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Earth and Planetary Science Letters 198 (2002) 257–266

EPSL

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Is amino acid chronology applicable to the estimation of the geological age of siliceous sediments?

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Received 1 August 2001; received in revised form 8 February 2002; accepted 11 February 2002

Abstract

There are few conventional dating methods that can be used to estimate the geological age of siliceous sediments on the order of 10^4 – 10^5 yr. In contrast, methods such as $\delta^{18}\text{O}$ are available for dating carbonate-containing sediments in this geological age range. We focused on amino acid chronology as an alternative dating method for siliceous sediments. We analyzed the enantiomeric ratio (D-isomer/L-isomer) of aspartic acid (Asp) in bulk diatom assemblages in two siliceous sediment cores collected at Station (St.) 3 (approx. lat. 50°N , long. 165°E) and St. 5 (approx. lat. 40°N , long. 165°E) in the northwestern North Pacific. Radiocarbon and paleomagnetic ages were also obtained from both cores to use as reference ages. Two models, a reversible first-order kinetic model and a parabolic model, were used to determine the relationship between the D/L ratios of Asp and reference ages from the core at St. 5. By using these models, Asp ages were then estimated for the core at St. 3, and these ages were compared to paleomagnetic ages from that core. There was a large difference between Asp ages estimated by the first-order kinetic model and the reference ages. On the other hand, Asp ages estimated by the parabolic model were consistent with the reference ages. Therefore, an Asp dating method using the parabolic model is suitable for dating siliceous sediments. However, although generally the D/L ratio of Asp increased with increasing depth in the core at St. 5, the ratio did not continue to increase below about 10 m depth. The D/L ratio of Asp and the paleomagnetic age at that depth were 0.37 and 350 kyr BP, respectively. Therefore, the Asp racemization reaction apparently does not continue to progress in diatom frustules older than this age. This finding implies that Asp chronology can be used to determine ages up to about 350 kyr BP in sediments composed of diatom ooze. Although the Asp dating method using the parabolic model has a limitation of 350 kyr BP for siliceous sediments, it is available for the estimation of ages on the order of 10^4 – 10^5 yr BP, which is beyond the time range (up to 50 kyr BP) datable by the ^{14}C method. © 2002 Elsevier Science B.V. All rights reserved.

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Keywords: amino acids; chronology; siliceous composition; Pacific Ocean

1. Introduction

On a geological time scale, the time interval from 10^3 to 10^6 yr BP is very important in paleoceanographic studies because it covers the glacial and interglacial periods, during which time the marine environment changed drastically. Although the precise age determination of geological samples is an absolute prerequisite to a discussion of the paleoenvironment, there are as yet no reliable direct dating methods that can be applied to marine sediments in the age range from 10^5 to 10^6 yr BP. Therefore, many researchers have investigated the suitability of amino acid chronology for covering the long time interval of 10^3 – 10^6 yr BP [1–4].

This chronology is based on the following principle: there are two enantiomers of amino acids in nature: L type (L) and D type (D). Living organisms, except for some bacteria, produce L-amino acids exclusively [5,6]. However, after the organisms die, the L-amino acids are converted to D-amino acids until such time as the L- and D-amino acid isomers become equimolar. The racemization reaction proceeds, according to the reversible first-order kinetic model, at a constant rate with time if the surrounding temperature is invariable [7,8].

This method has some advantages: (1) by using different kinds of amino acids, geological ages over the wide range of 10^3 – 10^6 yr BP can be estimated, beyond the time range for which the ^{14}C method is available (older than 50 kyr BP), and (2) the discrete age of cored sediments can be determined, unlike in the case of the $\delta^{18}\text{O}$ method. The age determination of geological materials by amino acid chronology has been studied mainly for carbonate fossils [3,9,10], for instance, foraminifera in marine sediments [11,12]. This chronology has not been applied to other types of marine sediments, in particular, siliceous sediments, which are distributed widely on the floors of the world's oceans, although the applicability of the method to such sediments has been supported [13,14].

