

## 18. ORGANIC CARBON $^{13}\text{C}$ VALUES FROM CRETACEOUS, TERTIARY AND QUATERNARY MARINE SEQUENCES IN THE NORTH ATLANTIC

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### ANALYTICAL METHODS

The experimental procedures used for the determination of  $^{13}\text{C}/^{12}\text{C}$  ratios are essentially those of Craig (1953) and Eckelmann *et al.* (1962). The sediment samples were acidified to eliminate carbonate (carbon dioxide), were dried, and were combusted over copper oxide at approximately 800°C. The produced carbon dioxide was purified by passing it over dry ice to remove water and over copper metal and manganese dioxide at 500°C to remove nitrogen oxides and sulfur dioxide.

The purified carbon dioxide samples were analyzed in a 60°, sector-type mass spectrometer similar to that described by Nier (1947), and described in detail by Nier, Eckelmann, and Lupton (1962). The mass spectrometric analyses are reported as per mil deviation (‰) from the  $^{13}\text{C}/^{12}\text{C}$  ratio of the Cretaceous belemnite, *Belemnite americana*, from the Peedee Formation of South Carolina. In practice, a commercial lubricating oil with an assigned value of -29.4 per mil relative to the Peedee belemnite is used as a laboratory standard. This lube oil standard was obtained from the Chevron Research Laboratories. The results are reported thus:

$$^{13}\text{(in per mil)} = \frac{^{13}\text{C}/^{12}\text{C} (\text{sample}) - ^{13}\text{C}/^{12}\text{C} (\text{standard})}{^{13}\text{C}/^{12}\text{C} (\text{standard})} \times 1000$$

Appropriate corrections for carbon-dioxide background in the mass spectrometer source, mixing of sample and standard due to leakage, and tailing under the mass 45 peak were made as described by Eckelmann *et al.* (1962).

The precision for complete analysis is  $\pm 0.2\text{‰}$ . The conclusions of this study are based on differences greater than  $\pm 1.0\text{‰}$  (5 times precision).

Recent observations (G. S. Bayliss, EPRCo, personal communication) indicate that some sediment samples, even after acidification, still produce appreciable carbonate carbon dioxide—this contamination results in isotopically heavy analyses. Apparently some carbonate carbon is protected during initial acidification by the presence of an organic or mucilageous coating. This problem is serious in carbonates but has not yet been a problem in clastics. However, to test for complete acidification of carbonate carbon we now routinely run (on selected samples as well as all isotopically-heavy results) the following procedure(s): Repeated digestion sequentially with 2N HCL and 30 volume percent  $\text{H}_2\text{O}_2$ . Titration of the liquor for  $\text{CA}^{++}$  ion.

Absence of  $\text{Ca}^{++}$  confirms complete acidification; thus, values of less than 5 ppm  $\text{Ca}^{++}$  are accepted.

### INTRODUCTION

Question: Does the  $^{13}\text{C}/^{12}\text{C}$  isotope ratio of combustible organic matter found in marine sediments vary with the original surface water temperature or is the ratio determined by the relative amount of terrestrial material?

Rogers and Koons (1969) had used carbon isotopic results on total organic carbon from Quaternary marine sequences in the Gulf of Mexico (both shelf as well as slope and abyssal samples) to suggest that the standard geochemical interpretation of  $^{13}\text{C}/^{12}\text{C}$  isotopic ratios on combustible organic matter in marine sediments was incorrect. They hypothesize that the ratio in marine sediments is determined by the variations in the original water temperature (that is, the temperature at which planktonic photosynthesis takes place) rather than by the variations in the amounts of terrestrially-derived relative to marine-derived organic materials incorporated in the sediments at a given location (Sackett, 1964).

Sackett and Rankin (1970) agree with the concept that the isotopic composition of sedimentary organic carbon may be related to the temperature controlled composition of the plankton cells living in the overlying photosynthetic zone, *but they do not believe* this is the controlling mechanism in the Caribbean-Gulf of Mexico system primarily because  $\delta^{18}\text{O}$  values do not support the large variations in surface-water temperatures derived from the observed range of  $\delta^{13}\text{C}$  values. However, they do agree with the concept that this  $\delta^{13}\text{C}$  parameter may be a useful paleotemperature tool for sediments deposited in the Antarctic regions and the central portion of large ocean basins where the terrestrial contributions are negligible.

Thus, the samples from DSDP, Leg 12 seemed an opportunity for further tests of the controls on  $\delta^{13}\text{C}$  values.

At Site 116 (Rockall Plateau) a pelagic Pliocene-Pleistocene sequence has been continuously cored. No ice-raftered or other land derived material was observed in the cores, so this high-latitude section then seemed to be a perfect one for answering the question.

The results from Site 116 can be compared with samples from Sites 111, 112, 118 and 119. Site 111 is atop an isolated knoll some 560 kilometers northeast of Newfoundland and 350 kilometers due north of the Flemish Cap. The knoll is, however, separated from the continental shelf by waters 2800 to 3400 meters deep. Pliocene and Pleistocene interglacial (?) deep-sea foraminiferal oozes alternate with glacial (?) clays with pebbles; the terrestrial material was transported by ice.

