

51. INORGANIC AND ISOTOPIC GEOCHEMISTRY OF SEDIMENTS FROM SITES 549 TO 551, NORTHEASTERN NORTH ATLANTIC¹

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ABSTRACT

Thirty-eight samples from DSDP Sites 549 to 551 were analyzed for major and minor components and trace element abundances. Multivariate statistical analysis of geochemical data groups the samples into two major classes: an organic-carbon-rich group (>1% TOC) containing high levels of marine organic matter and certain trace elements (Cu, Zn, V, Ni, Co, Ba, and Cr) and an organic-carbon-lean group depleted in these components. The greatest organic and trace metal enrichments occur in the uppermost Albian to Turonian sections of Sites 549 to 551. Carbon-isotopic values of bulk carbonate for the middle Cenomanian section of Site 550 (2.35 to 2.70‰) and the upper Cenomanian-Turonian sections of Sites 549 (3.35 to 4.47‰) and 551 (3.13 to 3.72‰) are similar to coeval values reported elsewhere in the region. The relatively heavy $\delta^{13}\text{C}$ values from Sites 549 and 551 indicate that this interval was deposited during the global "oceanic anoxic event" that occurred at the Cenomanian/Turonian boundary. Variation in the $\delta^{18}\text{O}$ of bulk carbonate for Section 550B-18-1 of middle Cenomanian age suggests that paleosalinity and/or paleotemperature variations may have occurred concurrently with periodic anoxia at this site. Climatically controlled increases in surface-water runoff may have caused surface waters to periodically freshen, resulting in stable salinity stratification.

INTRODUCTION

Thirty-eight samples from DSDP Sites 549 to 551 were analyzed for major and minor components and trace element abundances. About half of the samples were collected from black, laminated, organic-carbon-rich mudstone and marl intervals occurring in the mid-Cretaceous lithologic units at each site. The other samples came from light-colored, bioturbated, organic-carbon-lean intervals from Tertiary to Lower Cretaceous units at the sites. The primary objective of this study was to determine the effect of redox conditions on the geochemical variability (both inorganic and organic) of the sediments. In addition to elemental analysis, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements on bulk carbonate were obtained for cyclic interbeds of laminated, organic-carbon-rich and bioturbated, organic-carbon-lean chalky marls from Unit 5 at Site 550 and an organic-carbon-rich mudstone in Unit 5 at Sites 549 and 551. These data were used to assess the origin of the organic enrichment at each of the sites.

METHODS

The sediment samples were analyzed for 19 elements using DC-arc plasma optical emission spectroscopy (DCP-OES). Details of the analytical methods are described elsewhere (Bernas, 1968; Foster, 1971). In addition total organic carbon (TOC) and inorganic carbon analyses were conducted on the samples using LECO combustion. Inorganic carbon was assumed to be in the form of CaCO_3 . This was verified by the high correlation of Ca to inorganic carbon ($r^2 = 0.99$). Stable-isotope analyses of the carbonate fraction of some of the samples were also obtained. CO_2 gas was prepared by reaction of carbonate with phosphoric acid at 50°C (Killingley and Berger, 1979), and analyses for carbon and oxygen stable-isotopic compositions were carried out on a V.G. 602 mass spectrometer. The data are reported in delta (δ) notation relative to the PDB standard.

RESULTS AND DISCUSSION

Inorganic Chemistry

Site 549

Two lithologic units at Site 549, Units 5 and 10, were sampled for geochemical analyses (Fig. 1). The results are given in Table 1.

Unit 5 consists of gray and greenish gray nannofossil chinks, with a black carbonaceous mudstone interval occurring in Core 27. Two samples taken from this interval were found to be enriched in organic matter (average 5.7% TOC) of predominantly marine origin (Cunningham and Gilbert, this volume). Elements enriched in these sediments include Cu, Zn, Fe, V, Ni, Cr, and most notably Ba (concentrations up to 3,500 ppm). The concentration of these trace elements in organic-carbon-rich sediments and rocks is well established (see Arrhenius, 1952; Wedepohl, 1964; Calvert and Price, 1970; Vine and Tourtelot, 1970; Chester et al., 1978). The presence of biogenic siliceous debris and fine laminations in conjunction with enrichment in the above components suggests that these sediments were deposited under oxygen-deficient conditions possibly associated with high surface-water productivity (Waples and Cunningham, this volume).

Unit 10 consists of interbedded calcareous and non-calcareous mudstones to sandstones. Elemental analyses were conducted on three samples enriched in organic matter (average 3.4% TOC) of terrestrial origin. Burrow mottling and the absence of marine organic matter suggest that these sediments were deposited under well-oxygenated conditions (Waples and Cunningham, this volume). Compared to the overlying organic-carbon-rich sediments in Unit 5, these mudstones contain relatively low levels of Cu, V, Ni, Cr, and Ba. Concentrations of the other elements are similar to those in Unit 5.