Therefore, we examined the applicability of amino acid chronology to the determination of the age of siliceous sediments from the northwestern North Pacific over a 300-kyr time span. We used aspartic acid (Asp) because its racemization reaction rate is one of the highest of all amino acids [15], and thus Asp is suitable for age determination of sediments with ages on the order of 10^5 yr. By comparing the extent of the racemization reaction of Asp contained in diatom frustules with reference ages obtained by using the ^{14}C method (< 20 kyr) and magnetostratigraphy (> 20 kyr), we determined the racemization reaction rate constant for Asp in the sediments of a core by using a reversible first-order kinetic model. We also used an apparent parabolic model [16] to examine the relationship between the D/L ratios of Asp and the reference ages. We then estimated the Asp ages in a second core by using the two models, and compared the Asp ages with the paleomagnetic ages. The Asp ages estimated by the parabolic model were more consistent with the paleomagnetic ages than were those obtained by using the first-order kinetic model. Therefore, the parabolic model is better than the first-order kinetic model for estimating precise geological ages. Our findings suggest that amino acid chronology is applicable to siliceous sediments as well as to carbonate sediments within a time limit of approximately 350 kyr.

2. Materials and methods

2.1. Samples

Two piston cores at Stations (Sts.) 3 and 5, 1350 and 1750 cm long, respectively, were collected from the northwestern North Pacific (St. 3: lat. $50^{\circ}00'11''\text{N}$, long. $164^{\circ}59'37''\text{E}$, 5507 m water depth; St. 5: lat. $40^{\circ}00'26''\text{N}$, long. $165^{\circ}03'40''\text{E}$, 5498 m water depth) during cruise MR98-05 of the R/V *Mirai* (Fig. 1). The piston core at St. 3 was composed of gray to grayish olive diatom-

bearing hemipelagic clays and olive black organic silty clays. At St. 5, the major lithology was grayish olive pelagic siliceous clays and dull yellow to brownish black clays [17].

The sediment cores were cut into 2-cm-thick sections. Subsamples of about 7 g of wet sediment were suspended in Milli-Q[®] water and sieved through a screen (63 μm). Bulk sediments retained on the screen were then dried at room temperature. Microscopic observation showed that more than 99% of the bulk material on the screen consisted of diatom frustules, and the remaining 1% was composed of radiolarian tests, siliceous spicules, and terrestrial materials. The diatom assemblage from the core at St. 3 was composed mainly of *Coscinodiscus* spp. (including *Coscinodiscus marginatus*), *Neodenticula seminae*, *Rhizosolenia* spp. (including *Rhizosolenia hebetata*), and *Thalassiosira* spp. (including *Thalassiosira trifulta*), and that from the core at St. 5 was composed of *Coscinodiscus* spp. (including *C. marginatus*) and *Thalassiosira* spp. (including *T. trifulta*). After removal of all material except for the diatom fossils under an optical microscope, about 30 mg of bulk diatom frustules from each subsample was cleaned ultrasonically and ground into powder with a mortar and pestle of agate.

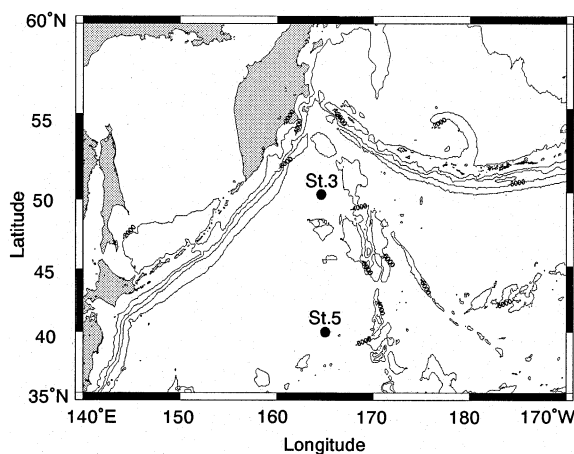


Fig. 1. Map showing the locations of Sts. 3 and 5, the sites in the northwestern North Pacific where the cores were collected during cruise MR98-05 of the R/V *Mirai*.