Site 112 is in the Labrador Sea, its location is 'nearer-to-shore' than Site 116, and the section contains much ice-rafted terrestrial material. Although Site 116 is at a higher latitude, the microfauna indicates that the water was warmer (Gulf Stream?) than at Site 112. Sites 118 and 119 are located further south in the Bay of Biscay. The

fauna is from warmer water, and no ice-rafted material has been observed. Only very little of the finest terrestrial material from the top of density currents might be mixed with pelagic sediments at Site 119; to the contrary, the nearby Site 118 showed a turbidite section and the samples consequently have much terrestrial material.

## RESULTS

### Site 111 (50° 25.57'N, 46° 22.05'W, Water Depth 1811 meters)

Pleistocene			
58258	111-1-3, 108-110 cm	-24.5	W/M
58259	111-1-3, 125-126 cm	-22.8	
58260	111-2-1, 30-32 cm	-25.8	—
58261	111-2-2, 54-60 cm	-25.6	
58262	111-2-3, 92-94 cm	-25.2	C/T
58263	111-2-4, 60-62 cm	-25.3	
58264	111-2-5, 35-37 cm	-25.5	—
58265	111-2-5, 38-39 cm	-25.3	
58266	111-2-6, 115-116 cm	-24.4	W/M
58269	111A-1-1, 131-133 cm	-24.5	
58270	111A-1-2, 52-54 cm	-24.6	W/M
58271	111A-1-3, 59-61 cm	-26.0	
58272	111A-1-4, 40-42 cm	-25.8	C/T
58273	111A-1-5, 64-66 cm	-25.0	
58274	111A-1-6, 90-91 cm	-24.8	—
58275	111A-2-1, 97-99 cm	-24.8	
58276	111A-2-2, 50-52 cm	-24.9	C/T
58277	111A-2-3, 56-58 cm	-25.0	
58278	111A-2-4, 39-41 cm	-25.2	C/T
58279	111A-3-1, 115-117 cm	-23.9	
58280	111A-3-2, 115-117 cm	-25.5	(W/M) <sup>1</sup>
58281	111A-3-3, 134-136 cm	-24.8	
58282	111A-3-4, 113-115 cm	-25.0	C/T
Pliocene (Glacial)			
58283	111A-4-1, 127-129 cm	-21.1	W/M
58284	111A-4-2, 39-41 cm	-24.0	
58285	111A-4-2, 89-91 cm	-24.8	
58286	111A-5-1, 117-119 cm	-24.9	
58287	111A-5-2, 113-115 cm	-24.7	
58288	111A-5-3, 116-118 cm	-24.4	
58289	111A-5-4, 120-122 cm	-24.7	
58290	111A-5-5, 113-115 cm	-24.7	
58291	111A-5-5, 148-115 cm	-23.3	
58292	111A-6-1, 87-89 cm	-23.7	
58293	111A-6-1, 135-137 cm	-24.7	
58294	111A-6-2, 31-33 cm	-24.3	
Pliocene (Transitional)			
58295	111A-6-2, 110-112 cm	-23.1	

<sup>1</sup> Letters in parentheses (W/M) indicate sample likely displaced or mixed.

Pliocene-Miocene (Pre-glacial)			
58296	111A-6-2, 142-143 cm Insufficient sample	—	
58296A	Composite Insufficient sample	-23.1	
58297	111A-6-3, 44-45 cm Insufficient sample	—	W/M
58298	111A-6-3, 127-128 cm Insufficient sample	—	
Eocene			
58299	111A-7-1, 117-19 cm Insufficient sample	—	
58299A	Composite	-25.0	
58300A	111A-7-1, 135-137 cm	-23.9	(Half of 58300: a light gray material)
58300B	111A-7-1, 135-137 cm	-25.6	(Half of 58300: a creamy white material)
58301A	111A-7-2, 52-54 cm	-23.6	(Half of 58301: a medium gray material)
58301B	111A-7-2, 52-54 cm Insufficient sample	—	(Half of 58301: creamy yellow material)
58302	111A-7-2, 57-59 cm	-24.9	W/M
58302A	Composite	-23.9	W/M
58303	111A-7-2, 104-106 cm Insufficient organic material		
58304A	111A-7-3, 87-89 cm	-24.0	
58305	111A-7-3, 122-124 cm	-24.8	
58306	111A-7-4, 51-53 cm	-25.1	C/T
58307	111A-7-5, 86-88 cm Insufficient organic material	—	
58308	111A-7-6, 139-141 cm	-24.9	
58309	111A-8-1, 97-99 cm	-25.9	
58310	111A-8-2, 124-126 cm	-25.8	
58311	111A-9-1, 77-79 cm	-27.0	
58312	111A-10-1, 125-127 cm	-26.4	C/T
58313	111A-10-2, 112-114 cm	-25.8	
58314	111A-10-3, 93-95 cm Insufficient sample	—	
58313A	Composite	-25.1	
58315	111A-10-4, 115-117 cm Insufficient sample		C/T
Maestrichtian			
58316	111A-11-2, 95-97 cm	-26.1	
58317	111A-11-3, 60-62 cm Insufficient sample	—	
58317A	Composite	-25.1	
58318	111A-11-4, 50-52 cm Insufficient sample	—	
58319	111A-11-5, 126-125 cm Insufficient sample	—	
58320	111A-11-6, 114-116 cm Insufficient sample	—	
Cenomanian			
58267	111-3-2, 37-39 cm	-24.4	
58268	111-3-2, 125-127 cm	-26.4	C/T
Site 112 (54° 01.00'N, 46° 36.24'W, Water Depth 3667 meters)			
Pleistocene			
58003	112-1-1, 59.0-61.5 cm	26.9/-26.82	C/T
58004	112-1-6, 8.5-11 cm	-26.65	
58005	112A-1-1, 126-129 cm	-25.8	
58006	112A-1-2, 1.5-4.5 cm	-25.9	C/T
58007	112A-1-3, 1-5 cm	-25.7	
58008	112A-1-4, 5-8 cm	-25.5	
58009	112A-1-6, 4-7 cm	-25.1	
58010	112A-1-5, 8-11 cm	-25.0	