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Site 550

Lithologic Units 1 to 5 at Site 550 were sampled for geochemical analyses (Fig. 1). The results are given in Table 1.

Units 1 to 3 are represented mainly by marly nannofossil chalks and mudstones. The minor amount of organic matter in these sediments (average <0.1% TOC) is composed exclusively of terrestrial components (Cunningham and Gilbert, this volume). No exceptional elemental enrichment is found in these units except for the relatively high concentrations of Sr (average ~1,900 ppm) in the nannofossil chalks of Unit 1a. These values are similar to those reported for coccolith tests that have undergone relatively little diagenesis (Turekian, 1964). The concentrations of the other elements are fairly uniform in the samples from Units 1 to 3. However, Ti, Fe, Al, V, and Ba are enriched three to five times in the carbonate-poor samples (those with less than about 50% CaCO₃).

Unit 4 is represented by pale green nannofossil chalks and siliceous mudstones. A sample from a faintly laminated interval, rich in biogenic siliceous fragments (mainly radiolaria) and zeolites, was geochemically analyzed. It was shown to be enriched in CaCO₃ (69%), lean in organic matter, and generally low in trace elements except for Ba, which is exceptionally high at 5,296 ppm. Presumably this interval was deposited in conjunction with relatively high productivity in the surface waters but without the bottom-water oxygen depletion necessary to preserve the organic fraction.

Unit 5 occurs as a black, organic-carbon-rich mudstone (up to 10.94% TOC), with marine-derived components comprising about 30% of the organic matter (Cunningham and Gilbert, this volume). The two samples from this unit are highly enriched in Cu, Zn, Fe, V, Ni, and Ba in conjunction with their high TOC contents. Laminated fabrics, abundant biogenic siliceous material, and organic trace element enrichment indicate that the sediments were deposited in oxygen-depleted waters probably associated with high productivity.

Unit 6 is composed of white to pale yellow-orange chalk. Geochemical results on a sample from this unit indicate low organic content (0.04% TOC), high CaCO₃ content (78%), and relatively low levels of trace elements.

Grouping of Geochemical Components

Geochemical data recorded for the 38 samples were analyzed using the multivariate techniques of principal components analysis (factor) and cluster analysis. Factor analysis groups the variables (organic and inorganic geochemical data) into a smaller number of factors in which specific variables are highly correlated. Cluster analysis groups samples that have similar distributions of variables.

Factor analysis shows that a five-factor model explains most (81%) of the variance in the data. Much of the variability (61.1%), however, is controlled by just two factors. Cross-plotting the factor scores for the variables in Factors 1 and 2 causes geochemically significant group-

ings of the data to emerge (Fig. 2). Factor 1 shows a strong positive association of noncalcareous, terrigenous, clastic and biogenic siliceous components that is opposite to a strong negative association of biogenic, calcareous components rich in Ca, CaCO₃, Mg, and Sr. Factor 2 shows a moderately strong, positive association of organic matter, marine-derived kerogen, and associated inorganic elements (Cu, Zn, P, V, Ni, Co, Y, and Ba) that is opposite to a moderately strong, negative associ-