2.2. Amino acid analysis

Powdered samples of diatom frustules were hydrolyzed with 6 M HCl for 22 h at 105°C under an N₂ atmosphere in a tube with a Teflon-lined cap. We did not use hydrofluoric acid (HF) to extract amino acids from the diatom frustules, because the use of HF might have introduced error to the amino acid age. Kimber et al. [18] reported that HF treatment releases amino acids from the more tightly bound peptides within air-fall deposits and paleosols. Amino acids in deposits and paleosols transported from land have D/L ratios different from those of autochthonous marine organisms. Although the diatom frustules were ultrasonically cleaned in Milli-Q[®] water, there was still a possibility that the bulk diatom frustules were contaminated by terrestrial micro-particles. Therefore, to avoid contamination by amino acids of land origin, HF treatment of diatom frustules was not carried out in this study.

Hydrolyzed samples were passed through a cation exchange resin column (Bio-Rad Laboratories AG, 50W-X8, 50–100 mesh, H⁺ form) to purify them. Bulk amino acids eluted from the column were dried with a rotary evaporator in order to reduce their volume and then were converted to their *N*-trifluoroacetyl isopropyl ester derivatives. Asp enantiomers were analyzed with a CE Instruments HRGC 8000 series gas chromatograph equipped with a chiral fused-silica coating column Chirasil-L-Val (CHROMPAC, 0.25 mm i.d. \times 25 m long) and flame ionization detector to determine the D/L ratio of the Asp. The analytical error for the concentration of each Asp enantiomer, estimated by replicate measurements, was about 6%.

2.3. ¹⁴C and paleomagnetic ages

Radiocarbon ages were determined on bulk organic material from the core at St. 5 to use as reference ages for the modern period to 20 kyr BP (Fig. 2). A portion of the bulk sediment was treated with HCl vapor to remove inorganic carbon and then oxidized with copper oxide and Ag foil under vacuum in a Vycor tube at an elevated temperature (approx. 900°C) to liberate carbon

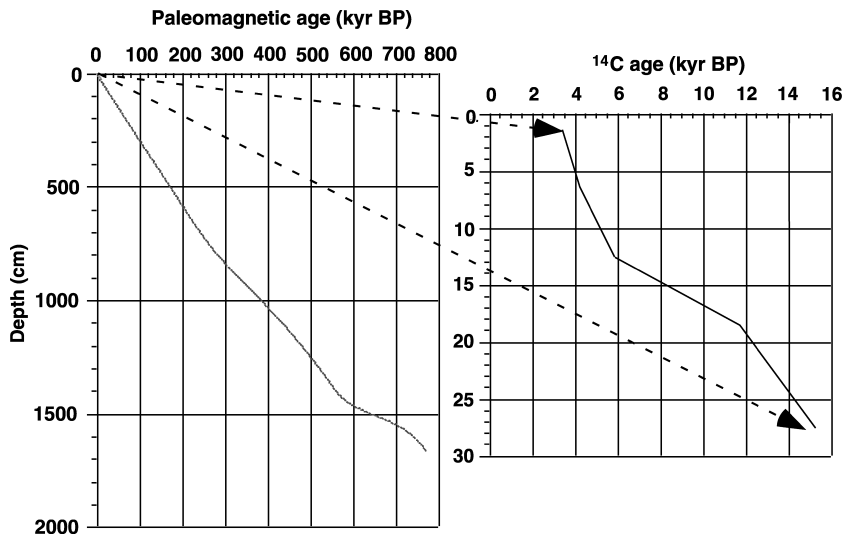


Fig. 2. The age model obtained by using ¹⁴C and paleomagnetic ages.

dioxide. The carbon dioxide was then converted to graphite carbon as described in a previous study [19]. ¹⁴C was measured as the ratio of ¹³C/¹⁴C with a Carbon Dating System Model-4130 accelerator mass spectrometer (High Voltage Engineering Europe Co. Ltd., 2.5 MV) at Nagoya University, Nagoya, Japan.

