64. CARBON AND ITS ISOTOPIC COMPOSITION IN PACIFIC OCEAN BOTTOM SEDIMENTS, LEG 56, DEEP SEA DRILLING PROJECT

E. A. Romankevich and M. P. Nesterova, P. P. Shirshov Institute of Oceanology, USSR Academy of Sciences, Moscow, U.S.S.R.
and
I. P. Shadsky and J. I. Grinchenko, I. M. Gubkin Institute of Petrochemical and Gas Industry, Moscow, U.S.S.R.

INTRODUCTION

We have analyzed inorganic and organic carbons and determined the isotopic composition of both sedimentary organic carbon and inorganic carbon in carbonates contained in sediments recovered from Holes 434, 434A, 434B, 435, and 435A in the landward slope of Japan and from Hole 436 in the oceanic slope of the Japan Trench.

Both inorganic and organic carbons were assayed at the P. P. Shirshov Institute of Oceanology, in the same sample, using the Knopp technique and measuring evolved CO_2 gravimetrically. Each sample was analyzed twice in parallel. Measurements were of a ± 0.05 per cent accuracy and a probability level of 0.95.

Carbon isotopic analysis was carried out on a MI-1305 mass spectrometer at the I. M. Gubkin Institute of Petrochemical and Gas Industry and the results presented as δC^{13} values related to the PDB standard. The procedure for preparing samples for organic carbon isotopic analysis involved (1) drying damp sediments at 60°C; (2) treating samples, while heating, with 10 N HCl to remove carbonate carbon; and (3) evaporating surplus HCl at 60°C. The organic substance was turned to CO_2 by oxidizing it in an oxygen atmosphere. To prepare samples for inorganic carbon isotopic analysis we decomposed the carbonates with orthophosphoric acid and refined the gas evolved. The δC^{13} measurements, including a full cycle of sample preparation, were of a ± 0.5 per cent accuracy and a probability level of 0.95.

RESULTS

The data on inorganic and organic carbon content of Leg 56 sediments and on organic carbon isotopes are summarized in Table 1. Lithology of organic carbon is presented in Figure 1.

Carbon Distribution

Sediments from the landward slope of Japan (Holes 434, 434A, 434B, 435, and 435A) contain inorganic carbon in quantities from less than 0.01 to 6.16 per cent, averaging 0.44 per cent. Sediments from the oceanic slope of the Japan Trench contain inorganic carbon (Hole 436) in amounts from less than 0.01 to 0.12 per cent, averaging 0.06 per cent. Quantities of organic carbon in the same holes in the landward slope vary from 0.14 to 1.29 per cent, averaging 0.85 per cent. Although these sediments clearly show certain maxima and minima in organic carbon content, there is no general pattern of distribution of organic carbon. The oceanic slope sediments (Hole 436) contain organic carbon in quantities from 0.08 to 0.73 per cent. There is an average of 0.12 per cent organic carbon in the middle Miocene sediments, which is low in comparison with younger strata. For example, the average value for Pleistocene sediments is 0.46 per cent. Sediments from the oceanic slope of the Japan Trench show low organic carbon content (0.29 per cent on the average) by contrast with the landward slope sediment.

Isotopic Composition of Organic Carbon

The isotopic composition (Figure 2) of organic carbon varies from -21.5 to -24.2 per mill in Holes 435 and 435A; from -18.6 to -25.2 per mill in Holes 434, 434A, and 434B; and from -22.1 to -25.5 per mill in Hole 436.

In general, the sediment layer shows a predominance of heavy organic carbon isotopes typical of organic substance of pelagic origin (Galimov, 1973). The general pattern of distribution throughout core samples reveals that the amount of isotope C^{12} increases with depth.