Pliocene (Glacial)			
58011	112A-3-1, 6-9 cm	-25.4	
58012	112A-3-3, 8-11 cm	-25.2	C/T
58013	112A-3-6, 4-7 cm	-25.2	
58000	112A-4-3, 2-5 cm	-25.2	C/T
58014	112A-4-5, 2-5 cm	-25.2	
58015	112-2-2, 7.0-9.5 cm	-25.2	
58016	112-2-3, 3.0-5.5 cm	-25.0	
58017	112-2-3, 1.5-4.0 cm	-24.9	C/T
58018	112-2-5, 4.0-6.5 cm	-24.9	
58019	112-2-6, 2.0-4.5 cm	-25.6	
Pliocene (Pre-glacial)			
58020	112A-5-2, 25-28 cm	-24.6	C/T
		—	?
58021	112A-5-2, 87-90 cm	-26.4	
58022	112A-5-3, 12-15 cm	-25.2	More terrestrial
58023	112A-5-5, 3-6 cm	-26.5	C/T
58024	112A-5-5, 134-137 cm	-25.7	
Upper Miocene			
58025	112-3-2, 40.0-42.5 cm	-26.4	
58026	112-3-3, 2.0-4.5 cm	-26.6	
58027	112-3-4, 2.5-5.0 cm	-25.5	C/T
58028	112-3-5, 5.5-8.0 cm	-25.4	
58029	112-3-6, 8.5-11.0 cm	-25.2	
Site 116 (57° 29.7'N, 15° 55.5'W, Water Depth 1161 meters)			
Pleistocene			
58047	116A-1-1, 60-63 cm	-21.5	W/M
58048	116A-1-2, 4-7 cm	-22.2	
58001	116A-2-2, 3-6 cm	-21.5	
58049	116A-2-3, 3-6 cm	-24.8	W/M
58050	116A-2-4, 3-6 cm	-23.6	
58051	116A-2-5, 6-9 cm	-24.2	
58052	116A-3-1, 27-31 cm	-24.8	W/M
58053	116A-3-2, 10-13 cm	-24.5	
58054	116A-3-5, 6-9 cm Insufficient sample	—	
58055	116A-3-6, 4-7 cm Insufficient sample	—	
58056	116A-4-1, 100-103 cm	-24.5	
58057	116A-4-2, 6-9 cm	-23.7	
58058	116A-4-3, 2-5 cm	-23.7	W/M
58059	116A-4-4, 16-18 cm	-23.7	
58060	116A-4-5, 2-5 cm	-23.2	
58061	116A-4-6, 7-9 cm	-24.8	
58062	116A-5-1, 54-57 cm	-23.2	
58063	116A-5-2, 4-6 cm	-24.2	W/M
58064	116A-5-3, 3-6 cm	-24.0	
58065	116A-5-5, 4-7 cm	-24.7	
58066	116A-6-1, 17-22 cm	-24.6	
58067	116A-6-2, 3-6 cm	-24.6	
58068	116A-6-3, 3-6 cm	-24.7	
58069	116A-6-4, 3-6 cm Insufficient sample	—	
58070	116A-6-5, 3-6 cm Insufficient sample	—	
58071	116A-6-6, 10-13 cm	-25.3	—

Pliocene (Glacial)			
58072	116A-7-2, 2-5 cm	Insufficient sample	—
58073	116A-7-3, 3-6 cm		-25.3
58074	116A-7-4, 2-5 cm		-25.2
58075	116A-7-5, 2-5 cm		-24.9
58076	116A-7-6, 2-5 cm		-25.2
58077	116A-7-6, 102-105 cm		-24.5
58078	116A-7-6, 132-135 cm		-24.7
58079	116A-8-2, 7-10 cm	Insufficient sample	—
58080	116A-8-3, 3-6 cm		-23.6
58081	116A-8-5, 5-8 cm		-24.2
58082	116A-8-6, 13-16 cm	Insufficient sample	—
58083	116A-9-1, 8-11 cm	Insufficient sample	—