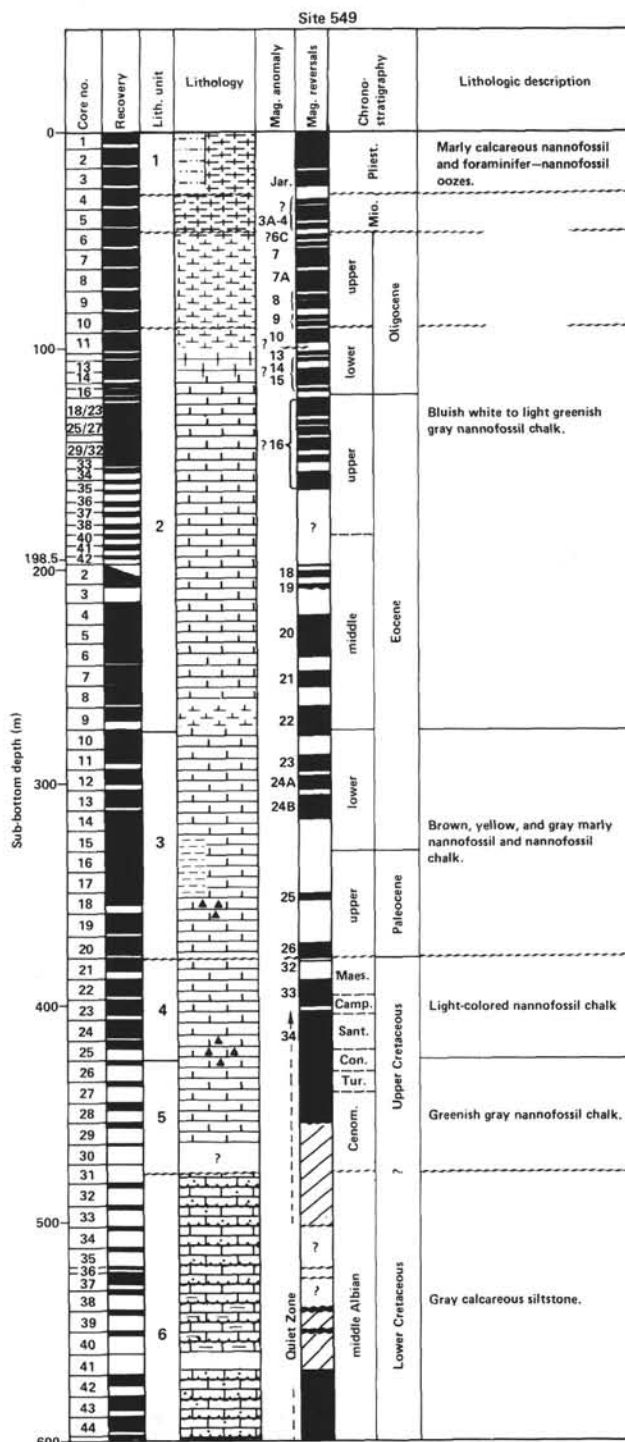


Figure 1. Lithologic and stratigraphic summary of Sites 549 to 551.

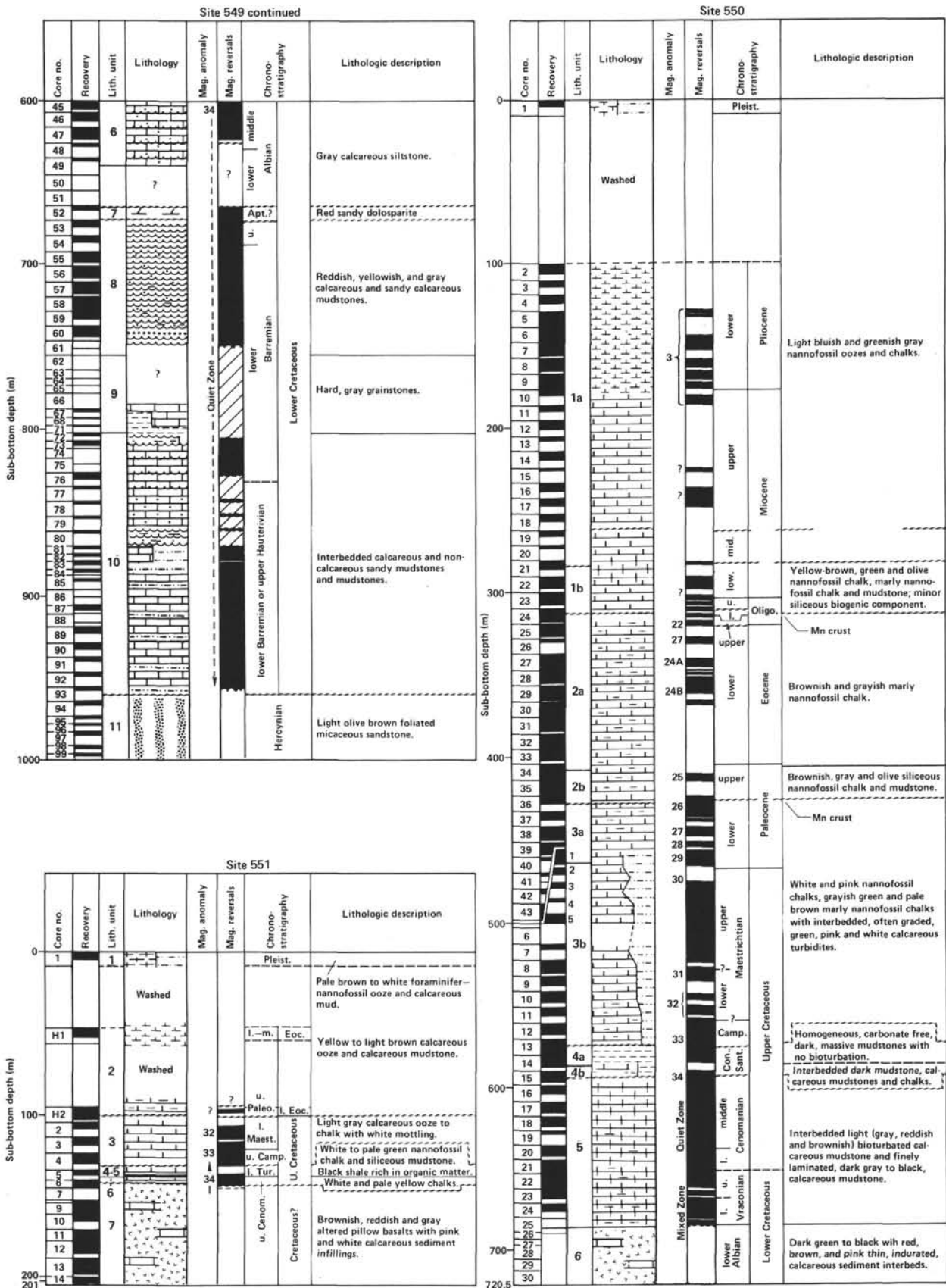


Figure 1. (Continued).