Isotopic Composition of Inorganic Carbon in Carbonates

The isotopic composition of carbon in two analyzed carbonate samples, as well as other characteristics of these samples and their matrices, are presented in Table 2 (see Whelan, this volume; Okada, this volume; and Site Summary Chart for Sites 434 and 435, back pocket, Part 1). One of the two samples, which is a carbonate concretion, was sampled from Hole 435 at a depth of 75.3 meters sub-bottom from a core of carbonate-free diatomaceous, clayey, methane-containing silt. The inorganic carbon of this sample is characterized by relatively light isotopic composition (-11.2 per mill). The other sample, a marl fragment, was sampled from Hole 434 at a depth of 244.5 meters sub-bottom from a core of diatomaceous clay containing 8.3 per cent $CaCO_3$. This core was free of methane and other gases, and the sample we tested consisted of heavier carbon isotopes (-5.9 per mill). The composition of carbon in this sample is closer to that of sedimentary pelagic carbonates, whose average istopic composition approaches zero (Galimov, 1968).

TABLE 1
Carbon and Isotopic Composition of Organic Carbon in Sediments from Leg 56

Section	Sub-bottom Depth (m)	Organic Carbon (%)	Inorganic Carbon (%)	Organic Carbon δC13 (per mill)
Hole 435				
4-1	28.0	0.96	1.16	-22.2
7-5	61.9	0.69	0.12	-21.5
12-2	105.0	0.86	1.35	-23.1
15-1	132.3	1.10	0.25	-21.5
Hole 435A				
3-4	163.7	1.29	0.17	-22.5
5-5	184.5	0.71	0.01	-22.5
6-2	189.6	0.76	0.03	-21.7
7-1	197.4	0.99	0.08	-22.7
10-1	225.8	0.98	0.16	-24.2
11-3	238.6	0.92	0.32	-22.4
Hole 434				
1-4	4.1	1.17	0.05	-21.8
4-1	26.0	0.63	0.10	-23.2
5-1	36.1	0.82	0.41	-25.2
7-1	54.8	0.63	0.21	-23.1
9-1	73.6	0.82	0.06	-23.0
12-1	102.8	0.75	0.12	-23.3
15-2	132.8	0.46	0.17	-18.6
19-1	169.2	1.09	6.16	-22.8
20-1	178.8	0.83	0.09	-22.9
22-1	196.8	0.83	–	-23.1
23-5	209.5	0.76	0.22	-22.8
25-1	226.3	0.73	0.87	-23.4
31-1	282.5	0.95	0.03	-22.9
Hole 434A				
1-4	1.0	–	–	-23.0
Hole 434B				
11-2	383.1	1.02	0.07	-23.2
15-3	422.3	0.84	0.11	-23.8
16-2	429.9	0.80	0.05	-23.9
24-1	505.2	0.94	0.35	-24.2
25-3	517.1	0.60	0.31	-25.1
Hole 436				
1-2	2.6	0.73	0.02	-22.6
3-1	18.5	0.58	0.05	-22.1
8-4	70.6	0.43	0.06	-22.3
9-2	76.8	0.12	0.01	-23.6
12-3	106.4	0.37	0.02	-23.0
13-5	116.2	0.40	–	-22.5
16-3	144.2	0.40	0.04	-22.1
25-1	227.1	0.26	0.06	-23.3
27-2	247.6	0.30	0.04	-23.1
28-1	255.6	0.22	0.04	-24.2
32-2	294.9	0.16	0.08	-24.2
33-3	305.6	0.12	0.05	-25.5
35-2	324.4	0.18	0.11	-24.2
36-1	332.3	0.08	0.12	-24.2
37-6	348.9	0.20	0.04	-23.1
40-6	376.2	0.09	0.08	–

