxylation of glutamic acid. The data suggest that the ratio of Glu/ $\gamma$ -ABA is dependent on the elapsing of geological time.

### Introduction

Current research is increasingly concerned with non-protein amino acids which are derived from products of biologically and/or chemically altered marine sediments. The two compounds,  $\beta$ -alanine and  $\gamma$ -amino butyric acid ( $\gamma$ -ABA) are often identified in marine sediments (Jones *et al.*, 1960; Itohara, 1967; Sasaki, 1973; Schroeder, 1975; Whelan, 1975), however, the exact source of the  $\beta$ -alanine and  $\gamma$ -ABA in marine sediments is not known with certainty.

Aizenshtat *et al.* (1973) have pointed out that the relative abundance of these amino acids increased gradually from 13 to 70% with depth in a sediment core. A similar pattern was also observed in Cariaco Trench sediment (~20%) by Hare (1973). Vallentyne (1964) concluded on the basis of his laboratory experiments that  $\gamma$ -ABA in fossil materials might be of diagenetic origin. These authors suggested that these compounds were derived from decarboxylation of aspartic acid and glutamic acid. On the contrary, Itohara (1973) proposed that  $\beta$ -alanine and  $\gamma$ -ABA are of biogenic origin, produced by microorganisms.

In present study, the contents of  $\gamma$ -ABA using a core sediment collected from the Okhotsk Sea are examined and the controlling factors affecting the diagenesis of amino acids in marine sediment are discussed.

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### Materials and Methods

A core sediment was collected at a station (53°53'N, 149°00'E) in the Okhotsk Sea by the Cruise 13 of R/V D. Mendellev from August to September, 1974. Core samples were cut at 5 to 10 cm intervals on board immediately after collection and stored at 3°C. The details have been reported by Maita *et al.* (1982).

The content and composition of amino acids in sediment samples were determined by analyzing 2 to 3 g of dried sediment. Weighed samples were put into a pyrex glass tube with 6N-HCl and norleucine as an internal standard. The glass ampoules were sealed after sweeping with nitrogen gas for 5 min. and the contents were hydrolyzed at a constant temperature of 105°C for 24 hours. After filtration through a glass fiber filter, the filtrates were adjusted to pH 2.0-2.2 and deionized by passing through a cation exchange (Dowex 50×8, 100 to 200 mesh, H type).

The loaded column was washed with 0.01N-HCl and the adsorbed amino acids were eluted with a large excess of 2N-NH<sub>4</sub>OH. The eluants were dried in a vacuum at a temperature below 50°C. The concentrates were redissolved in 5 ml of 0.01 N-HCl and analyzed by an automatic liquid chromatograph (Hitachi, Model 034) according to the method of Moore and Stein (1951). The content and composition of amino acids were estimated by comparison of peak area and retention time with those of known amino acids.

### Results and Discussion

The vertical distribution of the total amino acids,  $\gamma$ -ABA and Glu/ $\gamma$ -ABA, are shown in Fig. 1. A significant decrease of total amino acids and Glu/ $\gamma$ -ABA was observed in the subsurface. A rapid linear increase in the amount of  $\gamma$ -ABA

Table 1. Vertical changes of  $\gamma$ -ABA contents and Glu/ $\gamma$ -ABA in three sediment cores

| Location                      | Core depth (m) | $\gamma$ -ABA cont. (mole %) | Glu/ $\gamma$ -ABA | Age ( $\times 10^4$ yr) | Reference                 |
|-------------------------------|----------------|------------------------------|--------------------|-------------------------|---------------------------|
| Phytoplankton                 | —              | 0.2                          | 38                 | —                       | Chuecas & Riley (1969)    |
| Lake Biwa                     | 11             | 0.93                         | 7.9                | 1.5                     | Terashima & Mizuno (1974) |
|                               | 35             | 2.9                          | 2.9                | 8.0                     |                           |
|                               | 95             | 3.4                          | 1.9                | 17.5                    |                           |
|                               | 150            | 6.1                          | 0.9                | 35.0                    |                           |
| Okhotsk Sea                   | 0.05           | 0.7*                         | 7.9                | 0.025- 0.08**           | This work                 |
|                               | 0.7            | 2.0*                         | 3.7                | 0.7 - 2.2**             |                           |
|                               | 1.3            | 3.1*                         | 2.8                | 2.5 - 5.2**             |                           |
|                               | 3.2            | 4.6*                         | 1.1                | 5.2 - 11**              |                           |
| DSDP site 148 (Caribbean Sea) | 232            | 33                           | 0.17               | (Pliocene)              | Schroeder & Bada (1976)   |

\* Expressed as leucine equivalent

\*\* Calculated with sedimentation rate (30-100 mm/10<sup>3</sup> yr) after Lisityn (1972)