Table 1. Major and minor components (in wt.%) of samples from Sites 549 to 551.

Sample	Site	Section	Interval (cm)	Sub-bottom depth (m)																						
					Na ₂	K ₂ O	Al ₂ O ₃	SiO ₂	TiO ₂	MgO	Fe ₂ O ₃	MnO	P ₂ O ₅	CaO	CaCO ₃	TOC	MAR ^a	Ba	Co	Cu	Zn	V	Ni	Y	Sr	Cr
1	549	27-1	41-43	436.4	1.20	2.0	6.8		0.26	0.86	9.2	0.02	0.15	11.4	25.00	9.31	70	3485	21	98	132	312	204	24	480	76
2	549	27-1	43-46	436.5	1.90	2.4	11.4	78.8 ^b	0.66	1.50	5.2	0.02	0.57	2.3	1.50	2.09	50	1912	40	103	155	302	105	45	265	151
3	549	85-2	127-137	890.8	0.86	1.8	11.1	58.9	0.71	0.77	5.9	0.05	0.05	2.4	4.17	2.80	0	189	25	25	128	94	30	13	110	68
4	549	91-2	12-20	939.2	0.44	1.4	10.2	71.9	0.80	0.51	2.5	0.03	0.04	2.4	5.42	0.61	0	204	13	17	38	90	23	18	212	55
5	549	92-1	80-83	947.3	0.42	1.0	8.0	64.0	0.56	0.45	3.6	0.02	0.03	0.1	7.75	6.87	0	136	27	21	233	69	33	9	27	46
6	550	1-2	30-34	1.8	1.90	2.4	12.0	41.8	0.52	3.20	4.3	0.11	0.12	14.0	27.08	0.29	0	377	14	30	63	88	37	18	214	64
7	550	5-2	90-103	130.5	0.87	0.8	4.8	11.7	0.18	0.78	1.4	0.04	0.08	45.4	78.67	0.08	0	89	7	20	31	30	17	17	1705	29
8	550	17-2	90-105	244.5	0.77	0.7	3.9	10.4	0.14	0.70	1.3	0.10	0.09	43.2	44.92	0.07	0	93	11	15	27	26	29	17	2115	27
9	550	33-4	43-55	399.0	1.10	2.1	14.0	37.4	0.55	1.70	6.2	0.26	0.12	21.2	33.25	0.07	0	367	21	40	89	95	69	21	635	79
10	550	43-2	44-54	491.0	0.34	0.6	3.6	8.7	0.11	0.53	1.4	0.18	0.08	48.0	85.42	0.03	0	27	12	13	31	27	26	12	746	20
11	550B	8-5	90-100	529.5	0.82	2.2	13.9	32.1	0.47	1.30	5.5	0.09	0.10	28.0	42.92	0.05	0	171	43	24	80	180	89	15	634	59
12	550B	12-4	67-74	565.7	0.68	1.8	9.1	24.9	0.26	1.30	4.2	0.18	0.12	36.6	56.92	0.03	0	118	14	40	67	52	46	26	592	32
13	550B	13-6	45-56	578.0	1.60	3.5	19.1	61.1	0.71	2.50	4.2	0.03	0.07	0.8	0.58	0.55	0	291	33	32	91	146	72	15	236	93
14	550B	16-1	98-102	599.5	0.45	0.8	3.4	13.4	0.10	0.65	2.9	0.46	0.06	48.4	80.33	1.54	40	1413	31	39	57	187	68	15	795	94
15	550B	16-2	101-102	601.0	0.36	0.5	3.3	13.0	0.11	0.58	2.9	0.39	0.09	37.5	73.75	1.98	30	1903	47	44	135	200	120	17	725	44
16	550B	16-2	146-148	601.5	0.42	0.6	3.0	65.8	0.08	0.58	1.4	0.08	0.43	13.0	21.92	0.99	10	54	53	28	10	99	150	24	267	98
17	550B	17-2	0-10	608.1	0.46	0.8	4.6	22.0	0.15	0.71	1.5	0.28	0.06	39.1	64.67	0.06	0	81	5	28	16	27	15	15	677	21
18	550B	17-2	74-80	610.3	0.42	0.7	4.1	15.3	0.13	0.66	2.7	0.28	0.09	38.7	67.42	2.37	40	1433	19	58	100	290	98	19	705	50
19	550B	17-2	110-115	610.6	0.37	0.7	4.1	15.4	0.13	0.67	2.5	0.29	0.10	38.8	67.67	2.26	30	1444	47	57	234	276	127	20	658	55