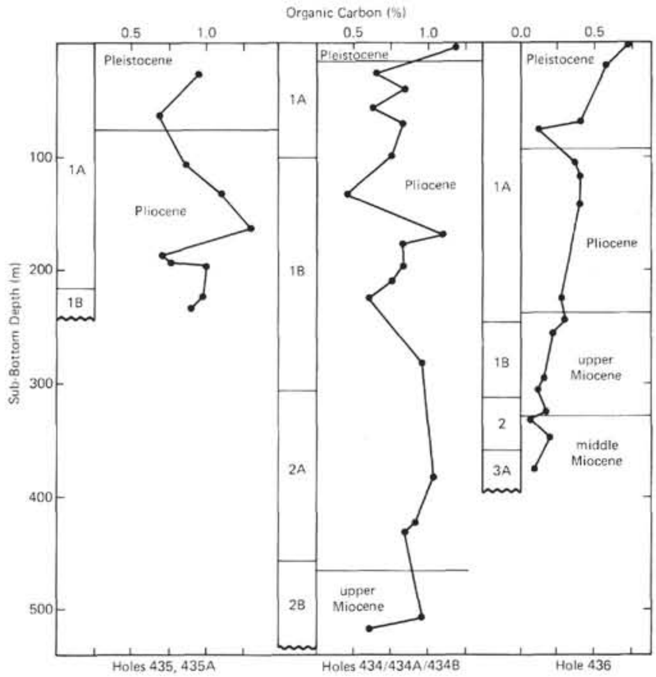

Figure 1. *Organic carbon in sediments of DSDP Leg 56. 1A: Clayey diatomaceous ooze; 1B: diatomaceous claystone; 2: radiolarian–diatom claystone; 2A: vitric diatomaceous claystone; 2B: tuffite; 3A: pelagic clay.*

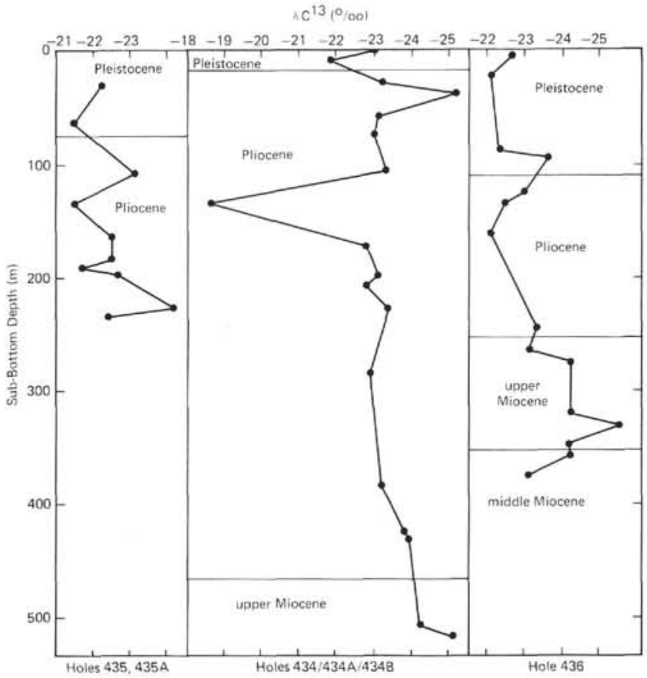

Figure 2. *Isotopic composition of organic carbon, DSDP Leg 56.*

DISCUSSION

The organic carbon of sediments cored from Hole 436 lightens isotopically as it decreases in quantity (see Figure 3). This tendency can be traced in samples from Holes 434A and 434B but is not evident those from Holes 435 and 435A. Because organic matter in the Japan Trench sediments is mostly planktonic in origin, additional amounts of allochthonous, isotopically light

TABLE 2
Characteristics of Sea Carbonates, Leg 56

Section/Sub-bottom Depth (m)	Carbonates $CaCO_3$ (%)	Carbonates δC^{13} (per mill)	Sediments Lithology	Sediments Organic Carbon (%)	Sediments $CaCO_3$ (%)	Sediments Methane
434-27-1 244.5 Marl	37.09	-5.9	Diatomaceous silty claystone	1.0	8.3	Present
435-9-1 75.3 Carbonate concretion	22.36	-11.2	Diatomaceous silty clay	0.6	0.2	Absent