Paleomagnetic ages were used for reference ages older than 20 kyr BP (Fig. 2). Normalized remanence intensities measured on the two piston cores collected at Sts. 3 and 5 were compared with standard paleointensity curves [20–22] and gave independent age estimations [23]. These two cores were found to be normally magnetized throughout the recovered sections, suggesting that both were within the normal Brunhes Chron (< 780 kyr). Troughs in the normalized remanence intensity curves of the cores, corresponding to geomagnetic excursions during the Brunhes Chron, were readily correlated with those of the standard paleointensity curves. These correlations yield the paleointensity stratigraphy [24], which can provide high-resolution dating of sediment cores even within the Brunhes Chron. We used the paleointensity stratigraphy results from the cores at Sts. 3 and 5 as reference ages for comparison with the Asp ages.

3. Results and discussion

3.1. D/L ratio of Asp in the diatom frustules

The vertical profile of the D/L ratio for Asp contained in the bulk diatom assemblage from the piston core at St. 5 is plotted in Fig. 3. The D/L ratio was not zero at the surface, perhaps

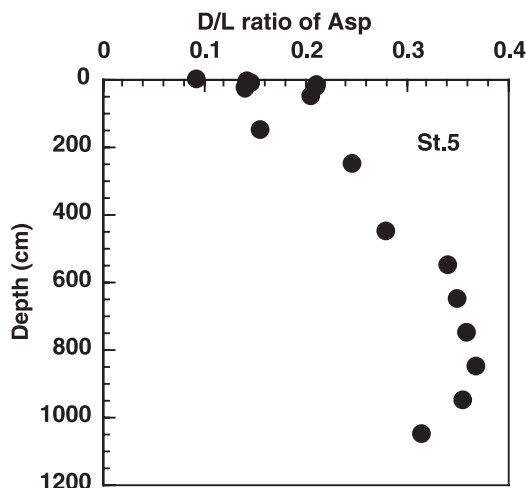


Fig. 3. Vertical profile of the enantiomeric (D/L) ratios of Asp in diatom fossils of the sediment core from St. 5.

because a small amount of D-Asp may have been produced during hydrolysis [25] or from bioturbation. The phenomenon that the D/L ratio at the core top is not zero has also been found in the case of foraminiferal tests at the core top. Non-zero ratios at the core top may be caused by a hydrolysis reaction. In addition, the D/L ratio of Asp in modern foraminifera is usually close to 0.07 [26], so it is also possible that some D-Asp originated from bacterial activity [27]. Therefore, the nonzero D/L ratio of diatoms at the core top might be influenced by a combination of a hydrolysis effect and bacterial activity. The D/L ratio of Asp increased with depth. While the increase in the D/L ratio was large, from 0.09 to 0.2, in the top 30 cm, the increase in the D/L ratio was slight and gradual at depths below 30 cm. On the other hand, no apparent increase in the D/L ratio was found below 950 cm. This pattern has been reported from previous studies of Asp [4,26] and isoleucine (Ile) [28] in foraminiferal tests. The racemization reaction rate of amino acids in fossils relates closely to the hydrolysis reaction rate of peptides and proteins, and the rates of both reactions become slow as geological age increases [3]. Furthermore, the oldest (stratigraphically) D/L Asp ratio was slightly lower than that of a sample immediately above (Fig. 3). According to Müller [28], ‘scattering’ from the expected Ile/Alle value becomes significant in mixed foraminiferal samples older than 150 kyr. This implies that the racemization reaction rate depends on the foraminiferal species and that the species dependence of the reaction gradually becomes more significant as older samples are measured. The species dependence of the racemization reaction rate might be because the dissolution effect is different for different foraminiferal species and, thus, the amount of leaching out of D- and/or L-amino acids from the foraminiferal tests is different for each species. Because the dissolution effect would alter the D/L value in the fossil, Müller [28] recommended that only one species be analyzed in order to estimate the amino acid age more accurately. Since our data were obtained from the frustules of multiple species of diatoms, it is likely that the dissolution effect observed with foraminifera also influenced the oldest D/L Asp value obtained at St. 5. How-

ever, for diatoms, it is almost impossible to perform an analysis by using only one species. Thus, to avoid estimating an incorrect age, we consider that this age at this depth (where the D/L ratio was 0.37) represents the apparent limit – the point at which the Asp racemization reaction is no longer progressing – for this piston core.

