Evidence of the Hypsithermal Verified Using the Racemization Rate Constant of Amino Acids: An Estimation of Paleo-Ground Temperatures

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The kinetics of a racemization reaction for aspartic acid in boreal terrestrial sediment core samples was investigated in detail to determine the rate constant (k_{ASP}) and the difference of the paleo-ground temperatures. The Arrhenius plot between the rate constant (k_{ASP}) and the literature data of corresponding temperatures is defined as

$$\text{Log } k_{ASP} = 16.1 - 5820/T$$

where T is the absolute temperature (K). From the beginning of the Holocene, estimated annual ground temperatures increased to reach the warmest period, after which a slight decrease was observed. The present findings are geologically consistent with the global transgression period called "the Hypsithermal".

Only the L-form of amino acids are usually found in the proteins of living organisms (except for glycine, which does not have a D- or L-form). However, over long periods of geological time, the L-amino acids undergo slow racemization, producing the D-form of amino acids.[1] The racemization reaction depends on time and temperature; thus, if one variable is known, the reaction can be used to calculate the other.[2] Pioneering studies have shown that the racemization reaction of amino acids can be used to estimate the paleo-temperatures.[2] In the present study, amino acid studies of the apparent rate constants, paleo-thermometry models, paleo-ground temperature models, and chronological implications for the Holocene period were systematically reviewed.[3,4]

The most useful amino acid for paleo-temperature studies is aspartic acid, because its racemization rate is the fastest of any stable amino acid.[5] Becaucse the diagenetic process may progress with depth; the D/L ratios were determined and used as indicators of the extent of organic matter alteration. Of particular interest is the racemization reaction of aspartic acid, which can be written as

$$\text{L-aspartic acid} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{D-aspartic acid} \tag{1}$$

where k_1 and k_2 are first-order rate constants for the interconversion of L- and D-enantiomers of aspartic acid. The first-order rate constant for the interconversion of aspartic acid (k_{ASP}) D- and L-enantiomers can be calculated from the following equation,

$$\ln[(1 + \text{D/L})/(1 - \text{D/L})]_t - \ln[(1 + \text{D/L})/(1 - \text{D/L})]_{t=0} = 2 \cdot k_{ASP} \cdot t \tag{2}$$

where t is the age in years, and D/L is the enantiomeric ratio of aspartic acid in the sediment. $\ln[(1 + \text{D/L})/(1 - \text{D/L})]_{t=0}$ is the initial value of the reaction. When age relationships can be established on a firm independent basis, the D/L ratios can be a guide to the paleo-temperature. Bada and McDonald (1995) calculated the preservation possibility of biomolecular chirality of amino acids in simulated past biota.[6] In the racemization reaction, the rate constant (k_{ASP}) maintained for various ground temperatures was estimated in a simulation of wet sedimentary organics. The minimum temperature at which the "wet" conditions could exist was assumed to be 252 K (−21 °C). Assuming an accurate calculation, the relationship between the rate constant (k_{ASP}) and the ground temperature profile was established.

In the present study the paleo-ground temperatures were deduced from the aspartic acid racemization reaction for a terrestrial sediment core during the mid-Holocene period, collected at Rikubetsu, Hokkaido, Japan. The present report provides geochemical evidence of a past warmer period, called "the Hypsithermal".[7]

Core samples of boreal terrestrial sediments from depths of 50–200 cm were analyzed. The drilling site was located at 43°28′0″ N, 143°44′5″ E, near Rikubetsu, which is one of the coldest cities in Japan, and is located near the center of Hokkaido.[8] In addition, the site is situated in a slight marshy area that is seasonally frozen to a depth of 80 cm, and is covered with ice during the winter. The altitude of the drilling site was 207 m, and the annual average temperature is 5.8 °C.[9] The sediment core samples were analyzed for age using ^{14}C radiocarbon dating by an accelerator mass spectrometric system (AMS).[8] The pretreatment[10] of the core samples and the separation of D- and L-aspartic acid enantiomers were carried out as described in preliminary report.[8] The determination of D- and L-aspartic acid was achieved using an RP-HPLC system, which was composed of high-performance liquid chromatograph pumps (TOSOH CCPM II), a reversed-phase column (YMC-pack Pro C18 4.6 mm i.d. × 250 mm), a pre-column derivatization system with OPA and N-AcCys, and a TOSOH UV 8020 detector.

