

48. RACEMIZATION OF ISOLEUCINE IN LEG 37, SITES 332 AND 333 CORES

Jeffrey L. Bada,¹ Scripps Institution of Oceanography,
University of California, San Diego, La Jolla, California
and

Eugene H. Man and Annita C. Walker, Department of Chemistry,
University of Miami, Coral Gables, Florida

INTRODUCTION

Deep-sea sediments and fossil skeletal remains have been shown to contain both D- and L-amino acids (see Bada and Schroeder, 1975; Schroeder and Bada, in press, for reviews). The nonprotein D-amino acids are produced by the slow racemization of the L-amino acids originally present in the sediment or skeletal material. The proportion of D- to L-amino acids steadily increases with geological age until an equilibrium ratio of 1.0 is obtained. (For amino acids with more than one asymmetric center, the equilibrium is slightly different from 1.0, i.e., the alloisoleucine/isoleucine equilibrium ratio equals 1.4.)

Recent studies have demonstrated that under certain conditions the amino acid racemization reaction can be used to estimate the age of fossil materials and also to deduce paleotemperatures (Bada and Schroeder, 1975; Schroeder and Bada, in press). Unlike radiometric dating methods, which use an immutable radioactive decay process, racemization dating uses a chemical change which is inherently temperature sensitive. Thus there are two variables which affect the extent of racemization of amino acids in fossil materials, time and temperature. By estimating temperature histories with various techniques, the racemization reaction can be used to estimate the age of the fossil. Alternatively, with well-dated fossils the racemization reaction can be used to estimate paleotemperatures. The amino acid racemization reaction not only provides a potentially important chronological tool, but is also a useful indicator of the temperature changes which occurred on the earth during glacial periods.

For deep-sea sediments, temperature is not normally an important factor, since the temperature of the deep ocean is constant at about 2°-4°C and evidence suggests that this situation has probably existed for the last several million years (Savin et al., 1975). In very long cores, however, such as those raised by the *D/V Glomar Challenger*, temperatures steadily increase with increasing depth of penetration into the sedimentary column, due to heat leaking out of the earth's interior through the oceanic crust and overlying sediment blanket. This warming usually averages a few hundredths of a degree centigrade per meter for most deep-sea locations. Thus, at 200 meters of penetration into the sedimentary column, temperatures have increased to 10°-15°C, and this should cause a corresponding increase in the rate of amino acid racemization (Bada and

Luyendyk, 1971). By determining the age of various sedimentary horizons using alternative methods, it should be possible to use the extent of amino acid racemization to calculate in situ temperatures in a sedimentary column and, consequently, the geothermal gradient. The value calculated by this method would be the average gradient over several hundred meters of sedimentary thickness, and this can be compared with the value obtained by direct temperature probes made in the first few meters of the sedimentary column (Bada, et al., 1974).

In this report we present results of racemization studies of isoleucine in foraminifera isolated from sediments from Sites 332 and 333 of the Deep Sea Drilling Project. The racemization data are used to estimate an average heat-flow value for these sites.

EXPERIMENTAL METHODOLOGY

Sediments used in this study were frozen immediately after the core was raised and were not thawed until the procedure described below was carried out.

Reagents were carefully purified to remove traces of contamination. Deionized water was doubly distilled in an all-glass apparatus; reagent grade hydrochloric acid was doubly distilled in glass. Ammonium hydroxide was prepared by dissolving gaseous ammonia into doubly distilled water under reduced pressure. All glassware was cleaned with chromerge (potassium dichromate in concentrated sulfuric acid) and washed with deionized water, followed by doubly distilled water. The analyses were carried out on a Beckman-Spinco Model 118 automatic amino acid analyzer.

The experimental procedure is essentially the same as the methods described in earlier publications (Bada and Man, 1973).

A sediment sample of approximately 20-25 g was slurried in 300-500 ml of distilled water and then carefully poured into a clean stainless steel sieve (approximately 62 μ m). The collected foraminifera were carefully washed with deionized water, followed by doubly distilled water, transferred to clean pyrex beakers, and then cleaned by several successive 10-min periods of ultrasonic vibration or until the supernatant was clear. This procedure removed any clay particles which might have clung to the foraminifera. After cleaning, the foraminifera were dissolved in 6M HCl and the HCl was then evaporated from the resultant solution. The residue after evaporation was dissolved in 6M HCl, and the resultant solution was then hydrolyzed for 24 hr in sealed glass tubes at 100°C. Following hydrolysis, the samples were desalted, as described

¹Alfred P. Sloan Fellow 1975-1977.

elsewhere (Bada and Man, 1973), using Bio-Rad AG-50W-X8 cation exchange resin.