Pliocene (Pre-glacial)			
58084	116A-9-2, 5-8 cm		-24.6
58085	116A-9-3, 5-8 cm		-23.2
58086	116A-9-4, 8-11 cm	Insufficient sample	—
58087	116A-9-5, 2-6 cm		-23.4
58088	116A-9-6, 2-5 cm	Insufficient sample	-23.8
58089	116A-10-1, 92-95 cm		-23.4
58090	116A-10-2, 6-9 cm		-24.0
58091	116A-10-3, 3-6 cm	Insufficient sample	—
58092	116A-10-5, 3-6 cm	Insufficient sample	—
58093	116A-10-6, 8-11 cm		-23.6

## Site 118 (45° 02.9'N, 9° 00.5'W, Water Depth 4901 meters)

Pleistocene			
58113	118-1-1, 110-113 cm		-24.9
58114	118-1-2, 1-4 cm		-25.0
58115	118-1-3, 5-8 cm		-25.0
58116	118-1-5, 1-4 cm		-25.2
58117	118-1-6, 7-11 cm		-23.8
58118	118-2-2, 7-10 cm		-23.1
58119	118-2-3, 7-10 cm		-23.6
58120	118-2-4, 2-5 cm		-22.4
58121	118-2-5, 2-5 cm		-23.5
58122	118-2-5, 98-101 cm		-22.3
58123	118-2-5, 115-118 cm		-24.5
58124	118-2-6, 11-14 cm		-23.3

Pliocene			
58125	118-3-1, 34-37 cm		-20.6
58126	118-3-2, 7-10 cm		-23.7
58127	118-4-1, 91-94 cm		-23.7
58128	118-4-2, 1-4 cm		-22.7
58129	118-4-3, 7-10 cm		-22.9

Upper Miocene			
58130	118-5-2, 1-4 cm		-23.2
58131	118-5-3, 8-11 cm		-23.8

## Site 119 (45° 02.3'N, 7° 58.8'W, Water Depth 4447 meters)

Pleistocene			
58139	119-1-1, 20-23 cm		-21.7

<sup>2</sup> Letters in parentheses (C/T) indicate sample likely displaced or mixed.

58140	119-1-2, 25-28 cm	-22.3	W/M
58141	119-1-3, 21-24 cm	-22.2	
58142	119-2-1, 89-93 cm	-23.2	
58143	119-2-2, 7-10 cm	-23.9	
58144	119-2-1, 87-90 cm	-23.7	W/M
58145	119-2-3, 0-3 cm	-23.9	
58146	119-2-5, 1-4 cm	-23.0	

## Pliocene

58147	119-3-1, 19-20 cm	-22.2	
58148	119-3-2, 4-7 cm	-23.2	W/M

## Upper Miocene

58149	119-4-1, 49-51 cm	-22.8	
58150	119-4-2, 7-10 cm	-23.2	C/T

These tabulated results may be better seen plotted with depth for each core hole, Figures 1 through 5. As may be seen from these figures only Holes 111, 112 and 116 have sufficient sample density to permit detailed stratigraphic interpretations; Holes 118 and 119 permit only generalizations.

## INTERPRETATION

All interpretations for this first paper must necessarily be preliminary and tentative. Precise interpretations require intimate correlation of the carbon isotopic results with the paleontology—paleontology which is not available yet.

In lieu of this we have delineated the intervals of more negative values as "C/T" indicating that the explanation may lie in either cold surface waters in the photosynthetic zone, or strong contributions of terrestrial organic materials.<sup>1</sup> More positive carbon isotopic values are labeled W/M to suggest that they can arise either from the effects of warmer surface waters in the photosynthetic zone or strong contributions of marine organic materials. Postulated breaks between C/T and W/M are dashed. Our previous experience indicates that single values, either high or low, in an otherwise consistent series are more likely from 1) displaced sediments or 2) mixed and relict faunas. Displaced sediments may incorporate organic carbon which was produced at another time and site; the paleontology may indicate either the site of original deposition or subsequent deposition or be mixed. Mixed and relict-faunas may arise due to very slow deposition and/or penecontemporaneous movements. Thus some reinterpretation of the significance of a paleontological designation may be required in these latter cases. The authors have included some of these possibilities in their hypothetical interpretations.

Overall, however, some general observations may be made. Sites 111, 116 and 118 exhibit 1 to 2 ‰ alterations between positive (W/M) and more negative (C/T)

values. Sites 112 and 119 show no such variations; Site 112 is uniformly cold water or terrestrial, Site 119 is uniformly warmer water or marine. Both show a subordinate trend toward heavier isotopes with depth.

Normally we anticipate from kinetic considerations that the gaseous products, chiefly methane, from decomposition of organic matter should carry away the lighter carbon isotope leaving the remaining organic matter enriched in  $\delta^{13}\text{C}$  as observed by Vinogradov and Galimov (1970). We too believe this secondary trend is due to "maturation-diagenesis" during the normal evaluation of organic matter in sediments.

There are, however, two exceptions to a general depth trend; at Site 112 near the pre-glacial to glacial transition within the Pliocene, there is an abrupt change to more negative values. These pre-glacial sediments are unexplicably either colder water or more terrestrial. In Core 119, samples from within the upper Pleistocene do not fall on any "maturation-depth" line but rather they are more positive suggesting either warmer waters or marine. These major changes, we believe, reflect the primary controls on carbon isotopic ratios.

## CONCLUSIONS

Surface water temperature control still appears to be most significant in explaining the observed variations. It explains:

(1) The alteration observable in the pelagic Pliocene-Pleistocene sequence at Site 116.