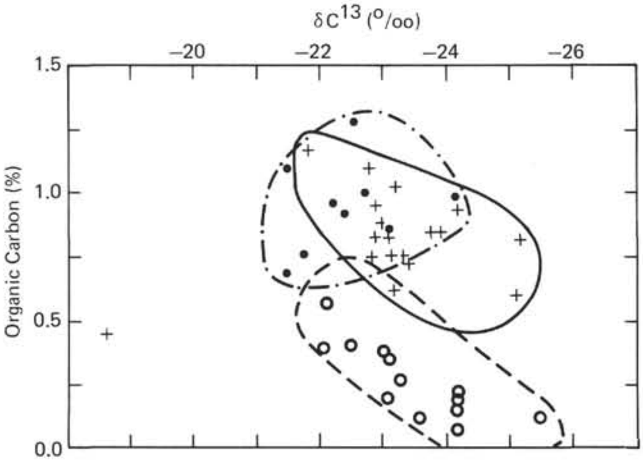

Figure 3. *Plat of organic carbon content relative to its isotopic composition for DSDP Leg 56 sediments (+, samples from Holes 434, 434A, 434B; •, samples from Hole 435, 435A; ○, samples from Hole 436).*

organic carbon should produce increased quantities of organic carbon as well as isotopic lightening. On the other hand, organic matter transformation during sedimentation and during the initial stages of diagenesis, which leads to a loss of unstable and isotopically heavy components of organic matter, will result in decreased amounts of organic carbon and in isotopic lightening (Shadsky et al., 1978). Thus these processes seem to be at odds with one another.

The relationship between isotopic composition of organic carbon and its presence in sediments revealed by Hole 436 samples proves that fractionation of carbon isotopes in the course of destruction of organic matter plays an important role in the formation of isotopic composition of organic carbon buried in oceanic slope sediments of the Japan Trench. The absence of such a relationship for the sediments of the landward slope may indicate the relatively substantial contribution of allochthonous isotopically light organic matter to the creation of those sediments. This allochthonous ingredient obviously possesses higher resistance to destruction than an autochthonous one.

The sedimentary section we examined is composed of similar diatomaceous clayey sediments interspersed with volcanic tuff. Carbonate concretions occur in the depositions of the landward slope (Holes 434, 434A, 434B, 435, and 435A). These sediments contain methane and other hydrocarbon gases, whereas oceanic slope sediments (Hole 436), although similar in other respects to those of the landward slope, contain no hydrocarbon gases (Whelan, this volume). Comparison of changes of isotopic composition of organic carbon and changes of methane content in sediments, exposed by Holes 434, 434A, 434B, 435, and 435A (Figures 4 and 5) shows that the extremes of these values coincide. Enrichment in C^{13} corresponds to extremely high magnitudes of methane in sediments during a gas-hydrate phase and shows limited migration.

It is known that the microbiological decomposition of organic matter, in which methane-producing bacteria take part, is accompanied by generation of isotopically light methane (δC^{13}, up to − 80 per mill) and of carbon dioxide whose isotopic composition is heavier than that of the original organic matter by 3 to 15 per mill (Nakai, 1961; Oana and Deevay, 1960). Calculation of the balance of stable carbon isotopes in such a decomposition system shows that the remaining organic matter should be enriched with heavy carbon isotopes. Hence the higher the generation of methane, the greater the enrichment of organic matter with heavy isotopes. Thus sample analysis may indirectly indicate the degree of active microbiological decomposition of organic matter taking place in the sediments under the influence of anaerobic methane-producing bacteria.

The difference between the average isotopic composition of carbon in organic matter of the sediments cored from Hole 435 (δC^{13} −22.4 per mill) and the isotopic