20	550B	17-3	108-110	612.1	0.41	0.6	3.7	14.9	0.12	0.62	2.1	0.32	0.06	42.1	76.25	1.72	20	1255	28	55	73	254	105	17	702	50
21	550B	18-1	6-10	617.1	0.44	0.8	4.5	15.6	0.14	0.71	2.7	0.27	0.07	38.1	71.08	2.19	30	1453	49	47	210	341	142	17	686	39
22	550B	18-1	41-45	617.2	0.42	0.9	4.7	18.4	0.16	0.77	1.7	0.26	0.05	36.6	66.42	1.86	30	1309	41	44	43	67	71	15	644	33
23	550B	20-3	30-45	638.4	0.58	1.4	8.0	26.4	0.31	1.10	1.8	0.17	0.10	27.7	52.50	0.98	0	981	32	43	74	82	57	24	521	39
24	550B	23-4	20-26	666.7	0.50	1.1	6.2	24.2	0.21	0.93	3.0	0.19	0.08	32.6	60.50	1.58	40	1160	26	44	70	127	77	23	469	46
25	550B	23-4	57-72	667.2	0.55	1.5	7.0	30.3	0.23	1.30	3.4	0.16	0.07	30.0	51.08	0.27	10	830	24	199	110	50	47	23	523	30
26	550B	24-1	26-37	671.3	0.55	1.5	7.3	28.6	0.26	1.10	2.6	0.20	0.10	34.0	55.42	0.21	0	1012	8	27	29	46	24	28	551	33
27	550B	24-2	46-49	673.0	0.61	1.6	8.6	27.2	0.32	1.40	4.0	0.17	0.09	35.5	52.00	2.02	40	2374	45	57	112	282	116	29	528	87
28	550B	24-2	55-59	673.1	0.56	1.5	7.4	24.8	0.25	1.20	3.2	0.20	0.11	35.1	55.67	1.68	30	1352	45	46	85	71	98	31	506	41
29	550B	25-2	97-107	682.5	0.55	2.1	8.0	23.1	0.27	1.40	3.2	0.21	0.08	40.6	58.42	0.95	10	1793	14	48	96	68	47	32	585	40
30	550B	25-2	137-143	683.0	0.49	1.9	7.7	21.4	0.26	1.10	3.9	0.19	0.33	36.3	55.92	1.91	30	1390	18	55	131	201	88	42	519	52
31	550B	25-3	60-68	683.6	0.39	1.7	5.8	16.6	0.20	0.86	3.3	0.23	0.06	36.0	68.58	1.69	40	1420	13	45	124	223	79	23	482	34
32	550B	25-4	56-65	685.1	0.71	2.2	8.3	30.7	0.30	1.30	3.1	0.13	0.05	28.5	48.17	0.38	0	1098	6	40	65	51	32	20	435	28
33	551	H1-1	100-111	48.1	2.50	2.9	15.2	50.2	0.72	2.70	5.3	0.07	0.12	8.7	14.83	0.30	0	388	12	35	82	128	45	20	209	86
34	551	4-3	50-64	127.1	0.82	0.7	2.4	7.1	0.07	0.64	0.9	0.18	0.05	44.7	55.50	0.06	0	100	3	19	14	3	11	11	883	<1
35	551	5-2	39-43	134.4	1.10	1.4	5.5	17.1	0.16	1.00	1.6	0.06	0.07	38.0	69.00	0.04	0	5296	<1	38	37	23	13	33	687	15
36	551	5-2	67-70	134.7	1.70	2.3	8.4	47.4 ^b	0.32	1.10	6.8	0.02	0.15	2.3	1.33	6.24	30	5496	27	115	392	600	221	29	286	91
37	551	5-2	103-112	135.1	2.10	2.8	10.3		0.35	1.30	3.9	0.02	0.14	3.3	2.33	6.66	20	746	21	117	264	630	239	26	305	90
38	551	6-1	95-104	146.0	0.62	0.7	2.9	12.2	0.10	0.57	0.7	0.03	0.07	35.3	78.00	0.04	0	1076	<1	13	18	15	1	17	549	6

^a MAR represents the percentage of total organic carbon (TOC) that is of marine origin based on optical characterization of kerogen. It is calculated as % amorphous + % algal + % round bodies.

^b Analyses provided by P. C. de Graciansky for 549-27-1, 50-51 cm and 551-5-2, 68-70 cm.