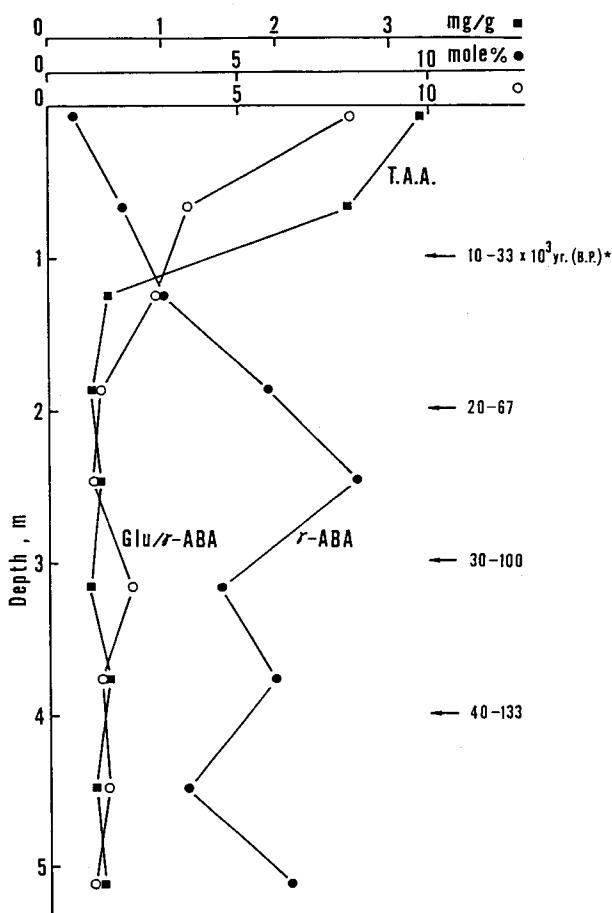


Fig. 1. Vertical distribution of total amino acids,  $\gamma$ -ABA and Glu/ $\gamma$ -ABA in the Okhotsk Sea sediment core.

Asterisk shows the age before of present

relative to other amino acids was observed from the surface to 2.5 m in the sediment core. It is suggested that  $\gamma$ -ABA is produced by the decarboxylation of glutamic acid.

The content of  $\gamma$ -ABA and the ratio of Glu/ $\gamma$ -ABA in sediment based on the work of several researchers is summarized in Table 1.

As shown in Table 1,  $\gamma$ -ABA content of phytoplankton is small (0.2%) and the ratio of Glu/ $\gamma$ -ABA is large ( $\approx 38$ ) (Chuecus and Riley, 1969). A rapid linear increase in the amount of  $\gamma$ -ABA was observed from the surface to deeper layers in core samples taken from Lake Biwa and the Okhotsk Sea (Table 1). On the contrary, Glu/ $\gamma$ -ABA ratio decreased with depth. Schroeder and Bada (1976) have reported that one third of the  $\gamma$ -ABA content was comprised of amino acids and the Glu/ $\gamma$ -ABA ratio was small ( $\sim 0.17$ ) in the pliocene marine sediment. These results suggest that the proportion of  $\gamma$ -ABA and the ratio of Glu/ $\gamma$ -ABA are related

geological time, although further experiments are still remained to establish the new geochronological method for deep sea sediment.

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### References

- Aizenshtat, Z., Baedecker, M.J. and Kaplan, I.R. (1973). Distribution and diagenesis of organic compounds in JOIDES sediment from Gulf of Mexico and western Atlantic. *Geochim. Cosmochim. Acta*, **37**, 1881-1898.
- Chuecus, L. and Riley, J.P. (1969). The component combined amino acids of some marine diatoms. *J. Mar. Biol. Ass. U.K.*, **49**, 117-120.
- Hare, P.E. (1973). Amino acids, amino sugars, and ammonia in sediments from the Cariaco Trench. *Initial Rep. Deep Sea Drill Proj.*, **20**, 940-941.
- Itihara, Y. (1967). Amino acids in the recent sediments. *J. Geol. Soc. Japan*, **21**, 247-254.
- Itihara, Y. (1973). Amino acids in the Cenozoic sediments of Japan. *Pacific Geol.*, **6**, 51-63.
- Jones, J.D. and Vallentyne, J.R. (1960). Biogeochemistry of organic matter—I. Polypeptides and amino acids in fossils and sediments in relation to geothermometry. *Geochim. Cosmochim. Acta*, **21**, 1-34.
- Lisityn, A.P. (1972). Sedimentation in the world ocean. *Society of Economic Paleontologists and Mineralogists, Special Publication No. 17*, 218 pp.
- Maita, Y., Montani, S. and Ishii, J. (1982). Early diagenesis of amino acids in Okhotsk Sea sediments. *Deep-Sea Res.*, **29**, 485-498.
- Moore, S. and Stein, W.H. (1951). Chromatography of amino acids on sulfonated polystyrene resins. *J. Biol. Chem.*, **192**, 663-681.
- Sasaki, K. (1973). Sedimentological study on amino acids in Neogene Tertiary sediments of Niigata Province, Japan. *Sci. Rept., Tohoku Univ. Ser III.*, **12**, 121-171.
- Schroeder, R.A. (1975). Absence of  $\beta$ -alanine and  $\gamma$ -aminobutyric acid in cleaned foraminiferal shells: Implications for use as a chemical criterion to indicate removal of non-indigenous amino acid contaminants. *Earth Planet. Sci. Lett.*, **25**, 274-278.
- Schroeder, R.A. and Bada, J.L. (1976). A review of the geochemical applications of the amino acid racemization reaction. *Earth-Sci. Rev.*, **12**, 347-391.
- Terashima, M. and Mizuno, A. (1974). Preliminary result of amino acid and amino-sugar determination on a 200-meter core sample from Lake Biwa. *In Paleolimnology of Lake Biwa and the Japan Pleistocene.* (ed. S. Horie), *Open-file Rep.*, No. 43, pp. 219-224., Ministry of Education, Japan.
- Vallentyne, J.R. (1964). Biogeochemistry of organic matter—II. Thermal reaction kinetics and transformation products of amino compounds. *Geochim. Cosmochim. Acta*, **28**, 157-188.
- Whelan, J.K. (1975). Gas chromatographic confirmation of amino acid structure via diastereomer preparation. *J. Chromatogr.*, **111**, 337-346.