

## Estimation of paleo-environment by amino acids in terrestrial sediments at Rikubetsu, Hokkaido, Japan

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### Introduction

Core sample such as terrestrial soil contains amino acids that come from biological activities. Protein associated with life are consisted in only L-form of amino acids; hence D/L ratio will be increased by geochemical racemization process. The rate constant  $K$  was determined by its enantio ratio (D/L) and age determination ( $t$ ). So far discussion of racemization rate constant have been reported, although terrestrial case have not been verified. Here we report paleo-environment from the distribution of amino acid concentration and the rate constant value of amino acid in terrestrial core sediments for Holocene period at Rikubetsu, Hokkaido, Japan. Specific decarboxylation of some proteinous amino acids in diagenesis were discussed for origins of non-proteinous amino acids.

### Experimental

Boring core samples (0-300 cm) at Rikubetsu, Hokkaido, Japan were obtained from Ohbayashi Co. After pulverized and dried, HF degradation (5M HF-0.1M HCl, 110C, 16hr) was performed to expose interior organics. Then, samples were acid-hydrolyzed with 6M HCl for 2hr and desalted with cation exchanged resin (AG-50W-X8, 200-400 mesh). Total hydrolyzed amino acids (THAA) were determined by an amino acid analyzer (Shimadzu LC-6A) by post column derivatization system with *o*-phthalaldehyde (OPA) and N-acetyl-L-cystein. Pre-derivatized sample for enantiomer separations were analyzed by RP-HPLC (Pump: TOSOH CCPM II, column: YMC-Pack ProC18), where gradient elution with 40mM acetic acid buffer (pH6.5) and 100% MeOH was applied. AMS-14C radiocarbon age determination and total organic carbon was also analyzed.

### Results and Discussion

THAA drastically decreased with sediment depth having positive correlation versus total organic carbon, however, slight anomaly was observed at a depth of 100-125 cm. The D/L ratio of amino acids gradually increased with depth had negative correlation with THAA. The D/L ratio of aspartic acid was used for calculating rate constant of racemization reaction.  $K_{asp}=2.6 \times 10^{-5}$  (9290yrBP) and  $3.8 \times 10^{-5}$  (4420yrBP) were obtained. The former was before Jomon-transgression (8000-6000 year ago) at Hokkaido, and the latter was after Jomon-regression (5000-4000 year ago)(Report of Kushiro museum, 1975). The anomaly of amino acids abundance might be consistent with the warmest period during Holocene. Accepting distribution of amino acids, it is estimated that temperature of the Hypsithermal period was warmer than that of Holocene beginning at Hokkaido. Specific decarboxylation of alpha-carbon in aspartic acid and glutamic acid for Beta-alanine and gamma-aminobutyric acid were identified in diagenetic process.

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