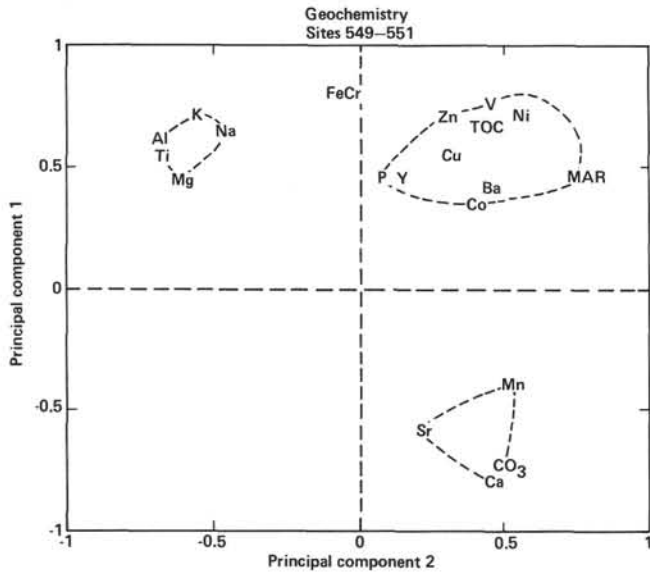


Figure 2. Cross-plot of factor scores for variables in principal components 1 and 2.

ation of terrigenous clastic components rich in Ti, Al, Mg, K, and Na. Fe and Cr plot midway between the terrigenous clastic and organic matter groupings, apparently indicating equal affinity for both of these sedimentary components.

The major groups of variables defined by factor analysis can be further differentiated by cluster analysis. A

six-cluster model provided the most geologically meaningful clusters of samples (Table 2). Clusters 1, 2, 3, and 5 are composed of trace metal-enriched samples generally containing high levels of organic matter (mean TOC 1.7–9.3%). The organic-carbon-rich, black mudstones and marls from Unit 5 at Sites 549 to 551 are grouped in Clusters 1 to 3. Differences in the concentrations of trace elements (especially Ba) control the nature of these groupings. Cluster 5 represents samples from Unit 5 at Site 550. These black marly chalks have lower mean TOC and trace metal concentrations than Clusters 1 to 3.

The overall marine organic matter enrichment (up to 70% of the TOC) and finely laminated structure of the samples in Clusters 1 to 3 and 5 suggests that they were deposited under anoxic conditions. The trace elements may have been concentrated by plankton and transported to the sediments as metal-organic carbon complexes (Martin and Knauer, 1973). Preservation of marine-derived organic matter in these sediments could then have contributed to their trace element enrichment. Recently, however, Holland (1979) has suggested that certain trace elements may precipitate directly from anoxic and reducing waters. Probably a combination of both factors acting simultaneously is a better explanation for trace element enrichment in these samples.

A wide variety of lithofacies from sandstones to mudstones and calcareous oozes characterizes the sediments from Sites 549 to 551 grouped in Clusters 4 and 6. The major factor they all share is their lack of organic matter (mean TOC 0.1–1.0%) and trace elements as com-

Table 2A. Arithmetic mean concentration of major and minor components in the statistical clusters.

Cluster	Sample number	Major and minor components (wt.%)												
		Na ₂ O	K ₂ O	Al ₂ O ₃	SiO ₂	TiO ₂	MgO	Fe ₂ O ₃	MnO	P ₂ O ₅	CaO	CaCO ₃	TOC	MAR
1	1	1.20	2.00	6.80	—	0.26	0.86	9.20	0.02	0.15	11.40	25.00	9.31	70
2	2, 15, 27, 29	0.86	1.65	7.83	35.5	0.34	1.22	3.83	0.20	0.21	28.98	46.42	1.76	35
3	35, 36	1.40	1.85	6.95	32.3	0.24	1.05	4.20	0.04	0.11	20.15	35.17	3.14	15
4	3, 4, 5, 6, 9, 10, 11, 12, 13, 16, 17, 33, 34	0.95	1.68	9.71	40.4	0.44	1.30	3.61	0.12	0.11	19.92	32.34	0.98	0
5	14, 18, 19, 20, 21, 22, 23, 24, 25, 26, 28, 30, 31, 32, 37, 38	0.60	1.30	5.96	22.2	0.20	0.93	2.72	0.21	0.10	33.84	59.83	1.71	25
6	7, 8	0.82	0.75	4.35	11.10	0.16	0.74	1.35	0.07	0.09	44.30	61.80	0.08	0

Table 2B. Arithmetic mean concentration of trace elements in the statistical clusters.