3.2. First-order kinetic model

In general, the relationship between the racemization reaction rate and the reaction time can be demonstrated by a reversible first-order kinetic model [15] and can be expressed by the following equation:

$$\ln[(1 + D/L)/(1 - D/L)]_t -$$

$$\ln[(1 + D/L)/(1 - D/L)]_{t=0} = 2kt \quad (1)$$

where k is the rate constant of the racemization reaction, and the y -intercept, $\ln[(1 + D/L)/(1 - D/L)]_{t=0}$, is the initial value of the reaction. The age of the sample, t (yr), can be calculated on the basis of the observed D/L value of the amino acid using Eq. 1, if k has already been determined. Therefore, it is necessary to determine first the value of k by using samples whose ages are already known. To determine the k value for Asp (k_{Asp}) for the first-order kinetic model, the $\ln[(1 + D/L)/(1 - D/L)]$ values of Asp were regressed against reference ages estimated by the ^{14}C and magnetostratigraphy dating methods (Fig. 4). Although the extent of the Asp racemization reaction and the paleomagnetic ages were significantly correlated, a discontinuity at about 30 kyr BP, with an inflection point where the D/L ratio equaled 0.22, was observed. Two k_{Asp} values were calculated: $0.50 \times 10^{-5} \text{ yr}^{-1}$ (the regression coefficient was significant at the 99% confidence level by F test) for the interval from the present to 30 kyr BP, and $0.58 \times 10^{-6} \text{ yr}^{-1}$ (significant at the 99% confidence level by F test) for ages from 30 to 370 kyr BP. In order to determine Asp ages, either $0.50 \times 10^{-5} \text{ yr}^{-1}$ or $0.58 \times 10^{-6} \text{ yr}^{-1}$ was selected as k_{Asp} , depending on whether the D/L ratio of Asp in the sample was, respectively, less than or greater than the inflection value (= 0.22).

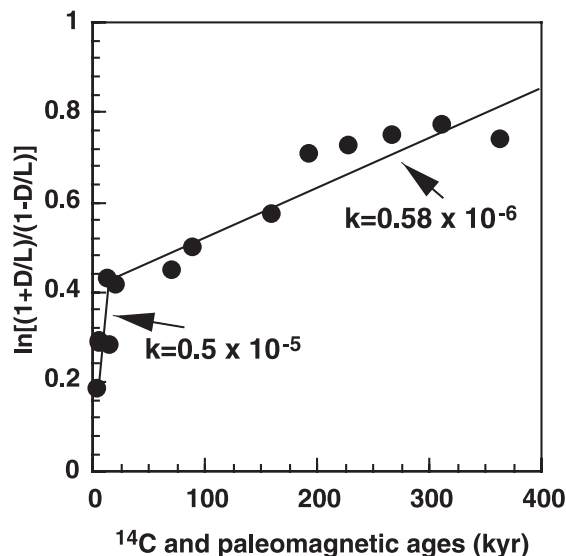


Fig. 4. Relationship between $\ln[(1+D/L)/(1-D/L)]$ of Asp obtained by using a first-order kinetic model and the ^{14}C and paleomagnetic ages from the sediment core from St. 5.