RESULTS AND DISCUSSION

The results of the alloisoleucine/isoleucine (alleu/iso) measurements we have carried out for sediments from Sites 332 and 333 are summarized in Table 1.

The measured ratio for Section 332-1-2 is compatible with values determined for an upper Pleistocene foraminiferal ooze collected from the Atlantic Fracture Zone in the Mid-Atlantic Ridge (Bada et al., 1970; Bada and Schroeder, 1972). The extent of racemization of isoleucine in Section 332-1-2 can be used to estimate the age of the sediment. This age is calculated using the kinetic equation (see Bada and Schroeder, 1972, for derivation)

$$\ln \frac{1 + (\text{alleu/iso})}{1 - 0.725 (\text{alleu/iso})} = 1.725 \cdot k_{\text{iso}} \cdot t \quad (1)$$

where k_{iso} is the first-order rate constant for the conversion of isoleucine to alleuisoleucine. For alleu/iso ratios less than ~ 0.35 , k_{iso} can be calculated from the equation (given in Bada and Schroeder, 1972)

$$\log k_{\text{iso}} (\text{yr}^{-1}) = 15.77 - 5939/T \quad (2)$$

where T is the temperature of the sediment $^{\circ}\text{K}$. Using a bottom water temperature of $\sim 4.5^{\circ}\text{C}$ (Hyndman, this volume) yields $k_{\text{iso}} = 2.4 \times 10^{-6} \text{yr}^{-1}$. Substituting this rate constant and the measured alleu/iso ratio for Section 332-1-2 into Equation 1 yields an age of $\sim 55,000$ yr.

The reproducibility of the alleu/iso measurements can be seen by comparing the ratios determined for sediments of approximately the same age at the two sites. In Hole 332A, Sections 2-5, 3-3, and 5-4 have an average alleu/iso ratio of 0.71 ± 0.02 . Similarly, at Site 333, Sections 5-3 and 6-2 have identical alleu/iso ratios. It is interesting to note, however, that Sections 333-5-3 and 333-6-2 have an alleu/iso ratio greater than that of 332A-5-4, even though the sediments from the two cores have approximately the same age. We attribute this difference to the fact that the Core 333 sediments come from a much greater depth in the sedimentary column and were thus exposed to higher temperatures. This is even better illustrated by comparing the k_{iso} values shown in Table 2.² The Site 333 k_{iso} values are all greater than those for Hole 332A, which is the expected result if the 333 sediments have been exposed to higher temperatures.

²As has been discussed elsewhere (Bada and Schroeder, 1972, 1975; Schroeder and Bada, in press), the racemization of isoleucine in foraminiferal tests does not obey reversible first-order kinetics (i.e., Equation 1) to equilibrium. However, since the k_{iso} values listed in Table 2 were calculated for samples which all have approximately the same age, the errors which arise from the kinetic complications should be minimal.

To further demonstrate that the higher alleu/iso ratios for the Site 333 sediments are due to temperature, we have used the data in Table 2 to calculate an average heat-flow value for Hole 332A and Site 333. Using the equation

$$\ln \frac{k_{333}}{k_{332A}} = \frac{E_a}{1.987} \frac{\Delta T}{T_1 T_2} \quad (3)$$

where $E_a = \sim 28$ kcal/mole (Bada and Schroeder, 1972) and $T_1 = T_2 = \sim 280^{\circ}\text{K}$,³ it is possible to calculate the difference in average temperature ($\Delta \bar{T}$) between Sections 333-5-3 and 333-6-2 (average $k_{\text{iso}} = 2.9 \times 10^{-7} \text{yr}^{-1}$) and Sections 332A-2-5, 3-3, and 5-4 (average $k_{\text{iso}} = 2.36 \times 10^{-7} \text{yr}^{-1}$). The calculated ΔT value is 1.2°C ; this represents the difference in average temperature that the sediments at the two different sites have been exposed to since their deposition. This difference in average temperature can be expressed as

$$\Delta \bar{T} = \bar{T}_{333 \text{ samples}} - \bar{T}_{332 \text{ samples}} \quad (4)$$