Cluster	Sample number	Trace elements (ppm)								
		Ba	Co	Cu	Zn	V	Ni	Y	Sr	Cr
1	1	3485.0	21.0	98.0	132.0	312.0	204.0	24.0	480.0	76.0
2	2, 15, 27, 29	1995.5	36.5	63.0	124.5	213.0	97.0	30.8	528.8	80.5
3	35, 36	5396.0	13.5	76.5	214.5	311.5	117.0	31.0	486.5	53.0
4	3, 4, 5, 6, 9, 10, 11, 12, 13, 16, 17, 33, 34, 14, 18, 19, 20,	192.5	21.2	27.1	72.5	84.5	49.7	16.7	418.6	55.5
5	21, 22, 23, 24, 25, 26, 28, 30, 31, 32, 37, 38	1210.8	25.5	58.1	105.4	181.9	84.6	22.5	565.6	45.0
6	7, 8	91.0	9.0	17.5	79.5	28.0	23.0	17.0	1910.0	28.0

pared to Clusters 1 to 3 and 5. The prevalence of bioturbation and pervasive terrestrial organic facies characterizing these sediments suggests that they were deposited under oxygenated bottom waters (Cunningham and Gilbert, this volume). Therefore, trace element enrichment by direct precipitation or burial of marine organic matter probably could not have occurred.

Isotopic Analyses

Cyclically Deposited Sediments in Unit 5, Site 550

Interbeds of laminated, organic-carbon-rich and bioturbated, organic-carbon-lean marly chalk of latest Albian (Vraconian) to Cenomanian age in Unit 5 at Site 550 reflect rapidly varying environmental conditions. It has been suggested that bottom waters periodically became reducing at 10,000- to 100,000-yr. intervals as a result of climatically induced variations in productivity and circulation as this unit was deposited (Cunningham and Gilbert, this volume). Indeed, organically associated trace metals Zn, V, Ni, Co, Ba, and Cr are enriched two to four times in the laminated (anoxic) versus bioturbated (oxic) intervals (Table 1).

In an effort to better assess the origin of cyclicity in Unit 5, stable carbon- and oxygen-isotope analyses were conducted on a series of samples through three complete redox cycles in Section 550B-18-1. The carbon-isotopic values remain fairly constant throughout the light/dark cycles at about 2.5‰, whereas the oxygen-isotopic signal shows a significant shift (up to 1‰) toward lighter values in the organic-carbon-rich intervals (Fig. 3).

Scholle and Arthur (1976, 1980) and Weissert et al. (1979) argue that positive $\delta^{13}\text{C}$ shifts in the stratigraphic

column, either locally or world-wide, may occur as a result of paleoceanographic events that cause the burial of marine organic matter. Surface waters become depleted in ^{12}C as marine organic matter (enriched relative to surface waters in ^{12}C) is removed. Conversely, the tests of planktonic calcareous organisms that are in isotopic equilibrium with surface waters become enriched in ^{13}C , thus causing a positive $\delta^{13}\text{C}$ shift in the isotopic record. The lack of $\delta^{13}\text{C}$ variability in Section 550B-18-1 suggests that isotopic fractionation did not occur in the surface waters, probably because variations in productivity and/or circulation were not great enough to change the bulk composition of the CO_2 reservoir.

Oxygen-isotopic ratios show a definite shift from background values of about -3.4‰ to maximum values of about -4‰ in the organic-carbon-rich intervals. Variation of oxygen-isotopic ratios may occur because of selective dissolution during burial diagenesis of the carbonates (Scholle, 1977a, b) or as a result of paleotemperature and paleosalinity variations in surface waters (Savin, 1977). If the fractionation resulting from diagenesis was minimal, the $\delta^{18}\text{O}$ shifts in sediments in Section 550B-18-1 indicate that warmer surface-water temperatures or decreases in salinity may have occurred during deposition of the organic-carbon-rich intervals. Climatically controlled increases in runoff, have been suggested as the cause of periodic stable salinity stratification and bottom-water anoxia in the northeastern North Atlantic during the mid-Cretaceous (Arthur, 1979). Elsewhere in this volume (see Cunningham and Gilbert) it is shown that productivity may have increased concurrently with the periods of bottom-water anoxia at this site. Nutrient loading of surface waters may have occurred in association with increased runoff, causing the periodic