(2) The lack of correspondence between sediment types and distinct  $\delta^{13}\text{C}$  values. Trends persist through sections of "silty and sandy clay with pebbles," and/or "foraminiferal-nannoplankton ooze," and/or disturbed "sediments." Observe in Sites 111, 112 and 116.

(3) The difference between Site 116 which is affected by the Gulf Stream and Site 112 where the waters were cooler. At Site 116  $\delta^{13}\text{C}$  values are generally less than -25 ‰ while those of Site 112 are greater than -25 ‰.

(4) The similarities between Sites 118 and 119 in spite of the nearly pelagic section at Site 119 and the turbidites at Site 118.

(5) The observation that "maturation-diagenesis" changes are second-order affects largely masked by more primary controls.

<sup>3</sup>Note that the use of the term "terrestrial" during the description of the cores in the Introduction referred only to the indicated source of the clastics, of the grains. No inference should be made about the source(s) of the comingled organics—their carbon may be of either terrestrial or marine photosynthetic origin. The purpose of this research is to help provide guides for interpretations of the source of organic materials.



Obviously, there are still anomalies in this data. We recommend that these  $\delta^{13}\text{C}$  results be integrated with the detailed paleontology before any precise answer be given to the original question.

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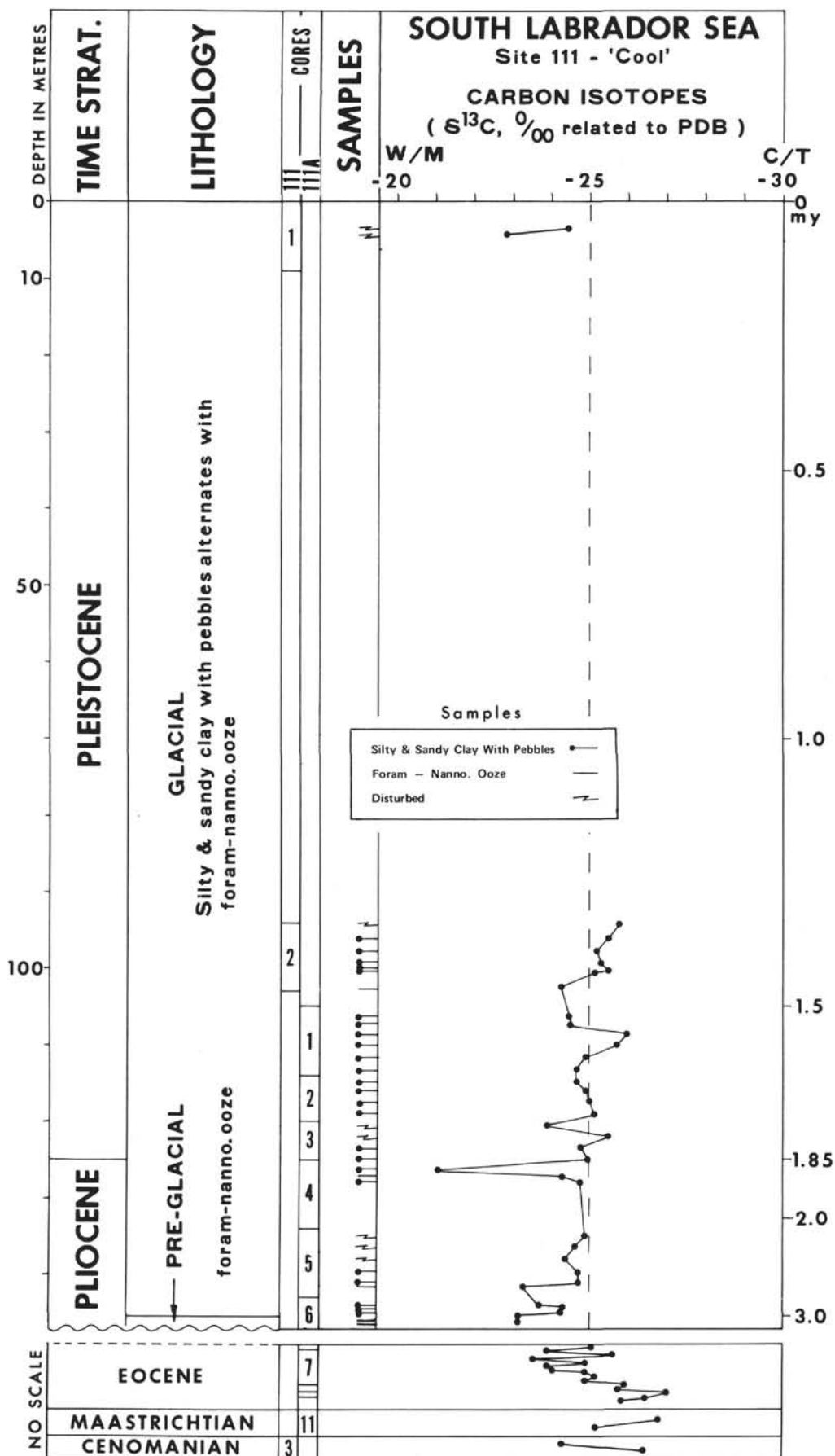


Figure 1.