A change in the k value during the period up to several hundreds of kyr BP, as was found in this study, was also found in earlier investigations on foraminiferal fossils [26,29]. One previous study on foraminifera [29] reported that the inflection point at which the k value changed might be caused by the combined effects of the diagenetic hydrolysis of amino acids and the dissolution of calcium carbonate in the foraminiferal tests. However, we consider that a dissolution effect, applicable not only to carbonates but also to silicates, cannot account for the appearance of the inflection point, because we found in this study of diatoms that the D/L ratio of Asp, 0.22, at the inflection point was very close to that determined for foraminifera, 0.24 [29]. Dissolution intensity and mechanisms and solubility in sea water are quite different between silicates and carbonates. If the dissolution effect is one of the main causes of the appearance of the inflection point, should both diatoms and foraminifera have similar Asp D/L values at the inflection point? Müller [28] predicted that the mechanism of the racemization/epimerization reaction occurring in fossil foraminiferal tests would be remarkably associated with diagenetic hydrolysis. Because polypeptides,

which in foraminiferal tests are less sensitive to diagenetic hydrolysis, increase in number with geological time, the rate of protein and peptide hydrolysis progressively decreases. Consequently, a reduction in the rate of protein hydrolysis, rather than an increase in the racemization reaction rate, may cause an inflection point to occur when the regression is calculated. This mechanism would also operate in the case of the racemization reaction of amino acids in silicates. As a result, the timing of the change in the value of k might be similar between silicates and carbonates.

Previous investigations of foraminiferal fossils obtained two k_{Asp} values, $0.94\text{--}1.01 \times 10^{-5} \text{ yr}^{-1}$ and $0.78\text{--}0.99 \times 10^{-6} \text{ yr}^{-1}$, for the past several hundreds of kyr BP, with an inflection point at several tens of kyr BP in each core [4,26,29]. However, k_{Asp} values obtained from foraminifera and diatoms are different in degree. For diatom fossils, the k_{Asp} values, $0.50 \times 10^{-5} \text{ yr}^{-1}$ and $0.58 \times 10^{-6} \text{ yr}^{-1}$, obtained before and after the discontinuity point, respectively, were smaller than those for foraminifera. In fact, there are differences in the roles of amino acids in diatom and foraminiferal tests [30,31], as follows: (1) the structure of the template protein is amorphous in diatoms, but is a β -sheet in foraminifera. The amorphous protein structure is more vulnerable to diagenetic hydrolysis than the β -sheet structure, and the change in the diagenetic hydrolysis rate affects the racemization reaction rate in the fossils. (2) Asp contained in silicate fossils is not bound to the silicate itself, but Asp contained in carbonate fossils is bound tightly to the calcium ion in the carbonate. Furthermore, crystalline water in silicate fossils would accelerate the racemization reaction of amino acids in diatoms, making it faster than that in carbonate fossils, which lack crystalline water. The progress of diagenetic hydrolysis of proteins in diatom frustules of young geological age might cause not only the racemization reaction rate of Asp to accelerate, but also the percentage of free D -Asp to increase. The free Asp in diatoms might be easily released from the fossils as the geological age increases, because the silicate test itself is amorphous and porous compared with the structured and massive carbonate test. It is likely that differences in the

two fossil types described above cause smaller k_{Asp} values to be observed for diatom fossils compared with those observed for foraminifera.

At St. 3, the Asp ages of three discrete samples of siliceous sediments were calculated by using k_{Asp} values $0.5 \times 10^{-6} \text{ yr}^{-1}$ and $0.58 \times 10^{-6} \text{ yr}^{-1}$. As a result, Asp ages were estimated to be 7.4, 79.6, 103.5, and 215.5 kyr BP at 0.5, 300.5, 400.5, and 700.5 cm depth, respectively (Table 1). The paleomagnetic ages at the same depths were 0.19, 79.8, 101.9, and 191.1 kyr BP, respectively (Table 1). The difference between the Asp and the paleomagnetic ages was 7.2, 0.2, 1.6, and 24.4 kyr at each respective depth. The Asp age at 0.5 cm depth was much smaller than the paleomagnetic age. A ^{14}C age, which would be more appropriate than the paleomagnetic age for ages in that range, was not obtained from the sample at 0.5 cm depth. Therefore, the paleomagnetic age at that depth is listed in Table 1, even though the paleomagnetic dating method is too imprecise to estimate ages younger than 20–30 kyr BP. The Asp age at 700.5 cm depth was much greater than the paleomagnetic age, although the Asp ages from 300.5 and 400.5 cm depth corresponded to the paleomagnetic ages within the margin of error. These results imply that the Asp racemization reaction in diatom fossils cannot be explained only by a reversible first-order kinetic model, and that the racemization reaction rate of Asp changes over geological time because of changes in the diagenetic hydrolysis rate.