Assuming that the average temperature of the cores from Hole 332A and Hole 333 can be roughly approximated as the mean value between the final temperature and the initial temperature, then for the Hole 333 samples

$$\Delta T_{333 \text{ samples}} = \frac{T_{\text{final}} + T_{\text{initial}}}{2} = \frac{\frac{q}{K} \cdot x_{333} + T_{\text{initial}}}{2} \quad (5)$$

where q is the heat flow in $\mu\text{cal}/\text{cm}^2 \text{sec}$, K is the mean thermal conductivity in $\text{mcal}/\text{cm sec } ^{\circ}\text{C}$, and x_{333} is the depth of burial of the Hole 333 samples in the sedimentary column in centimeters. A similar equation can be written for T_{332} . Substituting these expressions into Equation 4 yields (assuming that q for Holes 332A and 333 is roughly the same)

$$\Delta T = \frac{\frac{q}{K} \cdot x_{333} + T_{\text{initial}}}{2} - \frac{\frac{q}{K} \cdot x_{332A} + T_{\text{initial}}}{2} \quad (6)$$

Solving this equation for q yields

$$q = \frac{2\Delta T K}{(x_{333} - x_{332A})} \quad (7)$$

³The value of ΔT is fairly insensitive to the actual values used for T_1 and T_2 (a change of 1°C in the value of T_1 or T_2 gives a change of 0.01°C in ΔT). Thus, approximate estimates for T_1 and T_2 will suffice for the calculation.

TABLE 1
Isoleucine Racemization in Foraminifera From Sites 332 and 333
(nannoplankton zones given in Howe, this volume)

Site-Core-Section	Calcareous Nannoplankton Zone	Age (yr) ^a	Depth (m)	Alleu/Iso ^b
332-1-2	NN 21	<100,000	2	0.14
332A-2-5	NN 16	$\sim 3 \times 10^6$	72	0.69
332A-3-3	NN 16 (?)	$\sim 3 \times 10^6$	80	0.71
332A-5-4	NN 15	$\sim 3.3 \times 10^6$	99	0.73
333-2-2	NN 17	$2.5-2.8 \times 10^6$	147	0.66
333-5-3	NN 15 (?)	3.3×10^6	198	0.88
333-6-2	NN 15	3.3×10^6	210	0.88

^aEstimated by W. W. Hay from nannofossil zones.

^bThe amino acid analyzer chromatograms indicated that there was no β -alanine present. This demonstrates that the foraminiferal tests have been thoroughly cleaned of organic material associated with the non-carbonate mineral phases of the sediment (Schroeder, 1975).

TABLE 2
Values of k_{iso} Calculated for
Hole 332A and Site 333^a

Site-Core-Section	Depth (m)	k_{iso} (yr ⁻¹)
332A-2-5	72	2.4×10^{-7}
332A-3-3	80	2.4×10^{-7}
332A-5-4	99	2.3×10^{-7}
333-2-2	147	2.5×10^{-7}
333-5-3	198	2.9×10^{-7}
333-6-2	210	2.9×10^{-7}

^aThe k_{iso} values were calculated from Equation 1. See Footnote 2.

Using a K value of 2.6 mcal/cm sec °C for the Hole 332A and Hole 333 sediments (Hyndman, this volume), $x_{332} = 8.4 \times 10^3$ cm (the average depth of Sections 332A-2-5, 3-3, and 5-4) and $x_{333} = 2.05 \times 10^4$ cm (the average depth of 333-5-3 and 6-2), yields $q = \sim 0.5$ μ cal/cm². sec.

Direct downhole temperature measurements were made at both Hole 332A and Hole 333. The average heat flow for the two sites calculated from these measurements was ~ 0.6 μ cal/cm²sec (Hyndman et al., this volume), which is nearly the same as the value we have deduced from the difference in the extent of racemization of isoleucine in foraminifera at Hole 332A and Site 333. We feel that this close an agreement is remarkable, considering the uncertainties in our calculations, and strongly suggests that the difference in racemization of isoleucine between sediments of the same age at Sites 332 and 333 can be attributed to temperature.

The close agreement between the heat-flow value deduced from isoleucine racemization and the direct downhole temperature measurements suggests that racemization can be used to estimate reliable heat-flow values for other DSDP cores.

SUMMARY

In this report we have shown that at a particular site the alleu/iso ratios determined for foraminiferal tests of approximately the same age are identical and are thus

extremely reproducible. However, when alleu/iso ratios of tests of the same age from Sites 332 and 333 were compared, the ratios from 333 were found to be consistently greater than those from 332. We have attributed this difference to the fact that the Site 333 samples came from a much greater depth in the sedimentary column than those from Site 332 and have thus been exposed to a slightly higher average temperature. To verify this, we have used the alleu/iso ratios in the foraminiferal tests to calculate an average heat flow for Sites 332 and 333. The calculated value is in excellent agreement with that deduced from direct downhole temperature measurements.

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