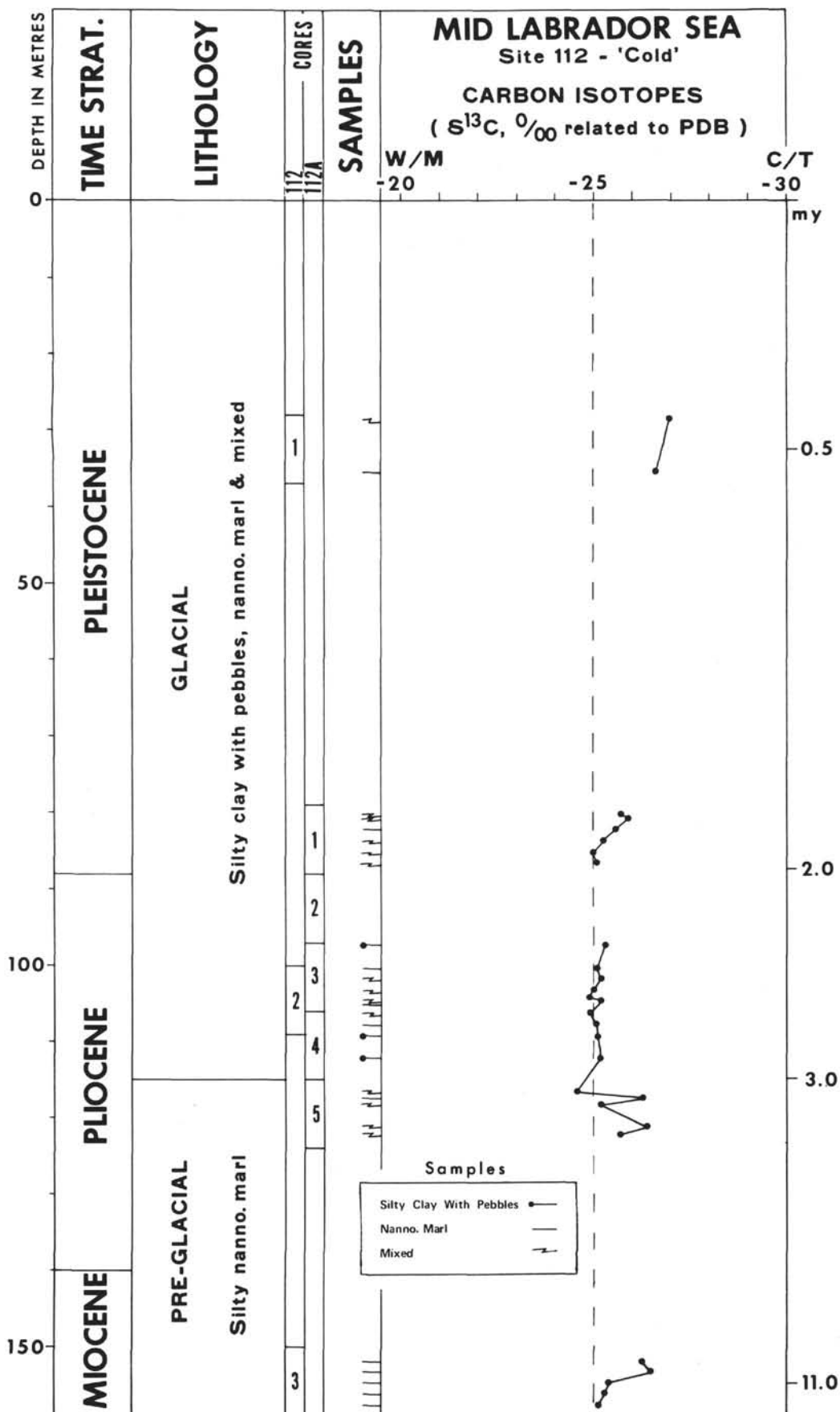


Figure 2.