3.3. Parabolic model and comparison with the first-order kinetic model

The amino acid racemization reaction theoretically progresses according to a reversible first-order kinetic model, and the progress of the Asp

racemization reaction in foraminifera younger than about 25 kyr BP is consistent with this theory [26]. However, a decrease in the racemization/epimerization reaction rate constant calculated by regression during geological time has been pointed out [29,32].

Some investigations have implemented other kinetic models, such as a parabolic kinetic model [16,33,34] and a multinomial model [35], which offer improved linearity between D/L ratios and reference ages. Therefore, we also investigated the relationship between the D/L ratios of Asp and the paleomagnetic ages from sediments at St. 5 using a parabolic model (Fig. 5). The linearity and the standard deviation of the slope of the relationship expressed by the parabolic model were compared with those of the first-order kinetic model. The relationship between the D/L ratio and age for the parabolic model is expressed by the following equation:

$$D/L = a\sqrt{t} + C \quad (2)$$

where t is the age (yr) of the sample, a is the slope (regression coefficient), and C is the y -intercept. The empirical equation for St. 5 using the parabolic model was:

$$D/L = 4.45 \times 10^{-4} \sqrt{t} + 0.122 \quad (3)$$

The correlation coefficient was 0.94, and the linearity was very high.

By using Eq. 3, Asp ages were calculated for the same samples of the St. 3 core as had been used for the first-order kinetic model, and then they were compared with the paleomagnetic ages (Table 1). The Asp ages were estimated to be 0.99, 80.1, 97.6, and 198.9 kyr BP. The differences between the Asp and the paleomagnetic ages were

Table 1
Comparison between Asp ages calculated by the two models and paleomagnetic ages from the piston core at St. 3

Depth (cm)	D/L of Asp	Paleomagnetic age (kyr)	First-order kinetic model (kyr)	Parabolic model (kyr)
0–1	0.134	0.19	7.4 ± 0.5	0.99 ± 0.1
300–301	0.246	79.8	79.6 ± 5.6	80.1 ± 5.6
400–401	0.259	101.9	103.5 ± 7.2	97.6 ± 6.8
700–701	0.319	191.1	215.5 ± 15.1	198.9 ± 13.9

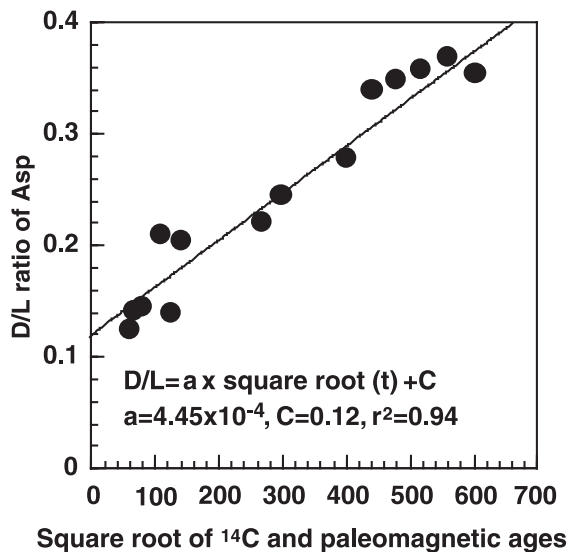


Fig. 5. Relationship between the D/L ratio of Asp obtained by the parabolic model and the square root of the ^{14}C and paleomagnetic ages from the sediment core from St. 5.