An Arrhenius plot of the Log k_{ASP} versus $1/T$ (K^{-1}) for temperatures, based on literature data,[6] is shown in Fig. 1. The data were fitted by the least squares method to give:

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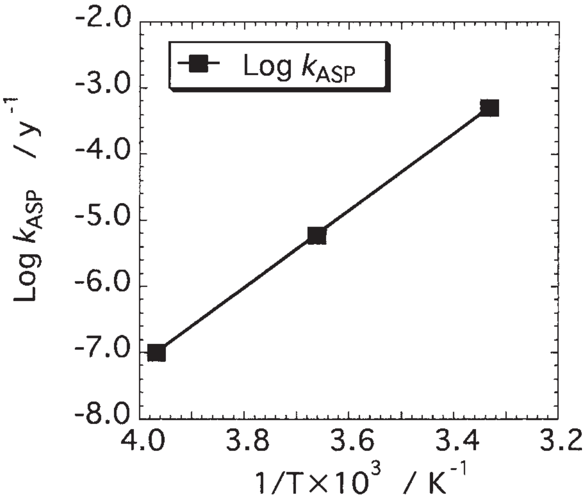

Fig. 1. Least squares fit of the Log k_{ASP} versus $1/T$ for temperatures. Each value of Log k_{ASP} and $1/T$ were determined in wet sediment conditions by Bada and McDonald (1995).[6]

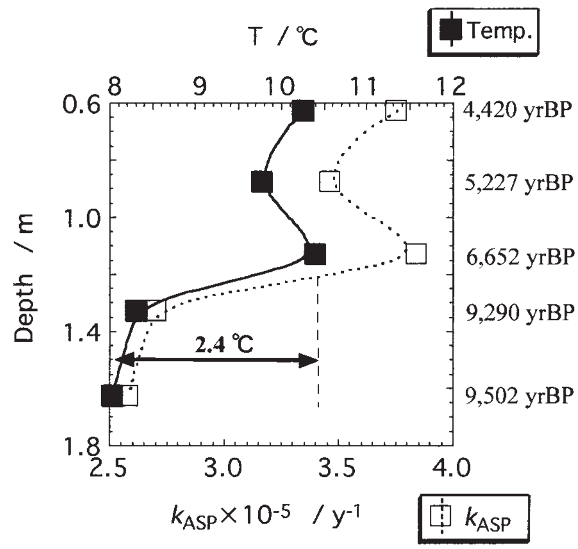

Fig. 2. Climatic variations of the paleo-ground temperature in the mid-Holocene estimated by the Arrhenius plot obtained from the Eq. 3.

$$\text{Log } k_{ASP} = 16.1 - 5820/T. \quad (3)$$

The values of k_{ASP} calculated from this equation are valid only for the region where the reaction follows reversible first-orer kinetics.[6] Radiocarbon dating confirmed the sediment age as being 4420 yBP and 9290 yBP at depths of 62 cm and 162 cm, respectively.[8] Parts of the k_{ASP} value were preliminarily determined from Eq. 2 using the measured D/L ratio for the sediment samples.[8] Linear profiles and good correlations ($r = 0.99$) between the age and the depth of the sediment were obtained. Using an accumulation rate of 0.2 mm·y^{-1} for the core sample, 5227 yBP and 6652 yBP were estimated at depths of 87 cm and 117 cm, respectively.

The climatic variations in the mid-Holocene were then estimated, as shown in Fig. 2. The ground temperatures at 6652 yBP and 9502 yBP were 10.4 °C and 8.0 °C, respectively. After the warmest time, ca. 6650 yBP, the ground temperatures slightly decreased to 9.8 °C, ca. 5227 yBP. The difference in the average ground temperatures (ΔT: $T_1 - T_2$) between 6652 yBP (T_2) and 9502 yBP (T_1) was shown to be +2.4 °C. The increasing temperature significantly impacted both the oceanic environment and the terrestrial meteorological profile. Statistical counting errors in the ^{14}C age determination resulted in an error of ±0.1 °C. The results obtained here indicate an increase in the average temperatures for the center of Hokkaido, following the termination of the last glacial period.

The temperature deduced from aspartic acid racemization appears to provide evidence that the atmospheric temperatures as well as paleo-ground temperatures had been increasing from the beginning of the Holocene. After ca. 9000 yBP, the paleotemperature drastically increased, resulting in a global transgression,[7] which is referred to as the Hypsithermal period (9000–6000 yBP). The present-day sea levels were reached along the southern African coastline ca. 6500 yBP; the sea level then rose further, depositing a series of beach rocks at an elevation of +2.8 m.[11] Therefore, the aspartic acid racemization reaction provides an important new tool for quantitative evaluations of the temperature variations that occurred in the terrestrial environment during the upper Pleistocene, following the Hypsithermal.

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