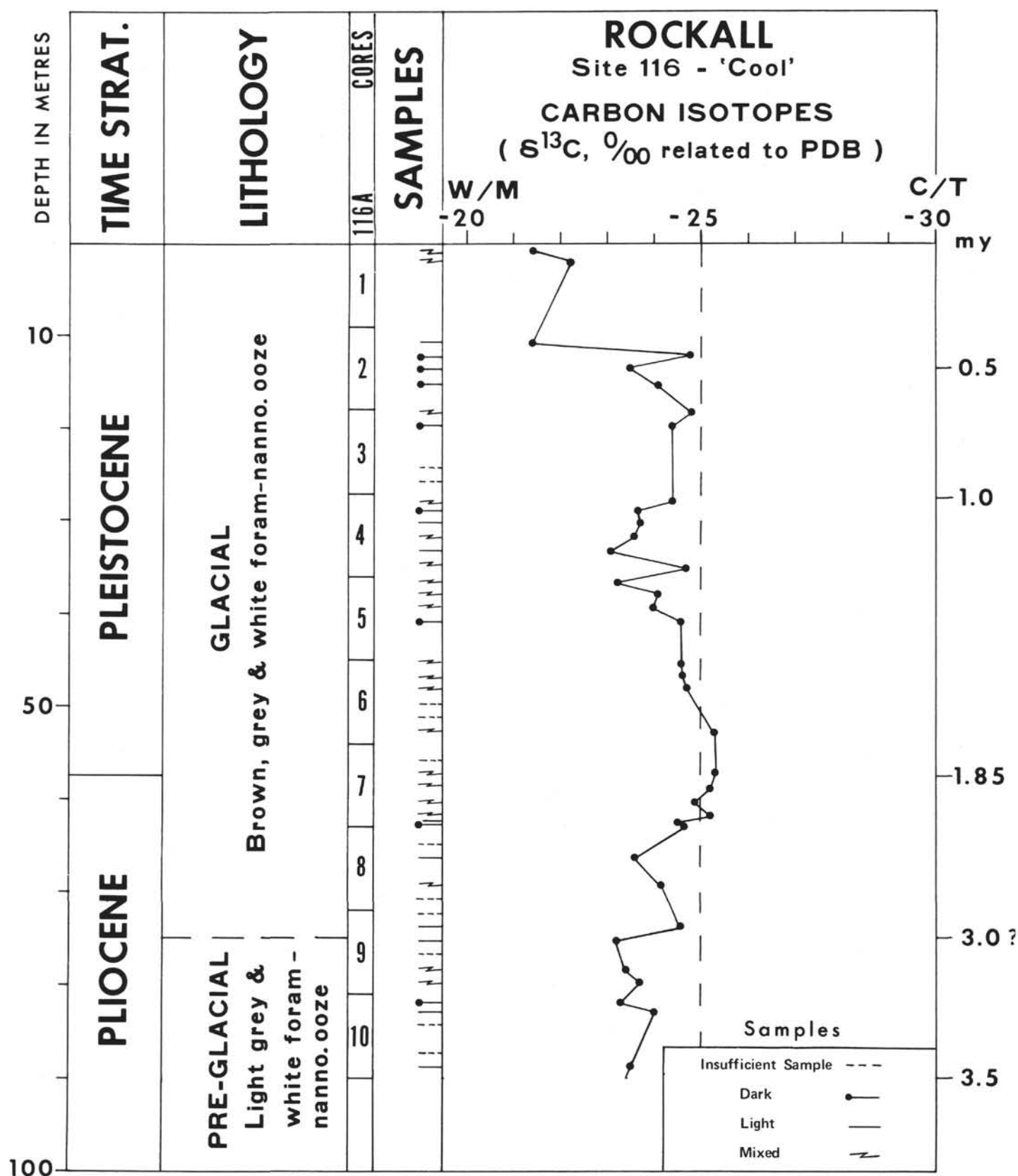


Figure 3.