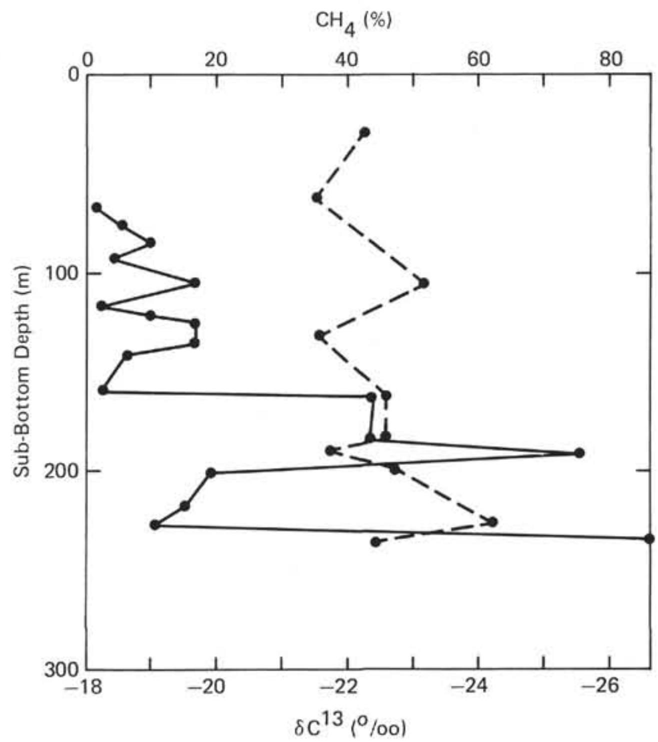

Figure 4. *Isotopic composition of organic carbon and methane gas content for Holes 435 and 435A sediments, DSDP Leg 56.*

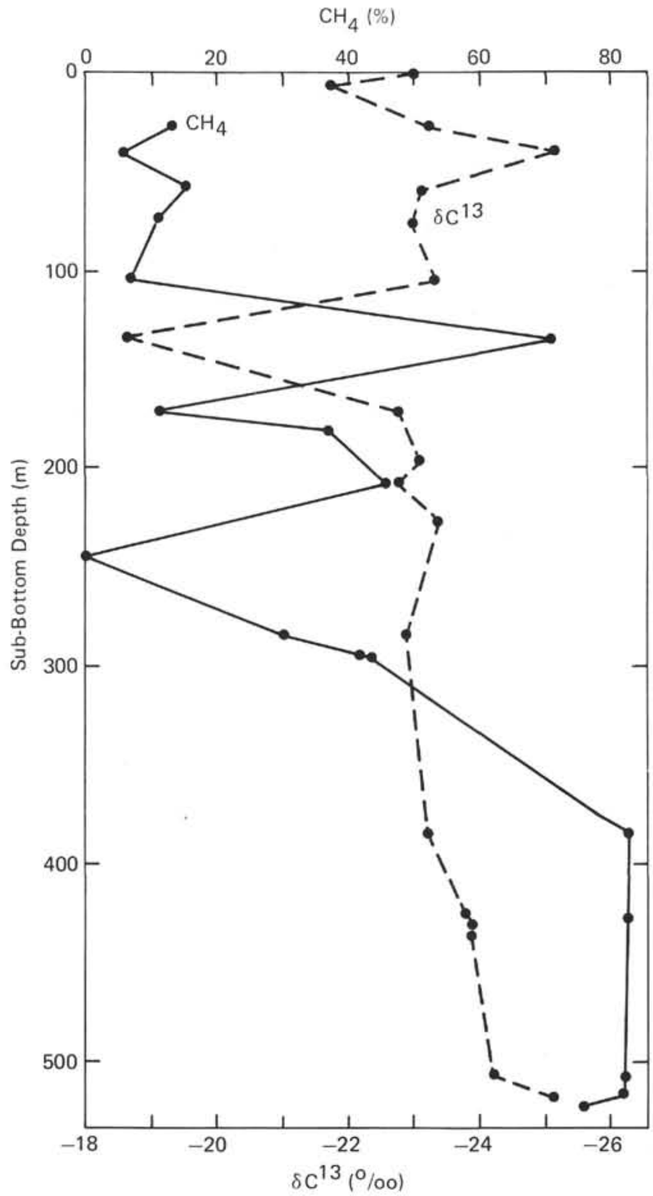

Figure 5. *Isotopic composition of organic carbon and methane gas content for Holes 434, 434A, and 434B sediments, DSDP Leg 56.*

composition of inorganic carbon from carbonate concretions in the same sediments ($\delta C^{13} - 11.2$ per mill) is 11.2 per mill. This value falls within the range of magnitudes characteristic of differences between isotopic composition of organic carbon and CO_2 produced during methane fermentation. Thus a carbonate concretion may in fact be a diagenetic carbonate which has emerged from metabolic CO_2. The essential irregularities that occur in the isotopic composition of organic carbon in the sediments from Holes 434, 434A, 434B, 435, and 435A can be attributed to the activity of methane-producing bacteria. Similar isotopic excursions occur in sediments from Hole 436 (Figure 2). Thus one may conclude that the methane which had been generated in oceanic slope sediments of the Japan Trench (Hole 436) subsequently escaped.

