20. CYCLICAL GEOCHEMICAL PROPERTIES OF ORGANIC MATTER IN CARIACO BASIN CORES — LEG 15, SITE 147

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Analyses of organic carbon and hydrocarbons in the first 127 meters of the Site 147 core, collected especially for organic geochemical studies, reveal trends that may reflect alternating high and low stands of the sea during late Pleistocene and Holocene times. Eight frozen samples were selected for this study of organic carbon, extractable bitumen, heavy hydrocarbons, gasoline-range hydrocarbons, and carbon isotope ratios of total organic matter and extractable hydrocarbons. The procedures we applied have been reported earlier (Dunton and Hunt, 1962; Gehman, 1962; Eckelmann et al., 1962). The results of organic carbon and hydrocarbon analyses are summarized in Table 1 and of isotope studies in Table 2.

Organic carbon contents of most of these samples are generally very high—higher than for other sediments previously collected from deep water (McIver, 1971); these high values reflect the silled, anaerobic conditions which apparently prevailed in this structural depression intermittently. Based on organic contents, these conditions must have existed during the deposition of the two deepest sediments we studied. However, the data suggest that these conditions were temporarily upset at the onset of the last glacial stage, which apparently occurred slightly above the 85 meter level in Hole 147B. Because of lower sea levels, streams carried more terrestrially derived organic matter into the basin. Terrestrial organic matter is isotopically light (Sackett, 1964), and a perturbation of the previous balance of terrestrial-marine matter toward more of the former would produce the observed lighter (more negative) organic carbon. In fact, the shift in the balance had apparently already begun in sample G, at 85 meters.

Isotopically lighter organic carbon may also be attributed, in part, to deposition from slightly warmer waters (as discussed by Rogers and Koons, 1969), but even though both mechanisms act to produce lighter organic carbon, the major control is probably the increased terrestrial contribution (Sackett and Rankin, 1970).

The input of terrestrial organic matter approached its maximum (insofar as can be seen with this sampling interval) in sample F at 62 meters. As Table 2 shows, it is at this depth that the organic carbon is lightest (-22.25 vs -20.75 above and -21.40 below). At the same time, the very stagnant conditions must have been replaced by relatively more oxidizing ones, because much less of the organic matter was preserved (0.62% organic carbon vs 2.24 and 1.30% above and below respectively). This zone, characterized by a more oxidizing environment and maximum influx of land-derived organic matter, probably corresponds to the Iowan glacial substage. In terms of organic character the sediment is still rich in organic matter relative to most other deep-sea cores (McIver, 1971).

The chemical evidence suggests that when the next younger sample (E, at 47 m) was deposited, the sea level may have already begun to rise again, the waters at the bottom of the basin were becoming more stagnant and reducing, and the earlier balance between terrestrial and marine organic matter was again achieved.

The isotopically lighter carbon in sample C (a slight reversal in the steady increase from sample F upwards) can be attributed to one of the last ice advances in the Wisconsin ice age. Finally, based on organic carbon contents, it appears that very reducing conditions have prevailed in the Holocene (samples A and B). Thus, we place the end of the last glaciation, 11,000 years ago, between 13 and 16 meters in Hole 147B, or slightly deeper than at 7 meters in Hole 147, as recorded in the shipboard findings of Edgar et al. (1971).

While these findings in Hole 147B are consistent with glacial-interglacial interpretations in the sister Hole 147, the boundaries are placed somewhat deeper based on our chemical studies. It is conceivable that if we had chosen closer sampling in our study, our interpretation of the order of events would have reflected more of the glacial history, i.e., glacial advances and retreats so well worked out for the Wisconsin. It may also have revealed even greater "cycles" in the organic parameters.

Very large bitumen extracts characterize the two uppermost samples, A and B (Table 1), and about 70 percent of this material, soluble in polar solvents, is insoluble in normal pentane; this insoluble material is classed as asphaltene. Such extracts, very rich in asphaltenes and soluble NSO's, but low in hydrocarbons, have been interpreted to be very young, virtually unaltered (i.e., thermally) deposits of organic matter mixed with inorganic sediment (McIver, 1971, 1973).

While the moderately low hydrocarbon contents (20 to 85 ppm) suggest that these sediments are not now capable of sourcing petroleum in commercial quantities, the high organic carbon and bitumen contents suggest that, given more time and exposure to higher temperatures, these sediments could be prolific hydrocarbon sources later in time. Nothing unusual is suggested by the relative amounts of saturate and aromatic hydrocarbons.

The gasoline-range contents of the samples suggest that thermal alternation (gasoline generation from heavier species) has barely begun. However, the highest value, 0.408 ppm for sample B, is anomalously high if this is truly a Holocene sample—as we have interpreted from the organic carbon and bitumen contents. As Dunton and Hunt (1962) point out, Holocene sediments do not have detectable quantities of hydrocarbons in this range. On the other hand, this unusual value may simply indicate that small

TABLE 1
Results of Geochemical Analyses, Site 147

Sample	Hole	Core	Section	Estimated Depth Below Sediment/ Water Interface (m)	Total Organic Carbon (%)	Total Extractable Bitumen (ppm)	Triple Solvent-Soluble Bitumen Composition			C_{13}^+ Hydrocarbon Composition		C4-C7 Gasoline-Range Hydrocarbons (ppm)
							C_{13}^+ Hydro-carbons (ppm)	Pentane Soluble NSO's (ppm)	Pentane Insoluble NSO's (ppm)	Saturates (ppm)	Aromatics (ppm)	
A	147B	1	2	4	3.92	2237	85	561	1591	47	38	0.064
B	147B	2	1	13	4.42	2313	76	633	1604	32	44	0.408
C	147B	2	3	16	1.35	347	30	165	152	16	14	0.132
D	147B	5	2	41	1.70	860	46	329	485	21	25	0.045
E	147B	5	6	47	1.30	549	35	221	293	16	19	0.041
F	147B	7	4	62	0.62	170	28	65	77	15	13	0.084
G	147B	9	8	85	2.24	423	44	181	198	18	26	0.194
H	147C	2	3	127	1.57	762	20	424	318	12	8	0.300

TABLE 2
$\delta C^{13}/C^{12}$ Versus Peedee Belemnite

Sample	Total Organic Carbon (avg. of 3 analyses)	Saturated C_{13}^+ Hydro-carbons (avg. of duplicates)	Aromatic C_{13}^+ Hydro-carbons (avg. of duplicates)
A	−20.45	−26.5	−24.7
B	−20.57	−26.9	−24.1
C	−21.70	−26.5	−24.3
D	−20.49	−27.3	−24.3
E	−20.75	−27.5	−24.7
F	−22.25	−27.2	−25.2
G	−21.40	−27.2	−23.9
H	−20.54	−27.3	−24.5

quantities of gasoline-range hydrocarbons are seeping upward from more mature sediments much deeper in the basin—as was found in a DSDP core in the Balearic Basin (McIver, 1973).

While the carbon isotope studies have been used to pick the glacial-interglacial boundaries, another interesting observation is that the saturated and aromatic hydrocarbons have such different C^{13}/C^{12} ratios than the total organic carbon. These differences, up to almost 7 per mil, are far outside the range reported by other investigators (Silverman and Epstein, 1958; Eckelmann et al., 1962). This suggests that the hydrocarbons may be only those preserved intact since they were deposited, and these have not been diluted or masked by any subsequent hydrocarbons formed by normal maturation, i.e., thermal cracking, of the heavier organic matter.

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