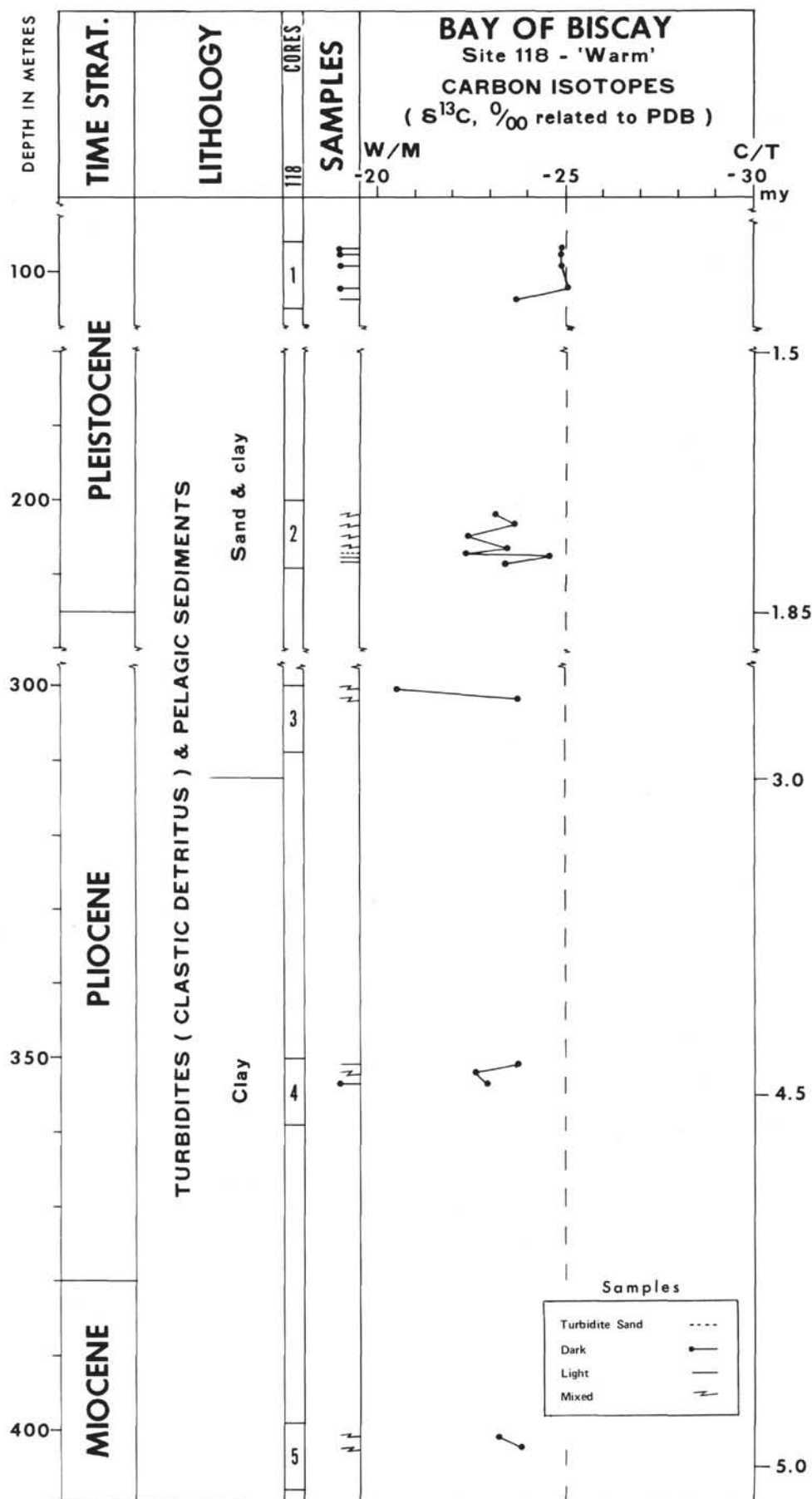


Figure 4.

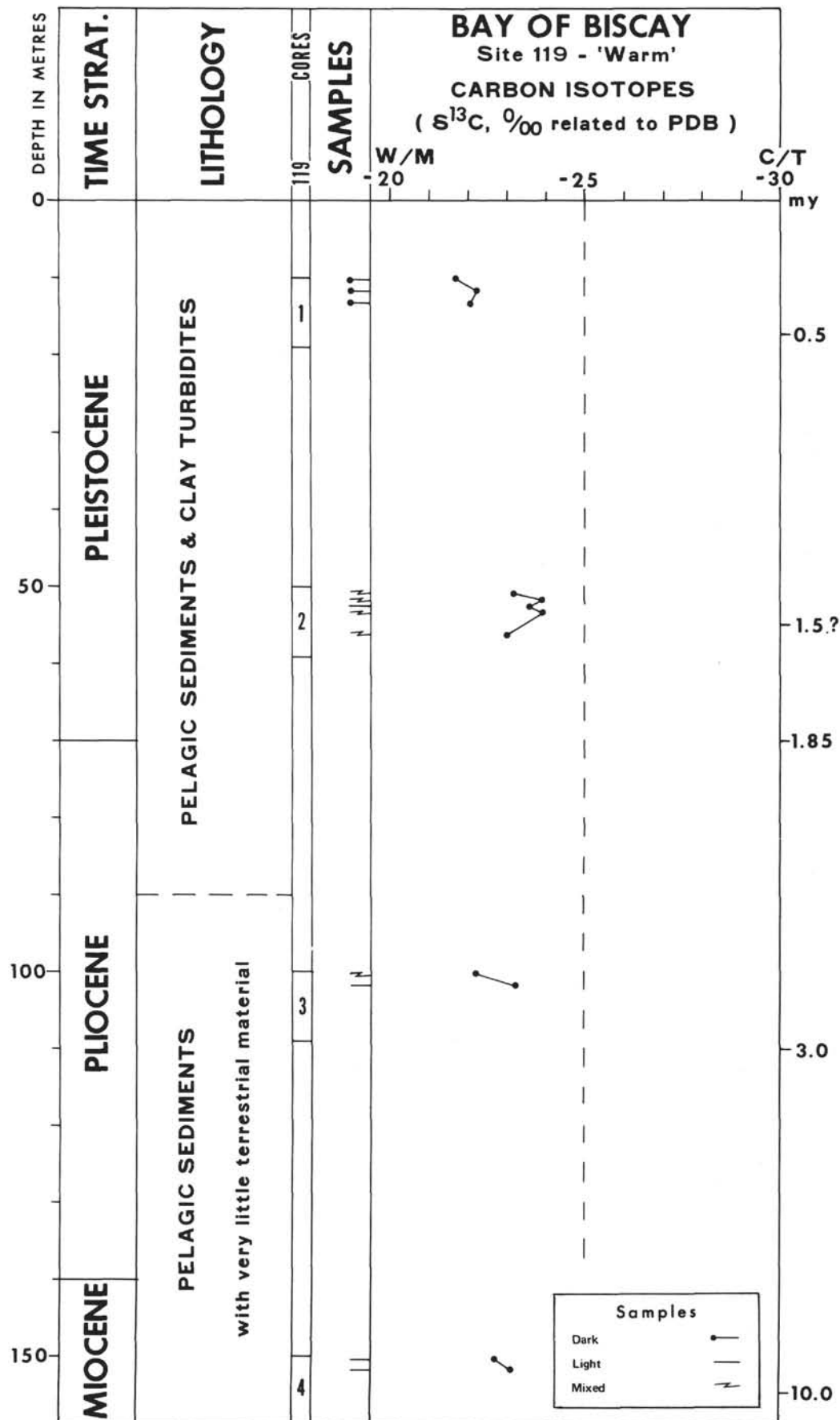


Figure 5.