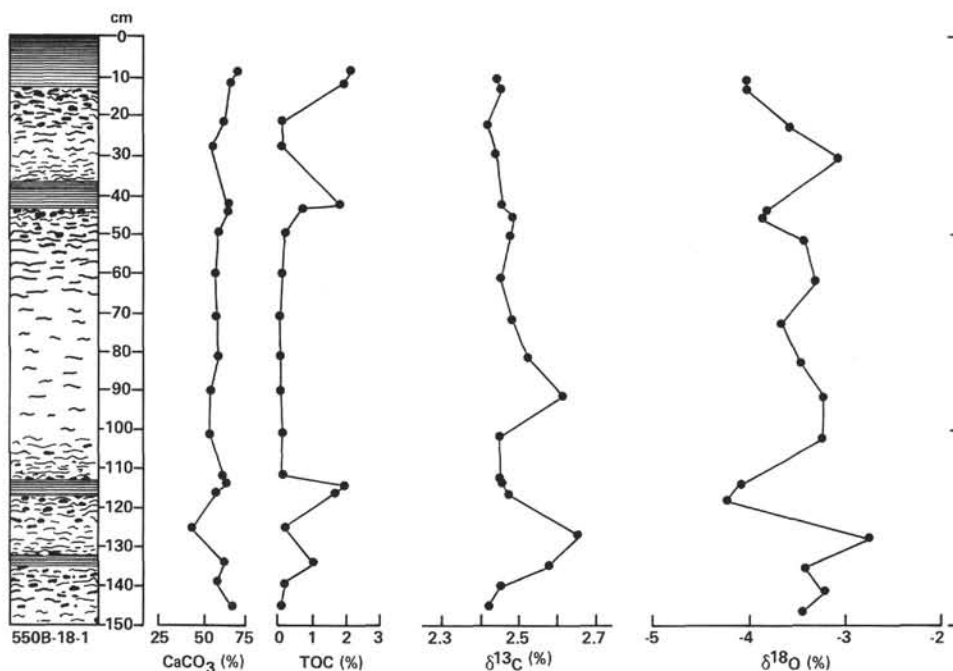


Figure 3. Variations in CaCO_3 , TOC, and carbon and oxygen isotopes for Section 550B-18-1. Beds alternate between finely laminated, organic-carbon-rich and bioturbated, organic-carbon-lean marls.

increases in fertility. Variations in productivity, however, were not great enough to cause carbon-isotopic fractionation in the surface waters.

Cenomanian–Turonian Black Mudstones, Sites 549 and 551

Carbon- and oxygen-isotopic values are significantly more positive in the late Cenomanian–Turonian black mudstones in Unit 5 at Sites 549 and 551 than in the middle Cenomanian marly chalks in Unit 5 at Site 550. The maximum $\delta^{13}\text{C}$ values, in Unit 5 at Sites 549 and 551, are +4.47 and +3.72‰, respectively, whereas that in Section 550B-18-1 is +2.7‰ (Table 3). Maximum $\delta^{18}\text{O}$ values range from -0.76 and -2.22‰ in Unit 5 at Site 549 and 551, respectively, to -2.68‰ in Unit 5 at Site 550 (Table 3). Carbon-isotopic values for the Cenomanian–Turonian black mudstones collected on Leg 80 fall into the range noted for this horizon elsewhere in the world (Scholle and Arthur, 1980), indicating that they are coeval with the worldwide “oceanic anoxic event” proposed by Schlanger and Jenkyns (1976) and Arthur and Schlanger (1979).

CONCLUSIONS

1. Multivariate statistical analysis of geochemical data causes samples to be grouped into two major classes: an organic-carbon-rich group (>1% TOC) containing high levels of marine organic matter and certain trace elements (Cu, Zn, V, Ni, Co, Ba and Cr) and an organic-carbon-lean group depleted in these components.

2. Enrichment of the above trace elements in the organic-carbon-rich samples may occur because of preservation of marine organic matter enriched in these elements or by direct precipitation from anoxic and reducing bottom waters.

3. The samples lacking in organic matter show enrichments in Ti, Si, and Al, if they contain a large fraction of siliciclastic material, or Ca and Sr, if they are mainly carbonates.

4. Variation in the $\delta^{18}\text{O}$ of bulk carbonate for Section 550B-18-1 suggests that paleosalinity and/or paleotemperature variations may have occurred concurrently with periodic anoxia at Site 550. Climatically controlled increases in surface-water runoff may have caused surface waters to periodically freshen, resulting in stable salinity stratification.

Table 3. Comparison of carbon- and oxygen-isotopic values for Cenomanian to Turonian sediments from Sites 549 to 551.

Sample (interval in cm)	Age	TOC (%)	CaCO ₃ (%)	$\delta^{13}\text{C}$ (‰)	$\delta^{18}\text{O}$ (‰)
549-27-1, 40–43	late Cenomanian– Turonian	9.31	25.00	+4.47	-1.72
549-27-1, 43–46	late Cenomanian– Turonian	2.09	1.50	+3.35	-0.76
550B-18-1, 125–126	mid-Cenomanian	0.20	43.00	+2.70 ^a	-2.68 ^a
551-5-2, 67–70	late Cenomanian– Turonian	6.24	1.33	+3.72	-2.22
551-5-2, 103–112	late Cenomanian– Turonian	6.66	2.33	+3.13	-2.53

^a Maximum value from Section 550B-18-1.

5. Carbon-isotopic values for the black mudstones in Unit 5 at Sites 549 and 551 indicate that they were deposited during the global “oceanic anoxic event” at the Cenomanian/Turonian boundary defined and discussed by Schlanger and Jenkyns (1976) and amplified by Arthur and Schlanger (1979).

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