0.8, 0.3, 4.3, and 7.8 kyr, respectively. As mentioned above, since the age estimated at 0.5 cm depth by the paleomagnetic dating method has a large error, we omit that point from our discussion here. The Asp age thus corresponded to its respective paleomagnetic age within the margin of error for all other samples. The Asp ages estimated by the parabolic model were therefore closer to the paleomagnetic ages than those obtained by using the first-order kinetic model. The distance of each Asp D/L ratio point from the regression line was assessed as a magnitude of the standard deviation of the slope and expressed as a percentage error. The standard deviation of the regression coefficient of the parabolic model was calculated to be 7%. On the other hand, the standard deviation of each k_{Asp} value calculated by using the first-order kinetic model was larger than that of the regression coefficient of the parabolic model because the data set that was used to calculate the standard deviation for the parabolic model was divided into two sets for the calculation of the standard deviations of the two k_{Asp} values. Therefore, the smaller mother group resulted in a large standard deviation for each of the k_{Asp} values.

The most critical factors that affect the racemization reaction rate of amino acids in natural samples are temperature and differences in sediment type (e.g. carbonate or silicate) [3]. Although St. 3 is about 10° of latitude north of St. 5, both stations have in common the following characteristics: (1) the sediments are composed mainly of diatom ooze, with similar species assemblages, and (2) temperature conditions are almost the same because water depth (approx. 5500 m) is about the same. Therefore, the racemization reaction in diatom frustules at both Sts. 3 and 5 progressed under similar conditions throughout the geological period studied, and the Asp ages at St. 3 estimated by the empirical equation derived from sediments at St. 5 were consistent with the paleomagnetic ages at St. 3.

4. Conclusions

The relationship between Asp D/L ratios and reference ages obtained by ^{14}C dating and magnetostratigraphy was investigated by using two models, a first-order kinetic model and a parabolic model. The former model is a theoretically correct model that can explain the mechanism of the racemization reaction of amino acids. In this study, the linearity of the relationship between the D/L ratio of Asp and the reference age was higher in the case of the latter model, and the standard deviation of the regression coefficient was smaller, when compared with the first-order kinetic model. Probably, the decision as to which model is appropriate for age determination should depend on the nature of the sediments (carbonate or silicate). For diatom ooze, we suggest that the parabolic model estimates ages more accurately than the first-order kinetic model. In addition, in samples from the core at St. 5 older than about 350 kyr BP, the D/L ratio of Asp in diatom fossils did not increase (Fig. 3); thus, the Asp racemization reaction apparently did not continue to progress in fossils older than that age. This finding implies that 350 kyr BP is the limit for the use of Asp chronology in diatom ooze sediments.

Few investigations have applied amino acid chronology to the determination of the geological

age of siliceous ooze. Possible reasons are as follows: (1) unlike in carbonate fossils, proteins and peptides in siliceous fossils are not tightly bound to a test [30], and (2) bulk analysis of the diatom assemblage is necessary, because, unlike in the case of the foraminifera, it is very difficult to select only a single species to analyze. Each reason is critical and contributes to the error in the determination of the amino acid age of siliceous sediments. However, the results of this study suggest that the application of amino acid chronology to the age determination of siliceous sediments is valid. In particular, it is suitable for the estimation of high-resolution ages on the order of 10^4 – 10^5 in siliceous sediments, for which $\delta^{18}\text{O}$, unlike in the case of carbonate sediments, is unsuitable. Furthermore, if the parabolic model developed in this study is confirmed to be commonly applicable to age determination of siliceous sediments in the North Pacific, we expect it to be a robust method for dating coastal siliceous sediments that have been precipitated under anoxic conditions and cannot be dated by using paleomagnetic or $\delta^{18}\text{O}$ chronologies.

Acknowledgements

We are grateful to Captain Hashimoto and the crew and scientists of the R/V *Mirai* for their help in sampling the piston cores. We thank our chief scientist on this cruise, M.C. Honda, the other scientists, and the marine technicians of Global Ocean Development Inc. and Marine Works Japan Ltd. for their support of all aspects of this study. Thanks are also due to N. Handa and J. Sachs, the reviewers of the manuscript, for their comments and suggestions for improvements. This study was supported by the Japan Marine Science and Technology Center under the project ‘Biogeochemical Study of the Western North Pacific and its Adjacent Seas’. [BOYLE]

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