We used the materials collected during the 46th voyage of the Soviet research ship *Vityaz* to study the isotopic composition of organic carbon present in Holocene sediments in the region of Kurilo-Kamchatck and the Japan Trench. Our analysis revealed, first, that in more pelagic environments the organic carbon is more enriched in the C^{12} isotope because of selective retention of lipids and their polymeric forms (isotopically light and stable fractions of organic matter) and, second, that irregularities of isotopic composition are due to differences in the thermal conditions in which organic matter was produced during photosynthesis in the warm Kurosio current on the one hand and the cold water of Oiyasio on the other (Shadsky et al., 1978). The data confirm that the tendency established for Holocene deposits (i.e., that C^{12} content increases in more-pelagic environments) is valid for Pleistocene sediments also (Table 3). Consequently, we conclude that on the whole there had been no great change in conditions throughout the Quaternary. In Pliocene sediments, far away from shore (Hole 436), the isotopic composition of organic carbon is the same as in the Quaternary depositions ($\delta C^{13} = -22.7$ per mill).

In comparison to Pleistocene deposits, the Pliocene sediments of the landward slope of Japan (Holes 434, 435, and 435A) are enriched by isotopically light organic carbon. One of the causes for isotopic lightening of organic carbon may be that during the Pliocene an isotopically light organic carbon was brought in by a cold current from colder waters of high latitudes where that carbon had been photosynthesized.

In the Miocene the organic carbon is isotopically lighter still by approximately 1.5 per mill, probably as a result of the following. In the Miocene the climate of the Northern Hemisphere was warmer and more humid than during subsequent periods. This enhanced the delivery to the ocean of allochthonous isotopically light organic matter, which is more resistant to biological destruction. Furthermore, methane fermentation, which produces an increase of heavy carbon isotopes, proceeded less actively in those sediments.

In Hole 436 sediments the settling of organic substances during the Miocene took place at a decreased rate. This resulted in precipitation of oxidized deep-sea red clays (see Site Summary Chart, back pocket, Part 1). These sediments, in contrast to Pliocene deposits, settled in pelagic environments far from land. Such lateral displacement of sediments bears out the hypotheses of plate tectonics.

ACKNOWLEDGMENTS

We wish to thank Professor A. A. Kartsev of the Gubkin Institute of Petrochemical and Gas Industry and Dr. A. A. Ivlev of the All-Union Scientific Research Geological Prospecting Oil Institute for their critical review of the manuscript. Thanks are also due Professor A. A. Murdmaa of the Shirshov Institute of Oceanology for his help with problems of taxonomy.

TABLE 3
Average Contents of Carbon and Its Isotopic Composition in Leg 56 Sediments

	Holes 435, 435A			Holes 434, 434A, 434B			Hole 436		
Age	Organic Carbon (%)	Inorganic Carbon (%)	Organic Carbon δC^{13} (per mill)	Organic Carbon (%)	Inorganic Carbon (%)	Organic Carbon δC^{13} (per mill)	Organic Carbon (%)	Inorganic Carbon (%)	Organic Carbon δC^{13} (per mill)
Pleistocene	0.82 (2)	0.64 (2)	-21.8 (2)	1.17 (1)	0.05 (1)	-22.4 (2)	0.46 (4)	0.03 (4)	-22.6 (4)
Pliocene	0.81 (8)	0.30 (8)	-22.6 (8)	0.80 (15)	0.54 (15)	-23.0 (15)	0.35 (4)	0.03 (4)	-22.7 (4)
Late Miocene				0.77 (2)	0.33 (2)	-24.6 (2)	0.20 (5)	0.06 (5)	-24.2 (5)
Middle Miocene							0.12 (3)	0.08 (3)	-23.6 (2)

Note: Numerals in parentheses refers to total number of samples averaged.

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